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The biogeochemistry of pristine, headwater Precambrian shield watersheds: an analysis of material transport within a heterogeneous landscape

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Abstract. The hydrology and elemental transport within five low order Precambrian shield catchments was investigated during 1988–90. Catchments were subdivided and instrumented to examine the vertical and horizontal fluxes of elements within and between two distinct landscape types: open, lichen-covered bedrock outcrops and patches of conifer forest. The dominant hydrologic pathways were Horton overland flow in the lichen-bedrock areas and shallow subsurface flow through organic rich LFH (forest floor) and Ah soil horizons in the forested areas. Annual runoff coefficients ranged from 0.3 to 0.7.

Runoff chemistry was acidic (pH 4.01–4.72), with organic anion equivalents ($RCOO^-$), comprising 60 and 69% of the anion charge total for bedrock and forest runoff, respectively. Forested plots exported more H^+ (2.6x), DOC (1.4x), Al (1.6x) and Fe (1.8x) and less N (0.40x), P (0.13x), particulate C (0.08x), Ca^{2+} (0.38x), Mg^{2+} (0.83x), Na^+ (0.85x) and K^+ (0.32x) per unit area than the bedrock-lichen plots. The catchments exhibited a net export of H^+ (34), Mg^{2+} (24), Na^+ (20), K^+ (4) (units in eq ha^{-1} yr^{-1}) and C (16), Si (5.6), Al (1.6) and Fe (0.47) (units kg ha^{-1} yr^{-1}). The catchments retained N (5.66), P (0.08), Mn (0.03) (units kg ha^{-1} yr^{-1}), and Ca^{2+} (37), and Cl^- (3) (units eq ha^{-1} yr^{-1}). The strong retention of Ca^{2+} within the treed soil islands resulted in extremely low export rates of base cations (−15 to 38 eq ha^{-1} yr^{-1}).

The spatial distribution and hydrologic and biogeochemical linkages associated with each landscape unit interact to control element transport within the study catchments.

Introduction

Undisturbed landscapes generally comprise heterogeneous vegetative and geomorphologic units which cycle and transport elements at different rates and magnitudes. Hydrologists have recognized the importance of this heterogeneity in theories of runoff generation (Dunne 1983). In contrast to distributed hydrologic approaches, catchment biogeochemical studies have traditionally employed a whole catchment input-output budgeting approach where the catchment is treated as a single black box (Bormann & Likens 1967). Ignoring spatial heterogeneity, the whole watershed mass balance approach cannot assess the internal fluxes of material associated with various combinations of landscape units and their role in determining runoff chemistry. The study reported in this paper, utilises a 'grey' box approach, examining the effect of two distinct landscape units on the transfer and retention of elements within low order catchments on the Canadian Precambrian shield to better explain the elemental export from this landscape.

Biogeochemical investigations in watersheds have shown that spatially discrete areas such as wetlands can modify runoff water quality (Devito et al. 1990). Knight & Fahey (1985) and Durand et al. (1991) demonstrated the role contrasting vegetation units play in modifying material fluxes from a catchment. LaZerte (1989) and Mulder et al. (1991) found the linkages between hydrologic flow paths and the spatial distribution of heterogeneous soils controlled the patterns of dissolved Al chemistry within shield catchments. The results of these and other studies indicate that the spatial heterogeneity present within a catchment must be considered in order to explain patterns of water chemistry within a system. Secondly, the linkage between biogeochemical processes and hydrologic pathways is required to develop empirical generalizations for various ecosystem types for the prediction of the effects of large scale environmental perturbations such as acid precipitation, changes in climate, and land use.

In this paper we present the results from a 3 year hydrologic and biogeochemical investigation of five low order Precambrian shield watersheds that illustrate the role that discrete landscape units play in element transfers within and from a catchment. The catchments are characterised by patches of treed soil deposits interspersed among large areas of crustose and fruticose lichen-covered bedrock. This is a common landscape type of northern Europe and North America where the continental tectonic plates are exposed. The primary objectives of the study were to: a) characterize and quantify elemental transport from pristine, acid-sensitive, Precambrian shield upland catchments; and b) to examine how the positioning and proximity of different lanscape units within a basin affected elemental exchange and ultimately the export of elements from this landscape.

Study area

The study area (Fig. 1) consists of four zero order (catchments U1—U4) and one first order catchment (U8), located in the Experimental Lakes Area (ELA), northwestern, Ontario (49°40′N, 93°43′W). The catchments are located on a granitic ridge top ≈ 40 m above a small headwater lake (L. 302). Subcatchment areas dominated by lichen-covered bedrock (U1b and U3b) and others containing forested soil deposits (U1f and U3f) were isolated into plots (see methods), and monitored separately within the

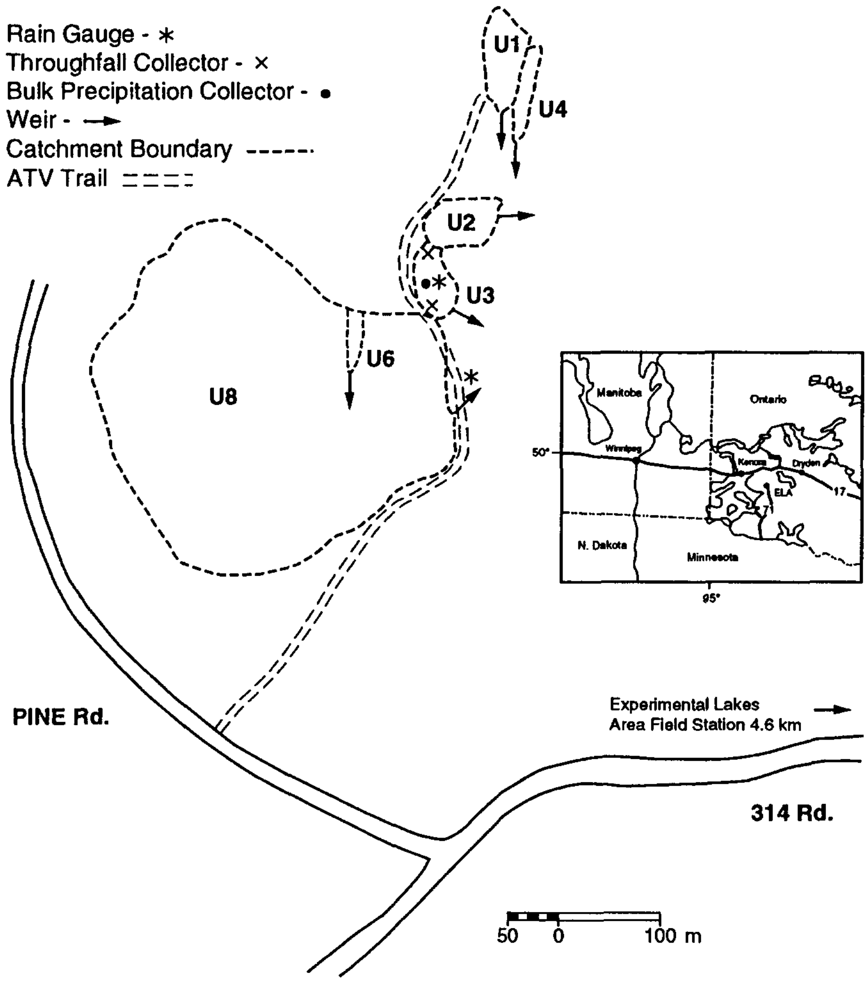


Fig. 1. L. 302 uplands experimental catchments, Experimental Lakes Area, northwestern Ontario, Canada.

larger catchments U1 and U3 (Figs. 2 and 3). Pertinent physiographic characteristics of the catchments are presented in Table 1.

The catchments, with the exception of U4, are largely underlain by leucocratic coarse grained meta-granites. Small areas of microcline feldspar meta-granites are found near the topographic highs of catchments U1, U2, U3, and U8. Catchment U4 is largely underlain by a quartzo-feldspathic orthogneiss (Ziervogel unpublished data).

Soils within the study watersheds are patchy and thin, consisting of truncated orthic humic regosols and sombric brunisols (Canadian Soil Survey Committee, Subcommittee on Soil Classification 1978). The upland soils are texturally classified as silt loams, and are of a glacio-lacustrine origin (Brunskill & Schindler 1971). The upland soil mineralogy comprises, by weight, quartz 75%, Al_2O_3 15%, Fe_2O_3 4%, K_2O 2.4% and Na_2O 1.7%. The <2 μm clay fractions make up 20—30% of the soil mass. The clay fraction comprises, in decreasing amounts, hydroxy-interlayered vermiculite, smectite and kaolinite. The Al-hydroxy interlayers within the vermiculite represent a potential source or sink for labile Al

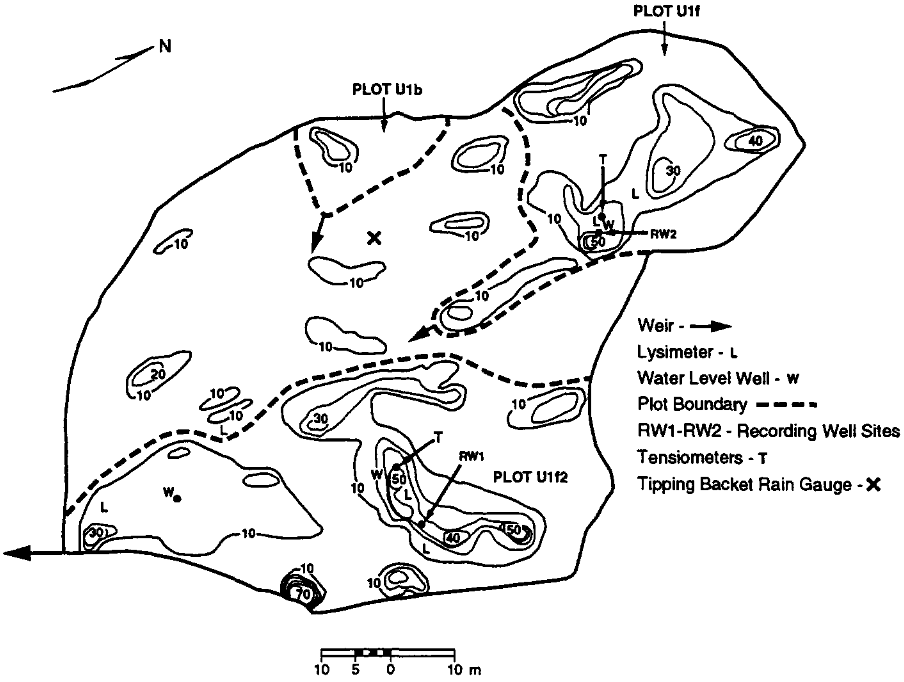


Fig. 2. The distribution and thickness of the surficial deposits contained in upland catchment U1, bedrock plot U1b and forested plots U1f and U1f2.

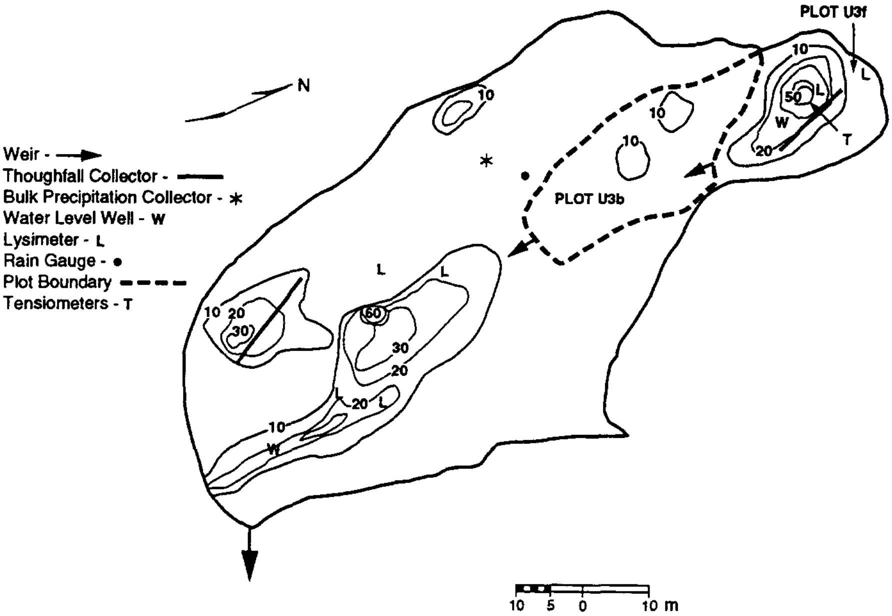


Fig. 3. The distribution and thickness of the surficial deposits contained in upland catchment U3, bedrock plot U3b, and forested plot U3f. Flow from the U3f forested plot passes through the downstream lichen-bedrock plot.

Table 1. Physiographic features of the study watersheds.

	Area m^2	Mean slope[1]	Bedrock %	Forest %	Mean soil depth (cm)
U1	5553	0.177	73	27	8
U1b	172	0.205	98	2	3
U1f	1102	0.093	62	38	11
U2	4694	0.178	65	35	11
U3	4006	0.169	79	21	8
U3b	266	0.187	100	0	4
U3f	381	0.053	60	40	13
U4	1730	0.230	60	40	10
U8	71970	—	—	—	—

[1] Mean slope = $oh*A_c^{-1/2}$, where: A_c is the area of the catchment in km^2, oh is the maximum altitude difference in km.

— not measured.

within the catchments. Chemical and physical characteristics of the catchment soils are presented in Table 2. Catchment soils are acidic with low CEC and base saturation values, and relatively high Al content. Both LFH and Ah soil horizons are highly permeable.

Table 2. Chemical and physical characteristics of the upland basin soils.

Soil horizon	LFH	Ah	C
N	8	18	2
Sand %	—	12	7
Silt %	—	57	70
Clay %	—	30	22
Bulk density kg m^{-3}	142.0	650.0	—
Saturated hydraulic conductivity (K_{fs}) $msec^{-1}$	5.20×10^{-2}	1.50×10^{-2}	4.90×10^{-4}
pH H_2O Ext.	3.91	4.12	4.49
Organic carbon %	31	7	1
CEC meq/100 g	17	5	1
Base sat. %	59	15	10
Al (KCl extractable) ug/g	47	36	13
Al ($Na_2P_2O_7$ extractable) % dry wt.	0.4	0.9	0.3
Al ($(NH_4)_2C_2O_4$ extractable) % dry wt.	0.0	1.3	0.5
SO_4 (H_2O extractable) ug/g	85.0	13.3	7.6
SO_4 (NaH_2PO_4 extractable) ug/g	0.0	152.0	31

— not measured.

Vegetation on the upland soil deposits consist of an overstorey dominated by *Pinus banksiana* and *Picea mariana* with a few *Pinus strobus.* The understorey vegetation consists of a shrub layer of *Acer rubrum, Prunus pensylvanica, Juniperus virginiana* and *Vaccinium angustifolium,* the herb *Pteridium aquilinum,* and a ground cover of *Cladina mitis* and *Pleurozium schreberi.* The exposed bedrock outcrops are dominated by *Andreaea rupestris Hedw., Polytrichum piliferum Hedw., P. juniperinum Hedw., Cladina mitis, Rihizocarpon geographicum (L.) DC* and *Racomitrium microcarpon* (Vitt 1991). The catchments have never been logged and the last forest fire in the study catchments occurred more than 115 years ago (Schindler et al. 1980).

The mean annual temperature recorded at ELA during the 1970—90 period was 2.4 °C and total annual precipitation averaged 508 mm, of which 36% fell as snow (Beaty & Lying 1989; Beaty, unpublished data).

Methods

Precipitation quantity (April—October) was measured by standard Atmospheric Environment Service (AES) rain gauges located in catchments U8 and U3 (Fig. 1). Winter precipitation was recorded with a Nipher shielded snow gauge at the ELA meteorological station located 4 km from the upland catchments. During May to October bulk precipitation for chemical analysis was collected in a plexiglass collector, located on an island in Hayes Lake adjacent to the ELA research camp. Winter bulk precipitation samples were collected at the ELA meteorological station. Bulk precipitation samples for aluminum analysis were collected in a similar collector within catchment U3.

Throughfall chemistry and volume were collected from two plastic eavestrough collectors, 1.16 and 1.23 m^2, located in catchment U3 (Fig. 3). Discharge from the catchments and plots was calculated from continuous water level measurements behind 60° or 120° V-notch weirs at each outlet.

Soil leachates for chemical determinations were obtained from both zero tension and tension lysimeters. In each catchment, three to four zero tension lysimeters consisting of screened plexiglass boxes were installed at the base of the LFH (forest floor) soil horizon which varied from 5—25 cm in depth. Tension lysimeters consisting of alundum plates were installed in the Ah and C mineral soil horizons. Lysimeters were precleaned before installation and left to equilibrate in the ground for eight months prior to the commencement of sampling (Neary & Tomassini 1985). Significant contamination above blank values of TAl (85 μgl^{-1}), Si (0.6 mgl^{-1}), Mg^{2+} (0.04 mgl^{-1}) and Na^+ (0.23 mgl^{-1}) was detected from the tension lysimeter plates after precleaning. However, none of these elements were contributed at concentrations which were near levels recorded for soil waters in the study catchments. The average concentration of material leached from the lysimeter plate after lysimeter precleaning expressed as a percentage of average Ah leachate concentration was as follows: Mg^{2+} (6%); Na^+ (17%); TAl (5%) and Si (6%). In addition, leachate concentrations of major ions and Si from shallow tension lysimeters were comparable to those collected from nearby zero tension lysimeters at approximately the same soil depth. Three to six lysimeter plates were installed in each catchment. Zero tension lysimeters were sampled on an event basis, while tension lysimeters were sampled every two days during snowmelt and weekly thereafter. A vacuum of 9.65 kPa was applied to each plate.

All water samples were collected in clean polyethylene bottles and taken to the ELA analytical laboratory within a few hours of collection for sample processing. Rainfall runoff samples from each catchmnet were collected on an event basis. Each event during the study perod was sampled (51 in total). A 40 L plastic barrel lined with a plastic bag was used to sample the initial runoff for each storm event. Thereafter, samples were collected each half hour until peak flow and with declining frequency during the recession period. Runoff during snowmelt was sampled once or twice a day depending upon runoff volume. Particulate fluxes ($> 200\ \mu$m) were measured directly by weighing the material collected in a sediment trap below the U3 outlet weir.

Analyses for NO_3^- and NH_4^+ as N, dissolved nitrogen (TDN), dissolved phosphorus (TDP), pH, conductance and dissolved inorganic carbon (DIC) were performed at ELA usually within 24 hours of collection. All other analyses (except speciated aluminum), were performed at the Department of Fisheries and Oceans (DFO), Fresh Water Institute (FWI) analytical laboratory. Chemical analyses were performed using standard DFO analytic procedures as outlined in Stainton et al. (1974), with the following exceptions. Sulphate and Cl^- analysis were performed using ion chromatography (Tabatabai & Dick 1983). Total labile aluminum (TCVAl), and labile organic aluminum (OAl) concentrations, were determined at ELA using a manual catechol-violet ion exchange procedure similar to that reported by LaZerte et al. (1988). Inorganic labile alumium (IAl) was calculated as the difference between organic and total labile aluminum. Inorganic aluminum speciation and HCO_3^- were determined with the chemical speciation program ALCHEMI (Schecher & Driscoll 1987). Fluoride values used for the speciation of inorganic Al were not measured directly. Fluoride concentration were estimated through the following empirical relationship developed between sepcific conductance (measured at 25 °C) and total F^- as measured by potentiometric ion selective electrode analysis after TISAB addition:

$$\mathrm{F}\ \mu\mathrm{g/l} = \mathrm{SC} * 1.256927 - 8.30547\ (r^2 = 0.95, p \leqslant 0.001)$$

where SC = specific conductance (μS).

Total aluminum (TAl) was measured by DC plasma emission spectrometry at the FWI heavy metals laboratory. The non-labile, or acid soluble (ASAl) fraction of aluminum was calculated as the difference betwen TAl and TCVAl. Organic anion equivalents ($RCOO^-$), was estimated as the anion deficit (cation sum — inorganic anion sum).

Water and chemical fluxes were determined as follows. Atmospheric deposition and throughfall fluxes were calculated by multiplying concentrations from bulk precipitation and throughfall samples by the recorded depth of precipitation and throughfall, respectively. Concentrations from LFH leachates were weighted by the leachate volumes collected during each runoff event. This is valid because the LFH horizons are fibrous and undecomposed (bulk density 142 kg m^{-3}), therefore it can be assumed that water movement through the horizon is by gravity flow and hence unaffected by capillarity. The net flux of material through the LFH horizon was not calculated from the leachate volumes because there was a great deal of variability ($>100\%$), in the quantity of leachate retrieved from the different lysimeters and the lysimeters excluded lateral fluxes from upslope runoff or return flow from deeper mineral soil horizons. The concentrations reported, therefore, apply only to the gravitational water flux of throughfall through the understorey and LFH soil horizons. The flux of soilwater through the mineral soil horizons cannot be determined from the vacuum lysimeter data as the plates were not at equilibrium with local soil tensions. Arithmetic averages, however are utilised to characterize the water quality of Ah and C horizon soils.

Runoff fluxes were determined by multiplying the concentration of an element by the volume of discharge measured at each outlet weir. The runoff volume assigned to each sample corresponded to the sum of the discharge recorded from the mid point between the collection of the previous water sample to the mid point in time prior to the subsequent sample. Calculated fluxes were then divided by the area of discharge to express the flux on a unit area basis. Annual hydrologic budgets (November 1—October 31) were calculated in the following manner:

$$P - R = E$$

where P = precipitation, R = runoff and E = evapotranspiration. Net annual storage was assumed to equal zero for the hydrologic budgets. Annual chemical budgets were calculated in the following manner:

$$P_i - R_0 = RT$$

where P_i = material inputs from atmospheric deposition, R_0 = material export in runoff waters and RT = the amount material retained in the catchment.

The errors reported for the hydrologic and chemical budget terms equal the confidence limits, or one standard deviation around the measured values. Confidence limits for the hyrologic budgets were estimated by multiplying the individual measured terms for the budget by percentage errors derived from the literature and the individual rating equations

(Winter 1981; Labaugh & Winter 1984). Confidence limits for the chemical budgets were estimated by summing the individual error terms for the chemical analyses and hydrologic fluxes (Devito et al. 1990).

Results and discussion

We begin our analysis of the transformation and transport of elements amongst the various compartments that comprise the upland basins, by presenting the hydrologic characteristics and linkages in the study catchments first. Following this, the water chemistry associated with each compartment of the upland forest is examined. Element retention patterns of forested and bedrock plots are then compared, and an examination of the modifications to solution chemistry as water moves across the two different catchment landscape units follows. To conclude, element budgets of the study basins are presented and patterns of interannual and inter-catchment element retention are examined and contrasted with those of other catchments found on crystalline bedrock.

Hydrology

Precipitation and throughfall

Total precipitation inputs were similar among the study years (Table 3) and on average were 15% greater than the 19 year mean for ELA (Beaty & Lyng 1989). Snow comprised 33%, 44% and 22% of the annual precipitation for 1988, 1989 and 1990 and snowmelt contributed between 22% and 60% of the annual runoff from the catchments (Table 3).

Total throughfall depths during the growing season (May—Oct.), were almost identical in 1989 and 1990, 22 and 23 cm respectively, although expressed as a proportion of total precipitation they differed (52% in 1989; 65% in 1990). The 48% to 35% loss in precipitation is attributed to direct evaporation of intercepted water from the forest canopy. Earlier investigations within similar, adjacent, watersheds indicated stemflow was a minor component of the canopy flux in this area (Allan, unpublished data).

Runoff

Runoff from lichen-bedrock areas is produced as precipitation excess through Horton overland flow (Horton 1933), because of the zero infiltration capacity of the bedrock-lichen areas and either by shallow subsurface stormflow, or saturated overland flow (Dunne 1983), in the forested areas (Allan & Roulet 1993). The 1988, 1989 and 1990 annual hydrographs

Table 3. Annual hydrologic budgets for the study catchments (mm yr^{-1}), (± 1 SD estimated hydrological uncertainties).

	Precipitation (mm)	Runoff (mm)	Evapotranspiration[1] (mm)	Annual runoff coefficient
U1				
1988	589 ± 89	255 ± 16 (45)[2]	334 ± 57	0.43 ± 0.03
1989	601 ± 90	340 ± 14 (51)	261 ± 43	0.57 ± 0.02
1990	559 ± 84	196 ± 13 (22)	363 ± 62	0.35 ± 0.02
U1b				
1990	559 ± 84	335 ± 54 (10)	224 ± 50	0.60 ± 0.10
U1f				
1990	559 ± 84	168 ± 15 (23)	391 ± 70	0.30 ± 0.03
U2				
1989	601 ± 90	285 ± 11 (57)	316 ± 51	0.47 ± 0.02
U3				
1988	589 ± 89	267 ± 22 (49)	322 ± 50	0.45 ± 0.04
1989	601 ± 90	333 ± 17 (54)	268 ± 38	0.55 ± 0.03
1990	559 ± 84	247 ± 18 (24)	312 ± 54	0.44 ± 0.03
U3b[3]				
1990	559 ± 84	367 ± 33 (31)	192 ± 35	0.66 ± 0.06
U3f				
1990	559 ± 84	167 ± 16 (10)	392 ± 72	0.30 ± 0.03
U4				
1988	589 ± 89	183 ± 13 (56)	406 ± 70	0.31 ± 0.02
1989	601 ± 90	239 ± 11 (59)	362 ± 60	0.40 ± 0.02
1990	559 ± 84	172 ± 11 (30)	387 ± 66	0.31 ± 0.02
U8				
1987	488 ± 73	148 ± 8 (39)	340 ± 56	0.30 ± 0.02
1988	589 ± 89	240 ± 18 (51)	349 ± 61	0.41 ± 0.03
1989	601 ± 90	318 ± 13 (60)	283 ± 46	0.53 ± 0.02
1990	559 ± 84	197 ± 9 (38)	362 ± 60	0.35 ± 0.02

[1] Evapotranspiration was calculated as the residual in the water balance (Precipitation − Runoff = Evapotranspiration), assuming the annual change in water storage was equal to zero.

[2] Bracketed values represent percentage of annual runoff attributed to snowmelt.

[3] Values for plot U3b are calculated for U3b alone (266 m^2). The annual runoff coefficient (defined as runoff mm/precipitation mm), from the combined U3b and U3f plots (647 m^2) is 0.46.

from catchment U1 are presented in Fig. 4. The runoff response from all zero order catchments is extremely rapid and flow periods are of short duration. Prolonged periods with no or little flow were common, particularly in the autumn and winter months. The shallow subsurface and surface runoff pathways combined with the absence of any substantial soil

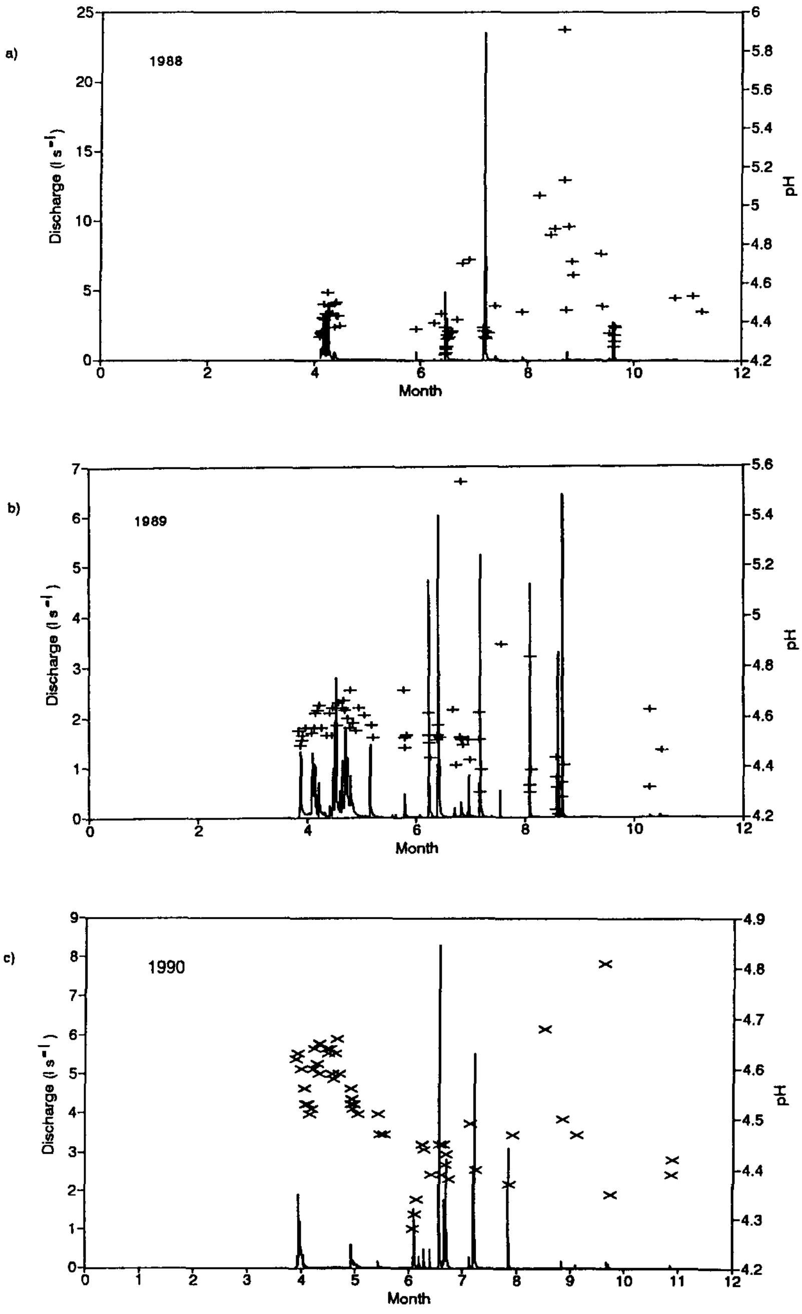


Fig. 4. 1988, 1989 and 1990 hydrographs and pH in runoff waters from catchment U1. pH values are presented to illustrate the acidic nature of upland runoff waters and sampling frequency of the event based monitoring program for each year.

water reservoirs are responsible for the relatively high peak flows and the short duration of each runoff period. Annual runoff coefficients varied from 0.31 to 0.57 for whole catchments while those for the bedrock plots U1b and U3b were higher, averaging 0.60 and 0.66 respectively (Table 3). Annual inter-catchment variability of runoff coefficients averaged 15% for the period 1988—90 with the most extensively forested catchment U4, consistently exhibiting the lower runoff coefficients.

Annual runoff coefficients from the study catchments tend to be higher than those of larger shield catchments monitored in the ELA area. The Northwest Inflow (56.38 ha), Northeast Inflow (12.43 ha) and the East Inflow (170.28 ha) of the Rawson Lake catchment have been monitored from 1967 until present (Beaty & Lyng 1989; Beaty, unpublished data). During 1989 annual runoff coefficients ranged from 0.29 to 0.35 for the Rawson Lake catchments and 0.40 to 0.57 for the study catchments. The higher runoff coefficients reflect the smaller size, lower storage capacity and rapid runoff response of these upland watersheds compared to that of the Rawson Lake catchments. Till deposits in the Rawson Lake catchments reach 15 m in depth and bedrock depressions can contain organic deposits up to 10 m deep, both forming potentially large soil and shallow groundwater reservoirs (Bottomley 1974; Kennedy 1974). Flow duration curves and cumulative flow distribution curves comparing the upland catchments U1 (0.56 ha) and U8 (7.19 ha), and the Rawson Lake EIF catchment (170.28 ha) during 1989 are presented in Figs. 5a and 5b. Despite differences in catchment size and thickness of surficial deposits, there is little difference between the flow duration curves for each catchment. All the catchments were either frozen or dry $\approx 70\%$ of the year during 1989 and no runoff was recorded. The U1 catchment does exhibit higher unit area discharges, with flows > 1 mm day^{-1} occurring more often than recorded for the first order catchments. However, the distribution of the flow throughout the year differed substantially between the three catchments. Flow was initiated earlier in the zero order U1 catchment and 25% of its annual runoff occurred after 99% of the annual runoff had occurred in the larger EIF catchment (Fig. 5b). The runoff distribution for the U8 catchment fell betwen these two extremes. The U1 catchment was more responsive to rain events, particularly those occurring later in the growing season and snowmelt accounted for a smaller percentage of its annual runoff total.

Water chemistry

The data collected from the upland catchments were analyzed to determine how precipitation chemistry changed as it passed through the catch-

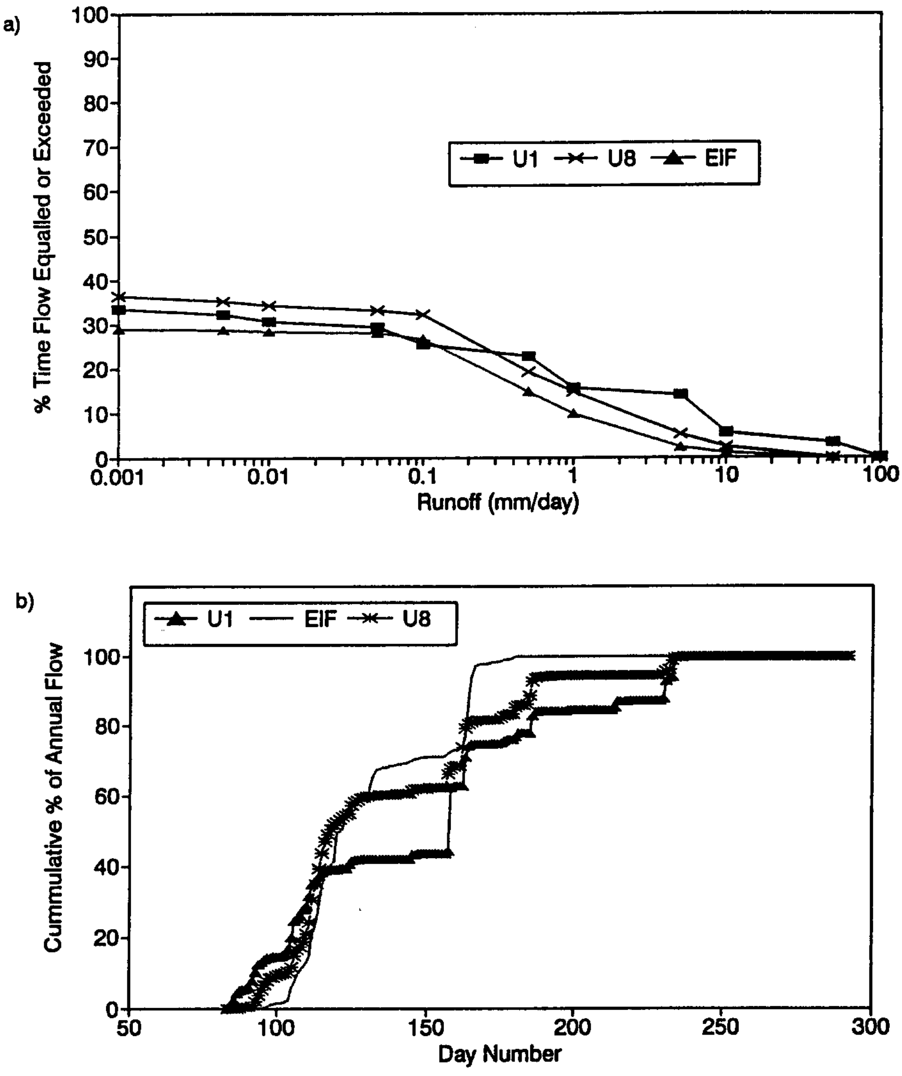


Fig. 5. The 1989 mean daily runoff flow duration curves and the annual flow distribution curves for the zero order, U1 (0.55 ha) and first order, U8 (7.20 ha) and East Inflow (170.28 ha) catchments.

ments. Average chemical concentrations for the various upland forest compartments are presented in Fig. 6a through 6h.

Precipitation

Precipitation chemistry at ELA is dominated by the Ca^{2+}, Mg^{2+}, NH_4^+, NO_3^-, and SO_4^{2-} (Figs. 6a, 6d and 6g). The atmospheric inputs of N and

SO_4^{2-} at ELA are ≈36% for SO_4^{2-}, and ≈98% for N of the loadings for eastern North America reported by Cronan et al. (1990). Bulk precipitation is the only water in the upland forest where inorganic nitrogen species NO_3^- and NH_4^+, dominate nitrogen water chemistry (Fig. 6a). Particulate phosphorus (Part. P) accounts for approximately 50% of the atmospheric input of phosphorus to the study catchments (Fig. 6b).

Lichen mat

The lichen mat covering the open bedrock surfaces received precipitation largely unaffected by the forest canopy. As precipitation passed through the lichen cover concentrations of organic nitrogen (TDN + Part. N − NO_3^- − NH_4^+), doubled and inorganic nitrogen fractions declined by two thirds (Fig. 6a). In general, the lichen mat had the same effect on water chemistry as the forest canopy (see below), with most chemical constituents, inorganic nitrogen being the exception, increasing in concentration (Figs. 6a—6g). Increases in concentration can be attributed to evaporative losses, the dissolution of aerosols, particulates, mineralization products and the weathering of primary and secondary minerals contained in and on the lichen-moss community. Alkalinity was consumed and pH declined as precipitation passed through the lichen mat (Fig. 6h). The increased acidity in solutions draining the lichen mat is attributed to organic acids such as oxalic acid which are produced by lichen colonies (Wilson et al. 1981).

Throughfall

Every chemical variable measured with the exception of NH_4^+, increased in concentration as throughfall moved through the forest canopy (Figs. 6a—6h). Ammonium exhibited a continuous decline in concentration as it moved through the entire forest system, reflecting biotic uptake and nitrification (Fig. 6a). Increased dissolved and particulate concentrations in throughfall water can be attributed to both evaporative losses and the flushing of aerosols and particulates and the leaching of foliar exudates from the forest canopy (Eaton et al. 1973; Lang et al. 1976). Our throughfall totals indicate a 48 to 35% evaporative loss as water moved through the forest canopy. The forest canopy can therefore be considered a source for elements whose volume weighted concentrations increased approximately two times or more over bulk precipitation. These included particulate nitrogen, phosphorus, carbon, H^+, Ca^{2+}, Mg^{2+}, K^+, Al, Fe, Mn, Cl^-, $RCOO^-$ and Si (Figs. 6a—6g). Dissolved nitrogen, Na^+, and SO_4^{2-} concentrations and alkalinity increased less than two times indicating little, or no contribution from the forest canopy (Figs. 6a, 6d, 6f and 6g). Several elements concentrations increased dramatically in throughfall

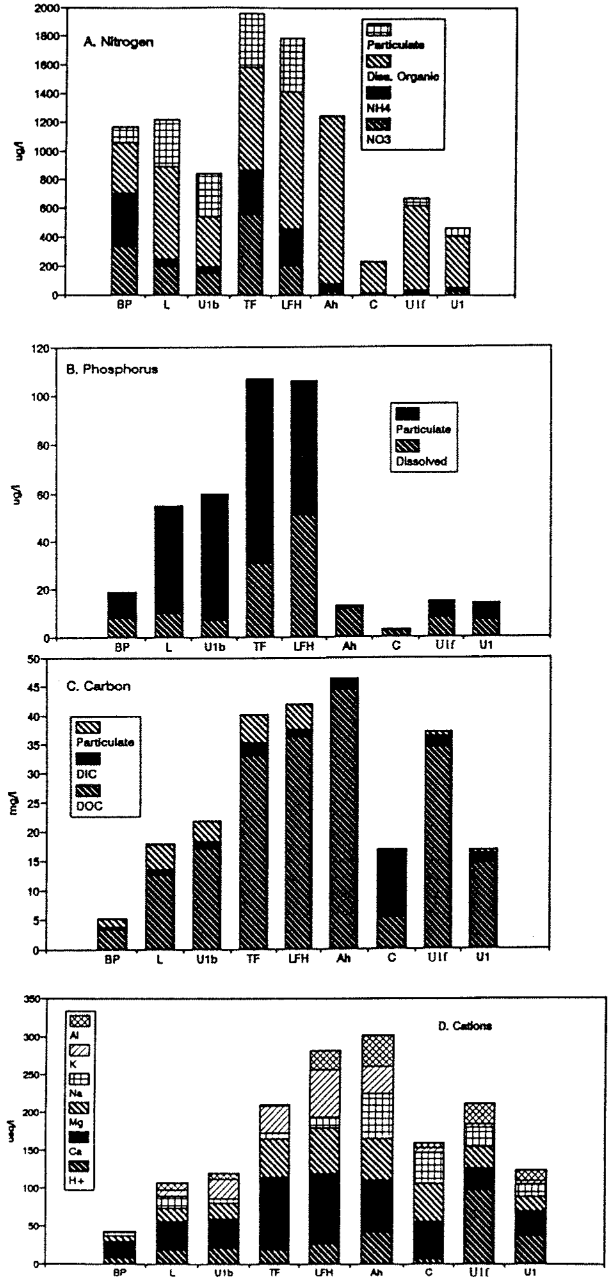
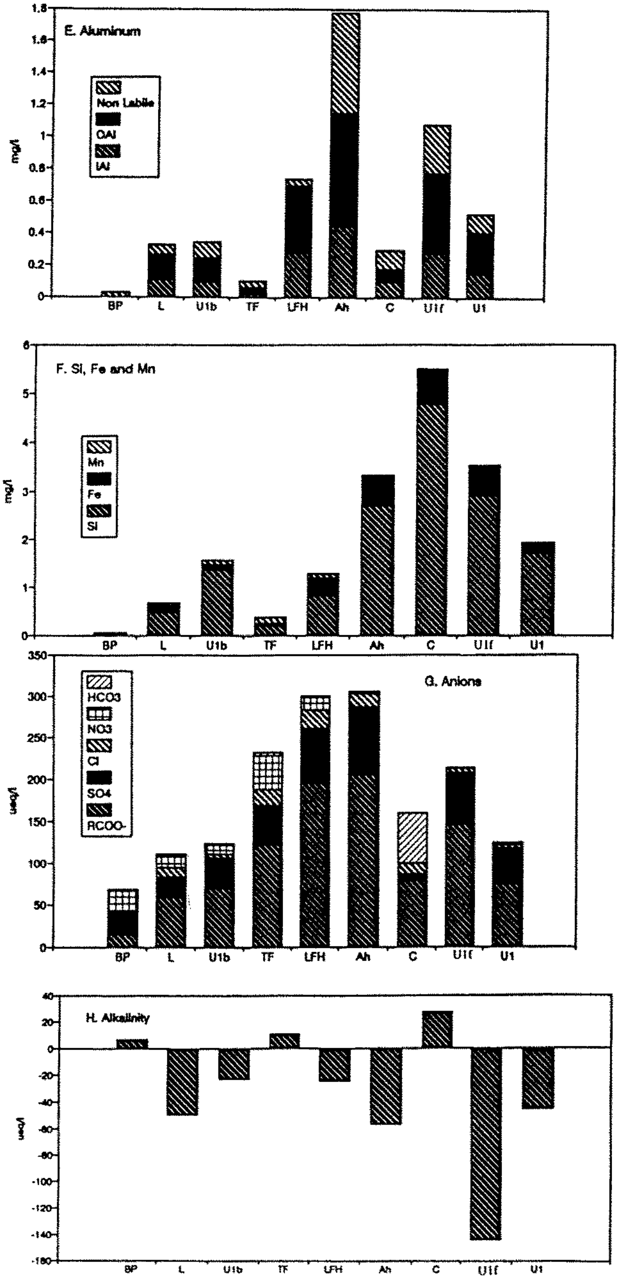


Fig. 6. Average concentrations of water chemistry for the various Precambrian shield upland catchment compartments. All values are volume weighted averages for 1989 and 1990 with the following exceptions: runoff waters from plots U1f and U1b are for 1990 and the Ah and C leachate values are arithmetic averages. BP = bulk precipitation, L =



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open lichen mat leachates, U1b = runoff waters from bedrock plot U1b, TF = throughfall, LFH = forest floor leachates, Ah = Ah soil horizon leachates, C = C soil horizon leachates, U1f = runoff waters from forested plot U1f and U1 = runoff waters from catchment U1.

waters, most notably K^+ (23x), Mn (13x), DOC (10x) and Part. P, Mg^{2+}, Cl^-, and $RCOO^-$ (all ≈ 7x).

Forest LFH

The changes in dissolved chemistry as water passed through the LFH soil horizon are a combination of the transformations occurring in the forest understorey and forest floor (Figs. 6a—6h). LFH leachate data presented in Fig. 6 represents the volume weighted concentrations of 130 samples collected from 14 zero tension lysimeters during 1989 and 1990. Sample volumes were not always sufficient to analyze the full suite of chemical variables and partial samples are included in this average.

Most parameters exhibited smaller changes in concentration in LFH horizon leachates when compared to the concentration changes associated with precipitation movement through the forest canopy. It is impossible to directly assess the role of the LFH, Ah and C horizon soils as a source or sink of material with our lysimeter data without direct water flux measurements. However, the magnitude of concentration change over throughfall values in some cases does suggest whether the LFH soil horizon acts as a source or sink of material. It appears that the LFH soil horizon was a source of Al, Fe and Si which increased 7, 6 and 4 times respectively (Figs. 6e and 6f). Sources of elements in the LFH horizon include the mobilization of aluminum and iron organic complexes, ion exchange with organic exchange sites and the dissolution of soil minerals. Inorganic nitrogen, particulate phosphorus, DIC, and Mn concentrations and alkalinity declined, indicating retention or consumption within the LFH horizon (Figs. 6a—6c, 6f and 6h). Retention of inorganic nitrogen and Mn reflects biotic uptake in the LFH horizon while the decline in particulate phosphorus and to some extent carbon may result from the 'filtering' of particulates by the forest floor and the screened surfaces of the zero tension lysimeters. Increases in acidity in LFH leachates results from increases in organic acidity which is reflected by a 37% increase in $RCOO^-$ over throughfall values (Fig. 6h). The decline in DIC concentrations exhibited in LFH leachates in comparison to throughfall reflect the degassing of CO_2 as water passes through the forest floor. The relatively smaller positive changes in concentration exhibited by organic nitrogen, dissolved phosphorus, DOC, H^+, Mg^{2+}, Na^+, K^+, Cl^- and SO_4^{2-} indicates that the LFH horizon had little effect on the magnitude of their fluxes within the study catchments (Figs. 6c, 6d and 6g).

Ah soil horizon

The Ah soil horizon is the dominant, and in most soil islands the only mineral soil horizon present. Water passing through this horizon often moves laterally along the Ah-bedrock interface before re-emerging through the LFH soil horizon as it exits a soil island. This soil horizon is also the dominant rooting zone for the forest vegetation and has high saturated hydraulic conductivities (Table 2).

Ah soil leachates are generally more acidic (1.6x), and had higher Na^+ (4.2x), Al (2.4x), Fe (1.6x), and Si (3.2x) concentrations in relation to LFH percolates (Figs. 6c, 6f and 6h). Phosphorus (0.26x), Ca^{2+} (0.74x), K^+ (0.57x) and Mn (0.44x) all declined in concentration in Ah leachates (Figs. 6b, 6d, 6f and 6g). The decrease in concentration as water moved through the mineral soil horizons does not necessarily indicate retention within this soil horizon. In some cases, runoff from upslope bedrock areas may serve to dilute soil water in the mineral soil horizons. Differences between the LFH and Ah soil horizon leachates may also be partly attributed to the different lysimeters used to sample each soil horizon. The tension lysimeters used to sample Ah and C soil waters collect both gravitational and capillary water while the zero tension lysimeters used in the LFH horizon sample gravitational water only. Capillary water might be expected to have higher concentrations of H^+, Fe, Na^+, Si and Al because of increased soil water contact. In addition, the tension lysimeter plates may contribute some Na^+, Al, Si and Mg^{2+} measured in Ah soil leachates. However, the potential Si and cation contamination is believed to be minor in relation to the high soilwater concentrations measured in the study catchments. Particulate nutrient concentrations are not presented for the mineral soil leachates as the tension lysimeter plates filter soil waters.

Organic nitrogen increasingly dominates dissolved nitrogen chemistry within the mineral soils, comprising 90% of the dissolved nitrogen fraction within the Ah horizon, while inorganic nitrogen concentrations declined by ≈90% when compared to that of LFH soil waters. Phosphorus values decline sharply (by 74%) as water passes through the mineral Ah soil horizon reflecting abiotic adsorption and biotic uptake (Fig. 6b).

Dissolved organic carbon reaches a maximum for soil waters within the Ah soil horizon. Sources of DOC and its associated organic acidity are the leaching of humus and/or the by-products of microbial metabolism. Ah leachates have the lowest pH of all soil waters with $RCOO^-$ comprising ≈65% of the anion charge total. Declining Ca^{2+} and K^+ concentrations in relation to overlying LFH soil waters indicate possible vegetative uptake within Ah soils. The dramatic increases in the concentrations of Na^+, Si and Al indicate the dissolution of primary and secondary aluminosilicate minerals and/or ion exchange reactions. Allan (1993) reported aluminum is contributed from soil aluminum-organic complexes and the dissolution of interlayer aluminum in secondary aluminosilicate minerals.

Aluminium concentrations peak within the Ah soil leachates with organic complexes (60%) dominating the labile fraction (Fig. 6e). Labile inorganic fractions of aluminum were under-saturated with respect to trihydroxide mineral phases within organic rich LFH and Ah soil leachates and forest plot runoff waters. Similar aluminum solubility behaviour have been observed for organic rich waters in other studies (e.g. Cronan et al. 1986; Helmer et al. 1990; LaZerte 1989; Sullivan et al. 1986). Inorganic labile Al fractions in the LFH and Ah soil leachates and all runoff waters were dominated by Al^{3+} (48—52%), with fluoride (21—15%) and hydroxy complexes (22—13%) comprising smaller percentages. Aluminum sulphate complexes were a minor component (<2%), of the labile inorganic aluminum total. The largest increase in Al fraction within the Ah horizon over the LFH horizon was attributed to ASAl.

C and Cg soil horizon

The C soil horizon has a relatively patchy distribution in the zero order catchments (U1—U4), and is found only under the deepest soil deposits. During early spring, before snowmelt H_2S was often detectable in C leachate samples. C horizon soils occasionally exhibit mottled patterns. The location and occasional anoxic conditions indicate that this horizon is at least partially isolated from the hydrologic flow paths operating in these catchments. C horizon soil leachates were far less acidic and more dilute than overlying Ah soil waters (Figs. 6a—6h). Alkalinity, DIC, Fe and Si all peaked in concentration in C horizon soil leachates (Figs. 6c, 6f and 6h). Increased DIC concentrations are associated with root and microbial respiration and the production of alkalinity within C horizon leachates. Sources of alkalinity include: 1) sulphate reduction; 2) the immobilization of DOC and its associated organic acidity through adsorption by reactive soil sesquioxides; and 3) the dissolution of aluminosilicate minerals. Low SO_4^{2-} concentrations and the presence of H_2S gas, combined with low DOC and $RCOO^-$ and high Si concentrations in C horizon soil waters indicate all three processes may be important.

The speciation of the inorganic labile aluminum fraction in C horizon leachates differed considerably from other soil waters. Aluminum-silicates (35%), hydroxy-aluminum complexes (32%) and aluminum-fluoride complexes (24%) dominated the labile inorganic fraction in the deeper mineral soils.

Forest plot runoff

Water exiting the forested U1f plot was extremely acidic with a volume weighted pH of 4.01 and pH often approaching 3.90. Forest runoff is dominated by organic acidity with $RCOO^-$ contributing 65% of the anion total in U1f runoff waters. The pH for forest runoff is lower than any recorded for soil leachates from the U1f plot. This high acidity of runoff in comparison to lysimeter solutions may reflect extended soil water contact, as water moves laterally through a soil island. Our lysimeter sampling design reflects vertical changes in water quality in the soil profile but cannot assess horizontal changes in water quality. The high organic acidity and Al concentrations present in Ah soil waters is reflected in forest runoff (Figs. 6c and 6e—6h). Forest runoff Si concentrations are higher than LFH soil water values and runoff acidity, DOC and Al concentrations are far higher than those measured in C horizon soil waters. This indicates that the lateral movement of water through Ah soil horizons is likely the primary flowpath in the treed soil islands and biogeochemical processes operating within this horizon determine the chemical character of runoff waters draining from the patches of upland forest.

Nitrate was selectively retained within the forested plot with volume weighted runoff concentrations 6 and 26 times lower than those of the whole catchment and bedrock plot runoff respectively (Fig. 6a).

Bedrock-lichen runoff

Runoff waters from the lichen-bedrock plot U1b were less acidic (0.22x) and more dilute in most elements when compared to waters draining the forested U1f plot (Fig. 6). As in soil island runoff waters, $RCOO^-$ dominates the anion chemistry of lichen-bedrock runoff. However, Ca^{2+} is the single dominant cation in bedrock-lichen runoff rather than H+ (Fig. 6d). Concentrations of biologically important elements such as inorganic nitrogen, Mn, and K^+ are higher in lichen-bedrock runoff than in the forest plot or the U1 whole catchment runoff (Figs. 6a, 6d and 6h).

Annual element retention in bedrock and forested plots

A major difference in material retention between the bedrock plot U1b, and the forested plot U1f, is the amount of particulate nitrogen, carbon and phosphorus exported (Table 4). The high particulate export from the bedrock plot in part, reflects the efficiency of overland flow in the transport of particulate material over the relatively unvegetated bedrock surfaces. The positive net export of particulate nutrients from plot U1b is at least partially attributed to the export of pollen and conifer litter which originated from the adjacent forest stands.

The net export of dissolved nutrients (NO_3^-, NH_4^+ and TDP), is also considerably higher in the bedrock plot than in forested plot (Table 4). This again is a product of the rapidity of runoff and minimal biogeochemical retention mechanisms on the bedrock surfaces. The preferential export of NO_3^- in relation to NH_4^+ in part, reflects the mobility of NO_3^-

Table 4. 1990 elemental budgets (kg ha^{-1} yr^{-1} or eq ha^{-1} yr^{-1}), (± 1 SD hydrologic, analytical and sampling uncertainties) for the bedrock-lichen plot U1b and the forested plot U1f.

	Bulk deposition	U1b bedrock	U1f forest
Nitrogen			
NO_3^- eq ha^{-1}	104 ± 20	37 ± 4	1 ± 0
NH_4^+ eq ha^{-1}	111 ± 21	11 ± 1	4 ± 1
TDN kg ha^{-1}	4.00 ± 0.76	1.82 ± 0.17	1.05 ± 0.09
Part. N kg ha^{-1}	0.69 ± 0.13	1.02 ± 0.16	0.09 ± 0.01
TN kg ha^{-1}	4.69 ± 0.98	2.84 ± 0.23	1.14 ± 0.10
Phosphorus kg ha^{-1}			
TDP	0.032 ± 0.006	0.022 ± 0.002	0.013 ± 0.001
Part. P	0.080 ± 0.015	0.176 ± 0.030	0.012 ± 0.001
TP	0.112 ± 0.024	0.198 ± 0.032	0.025 ± 0.002
Carbon kg ha^{-1}			
DIC	2.03 ± 0.39	3.00 ± 0.28	3.19 ± 0.33
DOC	15.11 ± 2.87	42.67 ± 4.11	58.07 ± 5.52
Part. C	9.69 ± 1.84	14.86 ± 2.53	1.26 ± 0.12
TC	26.83 ± 6.67	60.53 ± 6.92	62.52 ± 5.97
Cations eq ha^{-1}			
H^+	37 ± 10	64 ± 5	164 ± 14
Ca^{2+}	115 ± 22	128 ± 11	49 ± 4
Mg^{2+}	42 ± 8	59 ± 5	49 ± 4
Na^+	15 ± 3	52 ± 4	44 ± 4
K^+	7 ± 1	25 ± 4	8 ± 1
TAl kg ha^{-1}	0.16 ± 0.03	1.10 ± 0.09	1.81 ± 0.16
IAl	—	33 ± 3	48 ± 4
OAl kg ha^{-1}	—	0.53 ± 0.05	0.84 ± 0.08
Fe kg ha^{-1}	0.07 ± 0.01	0.58 ± 0.06	1.02 ± 0.09
Mn kg ha^{-1}	0.05 ± 0.01	0.05 ± 0.01	0.02 ± 0.00
Anions eq ha^{-1}			
Cl^-	12 ± 2	16 ± 1	10 ± 1
SO_4^{2-}	141 ± 27	121 ± 10	103 ± 8
$RCOO^{-1}$	—	198 ± 16	251 ± 20
Si kg ha^{-1}	0.09 ± 0.02	4.58 ± 0.38	4.89 ± 0.37

— not measured.

within natural systems (Johnson & Cole 1980). It is also possible nitrogen fixation by the blue green algae component of the lichen communities and subsequent mineralization and leaching of NO_3^- may contribute to the higher fluxes from the lichen-bedrock plot.

The forested plot, as would be expected, exported more DOC, H^+, Al (largely organically complexed) and Fe per unit area than the bedrock plot. Exports of DIC, Mg^{2+}, Na^+, IAl, SO_4^{2-} and Si were similar between the two plots.

Mass balance calculations indicate a net export of 85 eq ha^{-1} and a net retention of 29 eq ha^{-1} of base cations for the U1b bedrock plot and the U1f forested plot, respectively during 1990. The difference in base cation export between the two plots is accounted for by the retention of Ca^{2+} (66 eq ha^{-1}), likely through vegetative uptake in forest soils and higher losses of Mg^{2+} (10 eq ha^{-1}), Na^+ (8 eq ha^{-1}) and K^+ (17 eq ha^{-1}) from the lichen-bedrock surface. The net export of Si is similar between the forested (4.89 kg ha^{-1}), and bedrock (4.58 kg ha^{-1}) plots indicating that chemical weathering rates are similar between the two plots. If the dissolution of cations from aluminosilicate minerals is assumed to be similar between the bedrock and forested plots then the total removal of base cations by vegetative uptake in the forested U1f plot may be closer to 114 eq ha^{-1}. A large proportion of the difference in H^+ export between the forest and bedrock plots is attributed to the uptake of Ca^{2+} and K^+ by aggrading vegetation in exchange for H^+. The forested U1f plot exported more inorganic aluminum (15 eq ha^{-1}) than the bedrock plot which may reflect the exchange of H^+ for interlayer aluminum in the vermiculite clay fraction of forest soils.

Assuming the U1b lichen-bedrock plot was at steady state in terms of ion-exchange and vegetative uptake, the net weathering of the underlying microcline feldspar meta-granite surface resulted in the net export of 85 eq ha^{-1} of base cations, 105 eq ha^{-1} Al (assuming Al^{3+}), 18 eq ha^{-1} Fe^{2+} and 4.6 kg ha^{-1} of Si. As much as 70% of the total Al and all of the Fe were exported as organic complexes. Approximately 70% of the total export of base cations from the U1b bedrock plot could be attributed to atmospheric sources.

Horizontal changes in chemistry between bedrock and forest areas

The separation of the dominant landscape units allowed the examination of changes in water chemistry as water moved from one landscape unit through another. This allowed us to assess how the position of a landscape unit within a catchment affected runoff chemistry. This analysis was undertaken for two landscape combinations. The first, was to determine the influence of the lichen-bedrock surface on forest runoff and secondly to assess the effect of a forest plot on upslope bedrock-lichen runoff chemistry.

To assess the first situation the transfer of runoff from plot U3f (forested) across plot U3b (bedrock), was examined (Fig. 7a). Concurrent

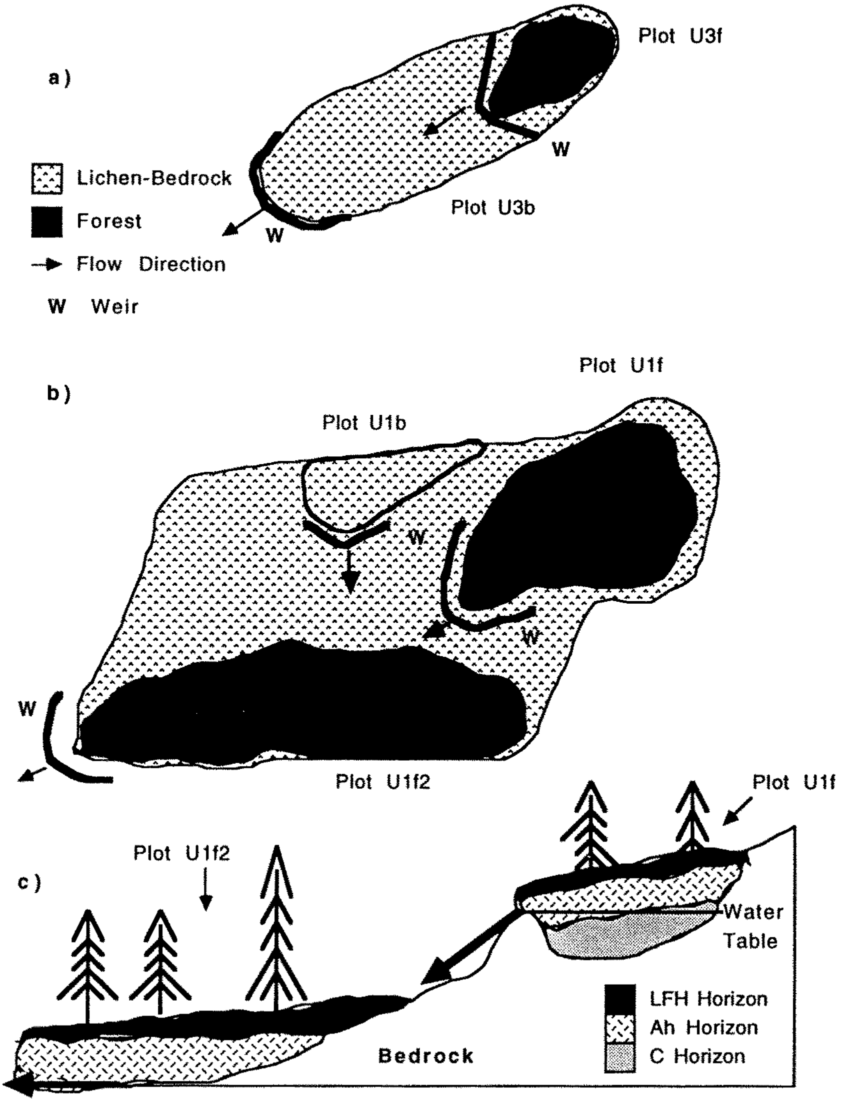

Fig. 7. Schematic diagram illustrating the combinations of forest and bedrock plots used to assess the changes in water chemistry as runoff passes through different landscape elements. Note the different subsurface hydrologic flowpaths in the U1f and U1f2 forest plots resulting from the presence of the bedrock sill beneath plot U1f (Fig. 7c).

water chemistry samples were compared when discharge at the U3b and U3f weirs were equal or discharge at the lower U3b was lower than the upslope weir. This occurred during the recession period of runoff events after runoff from the lower lichen-bedrock U3b plot, had ceased.

The changes in runoff chemistry from the forested plot U3f after having moved across the bedrock plot for six runoff events from 1989 are summarised in Fig. 8. Phosphorus, Fe, DOC, DIC, H^+, $RCOO^-$ and Al decreased while Ca^{2+} increased in concentration during all six events. During four of the events NO_3^- displayed little or no change in concentration. However, NO_3^- concentrations increased 20 and 37 times during two events which occurred after extended dry periods. All other chemical variables measured either did not change significantly or exhibited no consistent pattern of change.

The decrease in H^+ and Al^{n+} at the U3b outlet was largely balanced by the decrease in $RCOO^-$ and the increase in Ca^{2+}. Calcium appeared to be contributed to forest runoff through ion exchange rather than weathering reactions as Si concentrations did not increase as runoff moved across the bedrock-lichen surface. The ion exchange sites on the lichen-bedrock surface are initially exposed to runoff relatively high in Ca^{2+} from overland flow generated from lichen bedrock surfaces. During recession flows the ion exchange matrix on the lichen-bedrock surface is exposed to overland flow from soil islands which is characterised by high H^+ and Al^{n+} and low Ca^{2+} levels. Under these conditions ion exchange sites on the lichen-bedrock surfaces are likely not in a steady-state condition and Ca^{2+} on ion exchange sites would be expected to be exchanged for H^+ and Al^{n+}. The increase in pH attributable to the degassing of dissolved CO_2 as runoff exits the forest soils is insignificant. Aluminum and Fe associated with organic matter are likely precipitated on the bedrock surface as DOC is taken up by the lichen-moss community or degraded on the lichen-bedrock surface. Increases in NO_3^- concentrations after extended dry periods reflects the mobilization of mineralized nitrogen that accumulated between rain events.

To assess the effect of the forest stands on runoff from upslope bedrock-lichen areas, a mass balance for the May—October period, 1990 was constructed for the U1f and U1f2 forested plots within catchment U1 (Fig. 7b). Inputs to the forested plots consist of runoff from upslope bedrock-lichen areas (BR) and throughfall inputs (TF). Prorated hydrochemical inputs as measured at the bedrock plot U1b outlet weir were used to simulate inputs from bedrock-lichen areas to both forested plots. Canopy fluxes as measured by the throughfall collectors in catchment U3 were prorated and used to simulate atmospheric inputs to the forested areas within the U1f and U1f2 plots. In addition to the above inputs the lower U1f2 plot received runoff from the upslope forested U1f plot. Outputs from the U1f and U1f2 plots were measured at the U1f and U1 outlet weirs respectively. Differences between inputs and outputs could then be attributed to retention or mobilisation within the forest soil horizons. Results are summarised in Tables 5 and 6.

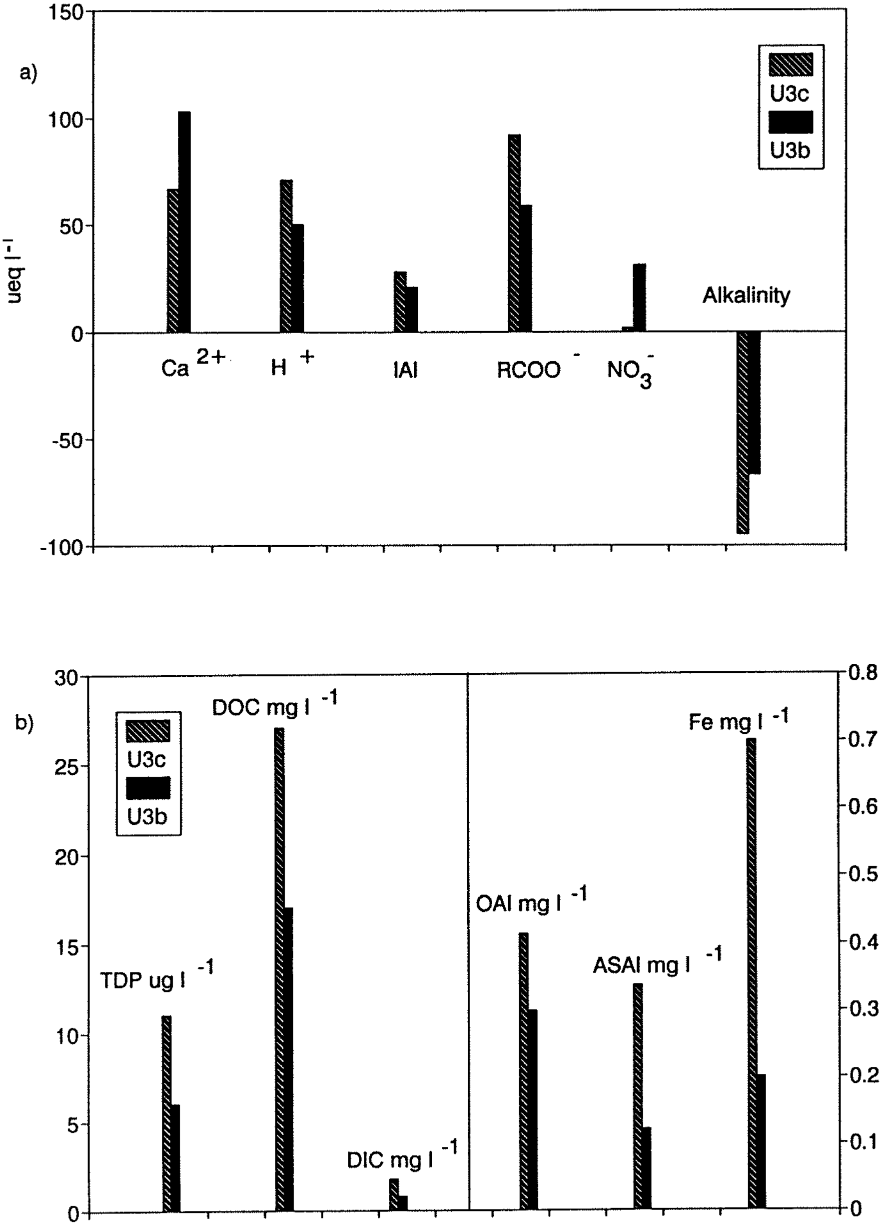

Fig. 8. Average change in U3f forest plot runoff chemistry after passing through the downslope U3b lichen-bedrock plot. Data summarises six runoff events that occurred between May 26 and August 20, 1989. Water samples were collected during recession flows when discharge at the lower U3b weir was $\leqslant$ to discharge measued at the upslope U3f weir.

Table 5. 1990 post snowmelt (May—Oct) elemental input/output budgets for the treed soil island areas in plot U1f. Units are in g or eq. Inputs to the soil island are from throughfall (TF) and upslope bedrock runoff (BR). Export from the treed island was measured directly at the U1f outflow. Retention in forest soils (R) = TF + BR − U1f. Negative numbers indicate a net export of material from U1f forest soils. Numbers in parenthesis indicate percentage of total inputs each input source contributed.

	TF	BR	U1f	R	%R
Nitrogen					
NO$_3^-$ eq	2.6 (52)	2.4 (48)	0.1	4.9	99
NH$_4^+$ eq	1.0 (61)	0.7 (39)	0.3	1.4	80
TDN g	102.9 (47)	114.4 (53)	94.1	123.2	57
Part. N g	28.9 (30)	67.9 (70)	7.4	89.4	92
TN g	131.8 (42)	182.3 (58)	101.5	212.5	68
Phosphorus g					
TDP	1.1 (44)	1.4 (56)	1.1	1.4	56
Part. P	7.0 (37)	11.8 (63)	1.0	17.8	95
TP	8.1 (38)	13.2 (62)	2.1	19.1	90
Carbon g					
DIC	218.0 (53)	193.0 (47)	314.7	96.3	23
DOC	2551.0 (49)	2697.0 (51)	5369.6	−121.6	−2
Part. C	355.2 (26)	1002.0 (74)	113.5	1244.2	92
TC	3124.2 (45)	3892.0 (55)	5797.7	1218.4	17
Cations eq					
H$^+$	1.4 (26)	4.0 (74)	15.2	−9.8	−181
Ca^{2+}	7.9 (50)	8.0 (50)	4.1	11.7	74
Mg^{2+}	3.8 (51)	3.6 (49)	4.1	3.2	44
Na$^+$	0.6 (16)	3.2 (84)	3.7	0.1	3
K$^+$	3.2 (68)	1.5 (32)	0.5	4.2	89
TAl g	8.7 (11)	68.3 (89)	161.8	−84.8	−110
IAl	0.2 (7)	2.3 (93)	4.3	−1.9	−76
OAl g	3.6 (10)	33.5 (90)	75.0	−37.9	−102
Fe g	5.1 (12)	37.2 (88)	91.5	−49.3	−117
Mn g	11.2 (77)	3.3 (23)	1.3	13.2	91
Anions eq					
Cl^{-1}	2.0 (69)	0.9 (21)	0.8	2.1	73
SO$_4^{2-}$	3.7 (34)	7.2 (66)	8.3	2.6	24
RCOO$^-$	9.8 (43)	12.8 (57)	23.1	−0.6	−3
Si g	16.4 (6)	281.4 (94)	421.9	−124.1	−42

Chemical variables strongly retained in forest soils in both forest plots included inorganic N, particulate nitrogen, phosphorus and carbon, Ca^{2+}, Mg^{2+}, K$^+$, Mn and Cl$^-$. There were significant differences in element retention between the two forest sites. The upslope U1f soil horizons

Table 6. 1990 post snowmelt (May—Oct) elemental input/output budgets for the treed area in the U1f2 plot. Units are in g or eq. Inputs to the treed island are from throughfall (TF), the upslope U1f forested plot (U1f) and upslope bedrock runoff (BR). Export was directly measured as U1 runoff. Retention (R) = TF + BR + U1f − U1. Negative numbers indicate a net export of material from U1f2 forest soils. Numbers in parenthesis indicate percentage of total inputs each input source contributed.

	Throughfall	BR	U1f	U1	R	%R
Nitrogen						
NO_3^- eq	6.6 (36)	11.8 (64)	0.1 (0)	0.7	17.7	94
NH_4^+ eq	2.6 (42)	3.3 (52)	0.3 (6)	1.6	4.6	74
TDN g	265.6 (29)	564.4 (61)	94.1 (10)	388.0	536.1	58
Part. N g	74.5 (18)	334.7 (80)	7.4 (2)	33.0	383.6	92
TN g	340.0 (25)	899.1 (67)	101.5 (8)	421.0	919.7	69
Phosphorus g						
TDP	2.8 (26)	6.9 (64)	1.1 (10)	4.0	6.8	63
Part. P	18.0 (24)	58.1 (75)	1.0 (1)	5.0	72.1	94
TP	20.8 (24)	65.0 (74)	2.1 (2)	9.0	78.9	90
Carbon g						
DIC	562.4 (31)	951.5 (52)	314.7 (17)	1675.0	153.7	8
DOC	6583.3 (26)	13305.3 (53)	5369.6 (21)	15655.0	9602.7	38
Part. C	916.5 (15)	4942.5 (83)	113.5 (2)	558.0	5396.5	91
TC	8062.3 (24)	19199.2 (58)	5797.7 (18)	17888.0	15171.2	46
Cations eq						
H^+	3.6 (9)	19.8 (51)	15.2 (40)	34.0	4.5	12
Ca^{2+}	20.4 (32)	39.3 (62)	4.1 (6)	29.3	34.5	54
Mg^{2+}	9.7 (31)	17.8 (56)	4.1 (13)	18.6	13.1	41
Na^+	1.6 (7)	15.8 (75)	3.7 (18)	16.4	4.6	22
K^+	8.3 (51)	7.5 (46)	0.5 (3)	2.5	13.8	85
TAl g	22.4 (4)	337.2 (65)	161.8 (31)	575.0	−53.6	−10
IAl	0.4 (3)	11.3 (70)	4.3 (27)	17.6	−1.6	−10
OAl g	9.2 (4)	165.3 (66)	75.0 (30)	266.0	−16.5	−7
Fe g	13.0 (5)	183.2 (63)	91.5 (32)	222.0	65.8	23
Mn g	28.8 (62)	16.3 (35)	1.3 (3)	10.0	36.4	78
Anions eq						
Cl^{-1}	5.2 (50)	4.5 (43)	0.8 (7)	3.3	7.3	69
SO_4^{2-}	9.4 (18)	35.6 (67)	8.3 (15)	34.4	18.9	36
$RCOO^{-1}$	25.3 (23)	63.0 (57)	23.1 (20)	81.8	29.6	27
Si g	42.3 (2)	1388.2 (75)	421.9 (23)	1978.0	−125.6	−6

acted as a significant source of H^+, Al, Fe and Si (Table 5) while the soils in the lower forest plot, U1f2, acted as sinks or minor sources of these elements to downslope runoff (Table 6). The downslope forest soils appeared to act as a sink for DOC, $RCOO^-$ and Na^+ whereas inputs were balanced by outputs in upslope U1f soils.

Possible explanations for the variation between the two sites include differences in the degree of hydraulic flushing (i.e. soil water contact), dissimilar hydrologic flow paths, differences in the relative proportions of bedrock vs throughfall inputs and differences in soil chemistry. During 1990 the soils in the lower forest island were potentially flushed (vol. soil/ vol. H_2O input), ≈ 1.6 times more than an equivalent soil mass in the upslope U1f plot. Increased hydraulic flushing would decrease soil/water contact duration resulting in more dilute and possibly less acidic soil waters. Hydrometric measurements indicate that drainage from the U1f plot is controlled by a bedrock sill (Allan & Roulet 1993). This sill prevents water from exiting the forest stand through the lower mineral soil horizons and routes runoff laterally through acidic surface Ah and LFH soil horizons rather than deeper, less acidic mineral soils nearer the base of the soil profile (Fig. 7c). Runoff exiting the U1f plot would then be expected to be aluminum rich and have high levels of organic acidity. Soil water in the U1f2 plot drains through the entire soil profile increasing soil-water contact with deeper, less acidic mineral soils. Runoff from the lower U1f2 plot would be expected to be less acidic as dissolved organic carbon and its associated organic acidity, Fe and Al is retained on reactive sesquioxides in the lower mineral soils.

The upper U1f forest soils were generally more acidic and had much higher exchangeable Al totals than downslope U1f2 soils (Table 7). The downslope soils appeared to have higher crystalline and amorphous Al, Fe and Si contents as well as more adsorbed SO_4^{2-}. We are unable to conclude that the above differences between the U1f and U1f2 soils are statistically significant owing to the small sample size from each site (N = 3) and the site specific variability. However, the range of values of the variables in Table 7 did not overlap between sites while all other measured soil variables exhibited similar values between sites. The differences in reactive soil aluminum and acidity combinedwith different subsurface hydrologic flow paths and flushing rates account for the differences in DOC, H^+, $RCOO^-$, Si, Fe and Al export between the two forested plots. The mass of Si weathered from the forest soils of the two forested plots was estimated as the difference between prorated Si exports from the U1b bedrock plot (representing Si export from lichen-bedrock areas of the U1f and U1f2 plots) and the total Si export measured at the plot outlet. Silica exports were 2.1 and 3.0 g^{-3} of soil for the U1f2 and U1f plots respectively. The lower Si mobilization in the downslope plot may reflect lower weathering rates as a consequence of the immobilization of organic acids in the mineral soils of the U1f2 plot.

Atmospheric deposition, washout from the forest canopy and weathering of the bedrock-lichen surfaces account for the majority of all the chemical elements exported from the two forested plots. Significant

Table 7. Soil characteristics of the Ah soil horizons in the treed island area of the U1f and U1f2 forest plots.

Soil parameter	Extraction method		U1f N = 3	U1f2 N = 3
pH	$CaCl_2$ ext.	$\bar{x}$	3.81	4.31
		Range	3.80—3.84	4.23—4.35
		CV[1]	6.5	14.0
Al meq/100 g	NaCl ext.	$\bar{x}$	7.59	1.76
		Range	7.53—7.72	1.26—2.22
		CV	1.8	39.0
SO_4 ug/g	NaH_2PO_4 ext.	$\bar{x}$	59	425
		Range	32.3—95.5	228.0—558.0
		CV	70.0	60.0
Al %Dry Wt.	$(NH_4)_2C_2O_4$ ext.	$\bar{x}$	1.56	2.13
		Range	1.03—1.81	1.97—2.24
		CV	39.0	3.1
Fe %Dry Wt.	$(NH_4)_2C_2O_4$ ext.	$\bar{x}$	1.01	1.80
		Range	0.33—1.34	1.35—2.46
		CV	85.0	34.0
Si %Dry Wt.	$(NH_4)_2C_2O_4$ ext.	$\bar{x}$	0.08	0.42
		Range	0.03—0.11	0.21—0.47
		CV	80.7	47.1

[1] CV = coefficient of variation.

amounts of Al, H^+, Fe and Si are exported from the forest soils of the upper U1f plot but only Al and Si are exported from downslope soils. The repeating sequences of forested soil deposits within this landscape appears to efficiently retain much of the dissolved and particulate material that is been transported within these catchments. Nitrogen, phosphorus and Cl^- from atmospheric deposition are strongly retained within the soil islands and base cations from both atmospheric deposition and weathering reactions in lichen-bedrock and forested areas are removed through vegetative uptake in the soil islands. The exchange of base cations for H^+ through vegetative uptake and the mobilization of degrading organic compounds from thin organic rich soils result in forest runoff waters with high levels of organic acidity and low concentrations of base cations. The position of the forest stand in relation to the bedrock areas and the underlying bedrock microtopography which controls water movement determine the soil islands element retention characteristics, hence both the heterogeneity and the spatial distribution of landscape elements need to be assessed to explain material cycling within these systems.

Whole watershed runoff

The runoff waters sampled at the outflow of the various catchments are a mixture of runoff that has passed through a series of bedrock-lichen and forested areas. Upslope runoff is integrated within forest soils in the lower part of each basin before exiting each catchment outlet. We again utilise the U1 catchment to characterise runoff from this landscape as it comprises our longest continuous period of monitoring.

Dissolved organic nitrogen comprised 78% of the total export of nitrogen from the U1 catchment (Fig. 6a). Particulate forms comprised 11%, 53% and 3% of the total export of nitrogen, phosphorus, and carbon respectively. The forest soils in the U1f2 plot, retained most of the particulate material exported from the upslope bedrock-lichen areas in catchment U1 (Figs. 6a—6c). Sulphate became an increasingly important anion in runoff chemistry as DOC and associated $RCOO^-$ was immobilised in the mineral soils of the catchment (Figs. 6c and 6g). Sulphate comprised 35% of the anion charge balance in runoff waters, compared with 22% of the anion total in LFH soil leachates. In general, the waters sampled at the U1 outlet were less acidic and lower in Al and DOC than runoff from the U1f forest plot (Figs. 6c—6e). Runoff from the bedrock-lichen areas contained more inorganic nitrogen, Ca^{2+}, K^+ and particulate material than whole catchment runoff (Figs. 6a—6d).

Annual chemical budgets

The annual chemical budgets for the study catchments are presented in Tables 8, 9 and 10. Annual mass balance estimates are not presented for catchments U3 and U4 and the U3b and U3f plots for 1989 and 1990 as these areas were utilised in a catchment manipulation experiment where H_2SO_4 and NH_4NO_3 were added to the U3 and U4 snowpack. Catchments U1 and U8 served as natural controls and were not affected by the manipulations. Catchment U2 was not monitored in 1988 and 1990. The single year records are included to provide insights as to the variability of annual element retention amongst the study catchments.

Chemical variables which exhibited consistent annual retention within the upland watersheds include nitrogen, phosphorus (Tables 8, 9, 10). Elements which switched among years from net accumulation to being in balance or showing a net loss were Ca^{2+}, Mg^{2+}, Na^+, Cl^- and SO_4^{2-}. Elements which consistently exhibited a net export from the watersheds

Table 8. 1988 elemental budgets (units in kg ha^{-1} yr^{-1} or eq ha^{-1} yr^{-1}), (± 1 SD hydrological, analytical and sampling uncertainties).

	Bulk deposition	U1	U3	U4	U8
Nitrogen					
NO_3^- eq ha^{-1}	173 ± 33	6 ± 1	6 ± 1	3 ± 0	4 ± 0
NH_4^+ eq ha^{-1}	196 ± 37	5 ± 1	6 ± 1	3 ± 0	4 ± 0
TDN kg ha^{-1}	8.44 ± 1.60	1.21 ± 0.08	1.53 ± 0.15	1.06 ± 0.10	1.23 ± 0.14
Part. N kg ha^{-1}	0.62 ± 0.12	0.17 ± 0.01	0.27 ± 0.02	0.23 ± 0.01	0.23 ± 0.03
TN kg ha^{-1}	9.06 ± 1.90	1.38 ± 0.09	1.80 ± 0.18	1.29 ± 0.12	1.46 ± 0.18
Phosphorus kg ha^{-1}					
TDP	0.055 ± 0.010	0.022 ± 0.001	0.027 ± 0.002	0.022 ± 0.002	0.019 ± 0.002
Part. P	0.058 ± 0.011	0.020 ± 0.001	0.029 ± 0.002	0.026 ± 0.002	0.024 ± 0.003
TP	0.113 ± 0.024	0.042 ± 0.002	0.056 ± 0.004	0.048 ± 0.004	0.043 ± 0.006
Carbon kg ha^{-1}					
DIC	2.12 ± 0.40	4.05 ± 0.28	4.72 ± 0.49	2.41 ± 0.23	4.81 ± 0.46
DOC	27.58 ± 5.24	40.82 ± 2.55	55.59 ± 5.01	34.53 ± 2.40	46.97 ± 4.80
Part. C	7.70 ± 1.46	1.57 ± 0.09	2.49 ± 0.19	2.18 ± 0.14	1.89 ± 0.20
TC	37.40 ± 9.04	46.44 ± 2.92	62.80 ± 5.41	39.12 ± 2.77	53.67 ± 5.46

Table 8 (Continued)

	Bulk deposition	U1	U3	U4	U8
Cations eq ha^{-1}					
H^+	73 ± 14	108 ± 6	125 ± 10	56 ± 4	94 ± 9
Ca^{2+}	169 ± 32	91 ± 8	115 ± 9	111 ± 7	104 ± 9
Mg^{2+}	53 ± 10	57 ± 3	67 ± 6	53 ± 3	81 ± 7
Na^+	53 ± 10	43 ± 3	48 ± 4	35 ± 2	44 ± 3
K^+	11 ± 2	15 ± 1	22 ± 2	16 ± 1	19 ± 2
TAl kg ha^{-1}	—	1.34 ± 0.09	1.58 ± 0.14	0.99 ± 0.07	—
Fe kg ha^{-1}	0.10 ± 0.02	0.37 ± 0.02	0.61 ± 0.05	0.24 ± 0.02	0.47 ± 0.05
Mn kg ha^{-1}	0.10 ± 0.02	0.07 ± 0.00	0.07 ± 0.01	0.06 ± 0.01	0.05 ± 0.01
Anions eq ha^{-1}					
Cl^-	22 ± 3	12 ± 1	15 ± 1	8 ± 1	11 ± 1
SO_4^{2-}	183 ± 16	125 ± 8	123 ± 8	102 ± 6	140 ± 10
$RCOO^-$	—	176 ± 14	239 ± 19	161 ± 10	191 ± 17
Si kg ha^{-1}	0.12 ± 0.02	4.37 ± 0.27	4.21 ± 0.33	3.20 ± 0.21	5.91 ± 0.63

— not measured.

Table 9. 1989 elemental budgets (kg ha^{-1} yr^{-1} or eq ha^{-1} yr^{-1}), (± 1 SD hydrological, analytical and sampling uncertainties).

	Bulk deposition	U1	U2	U8
Nitrogen				
NO_3^- eq ha^{-1}	150 ± 28	10 ± 1	12 ± 13	1 ± 0
NH_4^+ eq ha^{-1}	156 ± 30	6 ± 0	6 ± 0	5 ± 0
TDN kg ha^{-1}	6.23 ± 1.18	1.24 ± 0.05	1.64 ± 0.07	1.03 ± 0.05
Part. N kg ha^{-1}	0.55 ± 0.10	0.19 ± 0.01	0.25 ± 0.01	0.09 ± 0.01
TN kg ha^{-1}	6.78 ± 1.42	1.43 ± 0.06	1.89 ± 0.08	1.12 ± 0.06
Phosphorus kg ha^{-1}				
TDP	0.044 ± 0.008	0.019 ± 0.001	0.030 ± 0.001	0.015 ± 0.001
Part. P	0.050 ± 0.010	0.020 ± 0.001	0.035 ± 0.003	0.010 ± 0.001
TP	0.094 ± 0.020	0.039 ± 0.002	0.065 ± 0.004	0.025 ± 0.002
Carbon kg ha^{-1}				
DIC	2.02 ± 0.44	5.00 ± 0.20	5.03 ± 0.21	6.88 ± 0.28
DOC	16.74 ± 3.18	43.43 ± 1.72	65.43 ± 2.73	46.58 ± 2.12
Part. C	8.00 ± 1.52	1.71 ± 0.07	2.66 ± 0.17	1.10 ± 0.06
TC	26.76 ± 6.50	50.14 ± 1.79	73.12 ± 3.01	54.56 ± 2.18
Cations eq ha^{-1}				
H^+	52 ± 10	107 ± 4	174 ± 7	92 ± 4
Ca^{2+}	98 ± 19	101 ± 4	102 ± 4	113 ± 5
Mg^{2+}	30 ± 1	62 ± 2	74 ± 3	95 ± 4
Na^+	19 ± 1	52 ± 2	58 ± 2	70 ± 3
K^+	8 ± 0	14 ± 1	17 ± 1	13 ± 1
TAl kg ha^{-1}	0.14 ± 0.03	1.66 ± 0.07	2.19 ± 0.08	2.45 ± 0.11
IAl	—	47 ± 2	52 ± 2	77 ± 3
OAl kg ha^{-1}	—	0.82 ± 0.03	1.02 ± 0.04	1.17 ± 0.05
Fe kg ha^{-1}	0.10 ± 0.02	0.77 ± 0.04	1.15 ± 0.04	0.76 ± 0.03
Mn kg ha^{-1}	0.05 ± 0.01	0.05 ± 0.00	0.03 ± 0.00	0.03 ± 0.00
Anions eq ha^{-1}				
Cl^-	11 ± 0	14 ± 1	14 ± 1	22 ± 1
SO_4^{2-}	130 ± 5	133 ± 5	152 ± 6	191 ± 8
$RCOO^-$	—	232 ± 9	305 ± 12	251 ± 10
Si kg ha^{-1}	0.08 ± 0.002	5.23 ± 0.21	6.09 ± 0.22	8.00 ± 0.31

— not measured.

included carbon, K^+, Al, Fe, Si, and $RCOO^-$. A net export of H^+ occurred from all of the study catchments for each year with the exception of catchment U4 in 1988, which exhibited a net retention of H^+.

The annual precipitation depth was relatively constant for the study period, varying by only a factor of 1.08 (max/min), while the annual runoff totals varied by a factor of 1.4 to 1.7. This reflects the sensitivity of

Table 10. 1990 elemental budgets (kg ha^{-1} yr^{-1} or eq ha^{-1} yr^{-1}), (± 1 SD reflecting hydrological, analytical and sampling uncertainties).

	Bulk deposition	U1	U8
Nitrogen			
NO_3^- eq ha^{-1}	104 ± 20	1 ± 0	1 ± 0
NH_4^+ eq ha^{-1}	111 ± 21	4 ± 0	3 ± 0
TDN kg ha^{-1}	4.00 ± 0.76	0.81 ± 0.07	0.70 ± 0.08
Part. N kg ha^{-1}	0.69 ± 0.13	0.08 ± 0.01	0.06 ± 0.01
TN kg ha^{-1}	4.69 ± 0.98	0.89 ± 0.08	0.76 ± 0.09
Phosphorus kg ha^{-1}			
TDP	0.032 ± 0.006	0.010 ± 0.001	0.009 ± 0.001
Part. P	0.080 ± 0.015	0.013 ± 0.001	0.008 ± 0.001
TP	0.112 ± 0.024	0.023 ± 0.002	0.017 ± 0.002
Carbon kg ha^{-1}			
DIC	2.03 ± 0.39	3.32 ± 0.32	3.52 ± 0.30
DOC	15.11 ± 2.87	31.98 ± 2.89	31.45 ± 3.85
Part. C	9.69 ± 1.84	1.18 ± 0.10	0.73 ± 0.09
TC	26.83 ± 6.67	36.48 ± 3.31	35.70 ± 4.24
Cations eq ha^{-1}			
H^+	37 ± 10	66 ± 6	57 ± 5
Ca^{2+}	115 ± 22	61 ± 4	73 ± 6
Mg^{2+}	42 ± 8	39 ± 2	61 ± 5
Na^+	15 ± 3	34 ± 2	50 ± 4
K^+	7 ± 1	7 ± 0	11 ± 1
TAl kg ha^{-1}	0.16 ± 0.03	1.17 ± 0.10	1.64 ± 0.17
IAl	—	36 ± 2	61 ± 5
OAl kg ha^{-1}	—	0.54 ± 0.05	0.68 ± 0.07
Fe kg ha^{-1}	0.07 ± 0.01	0.44 ± 0.04	0.50 ± 0.06
Mn kg ha^{-1}	0.05 ± 0.01	0.02 ± 0.00	0.02 ± 0.00
Anions eq ha^{-1}			
Cl^{-1}	12 ± 2	7 ± 0	10 ± 1
SO_4^{2-}	141 ± 27	76 ± 5	126 ± 10
$RCOO^-$	—	163 ± 10	179 ± 14
Si kg ha^{-1}	0.09 ± 0.02	3.98 ± 0.30	6.55 ± 0.61

— not measured.

the watersheds to the timing and intensity of rainfall and snowmelt inputs as well as the magnitude of input. Atmospheric loading of all chemical variables exhibited a greater inter-annual variability than input volume did. Atmospheric inputs of dissolved organic nitrogen, Mn, and Na^+ all exhibited differences of 2 times or more from one year to the next. The retention or net export of NO_3^-, particulate nitrogen and carbon, phos-

Table 11. Inputs (I), export (E), and net losses or gains (G) of elements from terrestrial watersheds underlain by crystalline bedrock. Units for major ions are in eq ha^{-1} yr^{-1} units of kg ha^{-1} yr^{-1} are used for TN, TP, DOC, Si, Fe and TAl. (+) indicates net gain; (−) net loss.

	Watershed U1[1]			Watershed U8[1]			Rawson Lake NW1F[2]		
	I	E	G	I	E	G	I	E	G
NO_3^-	142	7	+135	142	2	+140			
NH_4^+	154	5	+149	154	4	+150			
TN	6.84	1.24	+5.60	6.84	1.12	+5.72	6.25	0.92	+5.33
TP	0.11	0.035	+0.08	0.11	0.028	+0.08	0.32	0.04	+0.28
DOC	19.8	38.7	−18.93	19.8	41.7	−21.9			
H^+	54	94	−40	54	81	−27	99	41	+58
Ca^{2+}	127	84	+43	127	97	+30	189	232	−43
Mg^{2+}	42	53	−11	42	79	−37	76	174	−98
Na^+	29	43	−14	29	55	−26	68	116	−48
K^+	9	12	−3	9	14	−5	28	20	+8
TAl	0.15	1.39	−1.24	0.15	2.04	−1.89			
Fe	0.09	0.53	−0.44	0.09	0.58	−0.49		0.58	
Cl^{-1}	15	11	+4	15	14	+1	60	15	+45
SO_4^{2-}	151	111	+40	151	152	−1	94	76	+18
Si	0.10	4.53	−4.43	0.10	6.82	−6.72	1.12	10.86	−9.74

Table 11 (Continued)

	Hubbard Brook Watershed 6[3]			Turkey Lake[4]			Sogndal[5] SOG1 and SOG3		
	I	E	G	I	E	G	I	E	G
NO_3^-	332	247	+85	398	211	+187	80	9	+71
NH_4^+	144	13	+131	221	8	+213	90	5	+85
TN									
TP	0.14	0.03	+0.11						
DOC	14.2	16.4	−2.2						
H^+	992	126	+866	461	9	+452	158	18	+140
Ca^{2+}	90	574	−484	196	1188	−992	55	161	−106
Mg^{2+}	41	230	−189	72	236	−164	80	91	−11
Na^+	65	287	−222	71	157	−86	395	425	−30
K^+	20	49	−29	32	46	−14	58	35	+23
TAl	0.23	3.20	−2.97						
Fe									
Cl^-	164	124	40	81	61	+20	418	409	+9
SO_4^{2-}	762	1087	−325	770	767	+3	230	209	+21
Si	0.37	35.60	−35.23					4.21	

[1] Summary of 1988—90 record for U1 and U8, this study.
[2] After Schindler et al. 1976, Table 5.
[3] After Likens 1985, Table II.B-6.
[4] After Nicolson 1988, Table 1.
[5] After Frogner 1989, Table 1.

phorus, K^+, Mn and Fe from catchment U1 and/or U8 all exhibited greater inter-annual variability than the variability in annual runoff. The inherent variability exhibited by these systems during a period of relatively constant precipitation indicates a much longer period of monitoring would be necessary to accurately determine average inputs and losses from these systems.

With few exceptions, the annual retention or net export of material was consistent between catchments (Tables 8, 9, 10). However, the yield per unit area of an element often differed by a factor of 2 or more between adjacent catchments.

Element retention in zero order and first order catchments

A summary of the elemental budgets for catchments U1 (zero order), and U8 (first order) is presented in Table 11. On a unit area basis catchment U8 exported considerably more Mg^{2+}, Na^+, TAl, SO_4^{2-} and Si than U1. All other parameters were exported from both catchments at similar unit area levels. The differences between catchments can be attributed to increased humic or mineral soil-water contact and a greater percentage of forest cover in the U8 catchment. The U8 catchment has a higher areal coverage of soil and soil deposits (> 1 m thick), than the zero order catchments. The only overland flow ever observed in the U8 catchment occurred in small areas near the catchment divides and the outlet weir. Runoff in the first order catchment U8 is routed through more extensive and possibly deeper soil pathways, contributing to longer soil-water residence times and an increased export of soil derived elements. The thicker soil profiles in catchmnet U8 also present a greater mineral surface area for weathering reactions.

The magnitude of SO_4^{2-} retention differs between the two catchments. Sulphate inputs are essentially balanced by exports over the 1988—90 period within catchment U8, while catchment U1 retained $\approx 25\%$ of its SO_4^{2-} input. Both catchments exhibited variable interannual retention of SO_4^{2-}, Ca^{2+} and Cl^-. They followed the same pattern of net retention during 1988 and 1990, and net loss during 1989. A possible explanation for these differences relates to the proportion of total annual runoff contributed by snowmelt. During 1989 51—60% of the annual runoff for catchments U1 and U8 was contributed by snowmelt compared to 45—51% and 22—38% for 1988 and 1990 respectively. The relatively large volumes of water, extremely high runoff coefficients (up to 80%) and minimal biologic demand during the snowmelt period may have resulted in the small positive export of SO_4^{2-}, Ca^{2+} and Cl^- observed for both catchments in 1989.

During 1988—89 the annual export of cations from catchment U1 and U8 averaged 332 and 389 eq ha^{-1} yr^{-1} (considering only the IAl aluminum component in the cation charge total), while the export of inorganic anions averaged 129 and 168 eq ha^{-1} yr^{-1}. The 56—61% anion charge deficit indicates that $RCOO^-$ is the single largest anion component of the runoff waters for the study catchments. For the three years of study 190 and 207 eq ha^{-1} yr^{-1} of $RCOO^-$ associated with DOC were exported on average from the U1 and U8 catchments respectively.

Comparisons with other catchments found on crystalline bedrock

An elemental budget comparison between the ELA Upland catchments and other catchments found in areas underlain by silicious bedrock is presented in Table 11. The ELA Upland catchments exhibit the lowest net base cation export rates of all the catchments examined with catchment U1 exhibiting a net retention of 15 eq ha^{-1} yr^{-1} and U8 a net export of 38 eq ha^{-1} yr^{-1}. The next lowest reported are those for the Sogndal watersheds SOG1 and SOG3, in western Norway and the nearby Rawson Lake catchment, which exhibit net cation export rates of 124 eq ha^{-1} yr^{-1} and 181 eq ha^{-1} yr^{-1}, respectively. The net base cation export rates for the Hubbard Brook (924 eq ha^{-1} yr^{-1}) and Turkey Lakes catchments (1256 eq ha^{-1} yr^{-1}) are much higher.

The low net base cation export rates characteristic of the study catchments can be attributed to the following factors. The ELA catchments are covered with snow 5—6 months of the year and receive a relatively low annual precipitation total, 510 mm. The ELA catchments also receive a low loading of strong mineral acids such as (H_2SO_4 and HNO_3) in comparison to the Hubbard Brook and Turkey Lake catchments. The thin patchy soil cover and high percentage of exposed bedrock surfaces also contribute to short soil-water contact times with a minimal volume of soil. However, the single most important factor in reducing the cation export from the ELA upland watersheds is the uptake of Ca^{2+} by aggrading forest vegetation in the treed soil islands. Tree surveys in the study catchments indicate juvenile *Picea mariana* are replacing the older *Pinus banksiana* stands within the various soil islands (Allan unpublished data). The net retention of base cations may reflect a successional change in vegetation in the study catchments. The net export of base cations from the U1b lichen-bedrock plot (85 eq ha^{-1} y^{-1}, Table 4) is higher than both the U1 and U8 catchments but less than the net base cation export rates reported for other catchments.

In addition to the net retention of Ca^{2+} in the study catchments, the net export of H^+ is also not exhibited by the nearby Rawson Lake catchment or the other terrestrial catchment examined (Table 11). The net export of H^+ is attributed to both vegetative uptake of base cations in exchange for H^+ and the mobilization of organic acids from catchment soils and lichen-bedrock surfaces. The thin patchy nature of the ELA upland soils precludes the large scale retention of mobile organic anions in deeper mineral soil horizons resulting in highly acidic organic rich soil waters been exported directly from surface LFH and Ah soil horizons.

The net mass export of dissolved material from the ELA upland watersheds is dominated by DOC (Table 11). This is in contrast to the results from Hubbard Brook where dissolved Si dominates the net mass loss of dissolved material (Likens 1985). The ELA upland watersheds export a much smaller amount of particulate material, ca. 4.3 kg ha^{-1} yr^{-1} as compared to 33.0 kg ha^{-1} yr^{-1} for the Hubbard Brook watersheds (Likens 1985).

All the catchments examined exhibit varying degrees of net retention of nitrogen (Table 11). The ELA upland catchments and the Sogndal catchments exhibit the greatest inorganic nitrogen retention, ≈ 90%. Both areas along with the Rawson Lake catchments, receive the lowest atmospheric loadings of inorganic nitrogen (296 and 170 eq ha^{-1} yr^{-1}), indicating that vegetation may be nitrogen limited in both areas. Total nitrogen retention is similar (≈ 82—85%) among the study catchments and the nearby Rawson Lake catchments.

Summary

The subdivision of the study catchments into horizontal and vertical compartments and the calculation of the elemental fluxes between these compartments emphasises the importance of the treed soil islands as areas of material retention in the upland Precambrian shield landscape. The vertical subdivision of the forest compartments indicate that several elements are actively cycled within the forest stands.

The high inorganic nitrogen, phosphorus, Mn, Ca^{2+}, Mg^{2+}, K^+, and Cl^- concentrations in throughfall and LFH soil waters combined with relatively low concentrations in forest runoff waters suggest an active cycling of these elements through biotic uptake between the forest canopy and the surface soil horizons (Fig. 6). The evidence for the non-conservative behaviour of Cl^- is perhaps surprising. In the upland catchments Cl^- concentrations increase by eight fold as water moved through the forest canopy and subsequently exhibited declines in mineral soil horizon percolates (Fig. 6). As discussed earlier this may indicate retention and, or dilution from upslope bedrock-lichen runoff. However, the mass balance data for whole catchments (Tables 8—11) and the individual forest stands (Tables 5 and 6), indicate a net retention of Cl^- within the catchments. Mass balance data from the nearbly Rawson Lake catchments also indicate a long term retention of Cl^- (Schindler et al. 1976). Our data for Cl^- is similar to that reported for the Hubbard Brook watersheds (Likens 1985), with Cl^- fluctuating between net accumulation and net loss annually, but exhibiting a long term net retention of 20—30%. The forest canopy was a major internal source of DOC, $RCOO^-$ and H^+ within this landscape.

The separation of the catchments into horizontal subunits identifies the bedrock-lichen subareas as a source of base cations, Al, Fe and Si which are dissolved from the underlying granitic bedrock by chemical weathering reactions involving H_2CO_3 from rainfall and organic acids derived from the lichen-moss community. The lichen-moss community on open bedrock surfaces is a major internal source of carbon, $RCOO^-$, phosphorus and H^+ within this landscape. At least some of the carbon and phosphorus probably originates as pollen and forest litter transferred laterally from adjacent forest stands. Organic acids are produced as a byproduct of the metabolic activities of lichen and from degrading organic material from the lichen-moss community on the open bedrock surfaces.

In general the upland forest soils act as sinks for most elements within the study catchments. Iron, Al, Si and H^+ exhibit net losses from soil deposits near the topographic highs of the study catchment, but later both Fe and H^+ appear to be at least partly retained within downslope soil deposits. The net export of base cations from the ELA upland catchments is low in relation to the rates reported for other catchments found on silicious bedrock. Approximately 100% of the Ca^{2+}, 53—80% of the Mg^{2+}, 53—70% of the Na^+, and 64—75% of the K^+ exported from these catchments are attributed to atmospheric inputs of base cations with the remainder derived from internal weathering processes.

The dominant hydrologic flowpath within the forest stands is via subsurface stormflow through the surface LFH and Ah soil horizons resulting in runoff waters that are carbon rich and dominated by organic acidity. Despite the rapid hydrologic responses and high runoff coefficients exhibited by these headwater areas our results indicate that in a relatively pristine area the small patches of upland conifer forest effectively retained atmospheric inputs of nitrogen, phosphorus and base cations and internally weathered base cations (Ca^{2+} and K^+ in particular). The synthesis of aggrading forest vegetation and the dissolution of degrading organic material and subsequent transport of mobile organic acids both contribute to the acidification of runoff waters from this upland Precambrian shield landscape.

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