

## Solid phase controls of dissolved aluminum within upland Precambrian shield catchments

CRAIG J. ALLAN<sup>1</sup> and N. T. ROULET<sup>2</sup>

*Department of Geography, York University, 4700 Keele St., North York, Ontario, Canada, M3J 1P3; <sup>1</sup> Present address: Dept. of Geography and Earth Sciences, University of North Carolina at Charlotte, Charlotte, North Carolina, USA 28223; <sup>2</sup> Present address: Dept. of Geography, McGill University Montreal, Quebec, Canada, H3A 2K6*

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**Abstract.** Solid phase controls of dissolved aluminum chemistry of soil and surface waters were investigated in several pristine, low order Precambrian shield catchments. Soil extraction and leaching experiments were conducted to quantify the various pools of solid phase soil aluminum and their relative mobility. Reactive soil aluminum (exchangeable + organic + amorphous forms), comprised < 20% of the total soil aluminum. Leaching soils with pH 3.0 HCl solutions indicated that  $\text{Na}_4\text{P}_2\text{O}_7$  extractable aluminum (largely organic complexes) was the most mobile form of reactive soil aluminum. Aluminum hydroxide from vermiculate interlayers was also mobilized from all soil horizons and its contribution to dissolved aluminum increased with soil depth. Runoff and soil waters from organic LFH and Ah soil horizons were highly undersaturated with respect to  $\text{Al}(\text{OH})_3$  solid-phases.

Several natural bedrock surfaces (metagranites) covered with moss or lichen were leached with HCl solutions. Significantly more aluminum was removed from bedrock surfaces colonized with the moss *Racomitrium microcarpon* compared to that of the lichen-covered surfaces. Aluminum removal increased dramatically as the acidity of the leaching solution increased to pH 3.0. Leachates solutions collected from bedrock surfaces became increasingly undersaturated with respect to  $\text{Al}(\text{OH})_3$  minerals at lower pH values. Aluminum solubility appears to be controlled by equilibrium with organic complexation, modified by kinetically constrained dissolution of interlayer aluminum.

## Introduction

Solubility of dissolved aluminum within soil and surface waters has been the subject of much research (Cronan et al. 1986, Lawrence et al. 1988, Neal et al. 1987 and others), because of potential acidification-induced aluminum toxicity to both terrestrial and aquatic biota (Driscoll et al. 1980, Hinrichsen 1986). In the present study we examine the relationship between the solubility of aluminum in soil and runoff waters of zero-order Precambrian shield catchments and the spatial distribution of solid phase aluminum compounds within the catchments. Potential sources and mobility of solid phase aluminum compounds from natural bedrock outcrops and forest soils are investigated.

Many studies indicate that the solubility of aluminum can vary spatially and temporally within soil and surface waters. Solutions often appear to be close to saturation with respect to some form of solid phase aluminum trihy-

dioxide ( $\text{Al}(\text{OH})_3$ ) (Christophersen et al. 1982, Nordstrom & Ball 1986). In these instances the solubility of  $\text{Al}^{3+}$  can be predicted by the relationship:

$$\text{pAl}^{3+} = 3\text{pH} - \log K$$

where  $K$  is the thermodynamic equilibrium constant.

Undersaturation with respect to  $\text{Al}(\text{OH})_3$  has been reported during episodes of high flow (Hooper & Shoemaker 1985, Sullivan et al. 1986). Hooper & Shoemaker (1985) hypothesized that kinetic constraints on the formation of labile aluminum may lead to the depletion of the pool of reactive soil aluminum causing apparent undersaturation with respect to  $\text{Al}(\text{OH})_3$  during periods of high flow. Sullivan et al. (1986) suggested that transient decreases in aluminum mineral saturation indices during high flow events are the result of the increased routing of runoff laterally through organic-rich surface soil horizons. Field investigations of low pH ( $< 4.5$ ), organic-rich soil and surface waters have indicated consistent  $\text{Al}^{3+}$  undersaturation with respect to a mineral  $\text{Al}(\text{OH})_3$  phase (Cronan 1980, Driscoll et al. 1985, LaZerte 1989).

The solubility control of dissolved aluminum in soil and surface waters by solid-phase organically bound aluminum has been suggested by several authors. Bloom et al. (1979) concluded that the exchange of aluminum from carboxyl sites on soil organic matter was the most important factor controlling soil solution  $\text{Al}^{3+}$  in acid soils with relatively low permanent cation exchange capacities. Mulder et al. (1989a), Dahlgren & Walker (1993) and Mulder & Stein (1994) presented experimental evidence indicating that pyrophosphate extractable, non-silicate, organically-bound aluminum is readily solubilized from sandy podzols in acidic soil solutions. Field investigations by Mulder et al. (1991) in both pristine and acid-impacted catchments in Norway indicated that dissolved aluminum concentrations in surface waters were influenced by Al-enriched, near-stream, organic soils during intermediate flow and by Al-depleted, forest floor solutions, during periods of high flow. Studies by Cronan et al. (1986), LaZerte (1989) and Helmer et al. (1990) concluded that a combination of mineral solubility and humic adsorption processes accounted for temporal and spatial variability in aluminum solubility in organic-rich waters. In some instances an apparent mineral solubility control may be misleading. For example, Walker et al. (1988) demonstrated that exchange reactions on clay mineral surfaces with exchange capacities approaching 50% saturation with aluminum could sustain aqueous aluminum concentrations similar to those reported for aluminum trihydroxide solid phases.

From these studies it is apparent that temporal variations in surface water aluminum chemistry must be considered in the context of the spatial distribution of multi-phase reactive pools of aluminum in catchment soils and

the dominant hydrologic flow paths in a catchment. This paper presents the results of laboratory and field studies of the aluminum chemistry in soil and surface waters of several pristine, low order, Precambrian shield catchments. The objectives of the study were to: 1) quantify the distribution and size of the pools of soil aluminum; 2) determine the relative ease of dissolution of various soil aluminum fractions; 3) examine the potential release of dissolved aluminum from natural bedrock surfaces; and 4) relate the spatial distribution of solid phase aluminum compounds to the observed solubility of aluminum in soil and surface waters within the study catchments.

## Study area

The study area is located at the Experimental Lakes Area (ELA) northwestern Ontario, Canada (49°40'N, 93°43'W). The catchments are characterized by small vegetated (conifer) soil islands (21–40% aerial coverage), interspersed amongst open areas of lichen-covered granitic bedrock. The overstory of the forested soil islands is dominated by black spruce (*Picea mariana*) and jackpine (*Pinus banksiana*). The open bedrock areas are covered by varying amounts of crustose and fruticose lichens, mosses and juniper shrubs.

The ELA upland watersheds are underlain by leucocratic coarse grained metagranites. Bedrock mineralogy consists of quartz, feldspars (microcline and andesine) and biotite. The underlying bedrock is unfractured and forms a water-tight seal beneath the catchments. The catchments contain deposits of glacio-lacustrine sediments up to 1 m thick in depressions on the underlying bedrock surface.

Catchment soils are thin and consist of truncated orthic humic regosols and sombric brunisols (CSSC, SSC 1978), with a silty loam texture and a 5–15 cm thick organic layer at the surface. Chemical and physical parameters of catchment soils are presented in Table 1. A typical soil profile consists of a surface LFH horizon underlain by one or more Ah soil horizons. The Ah horizons are characterized as a zone of maximum organic matter accumulation rather than a zone of organic matter eluviation (CSSC, SSC 1978). In deeper soil deposits, a C or Cg horizon may sometimes be present. Bulk Ah horizon soil chemistry ( $n = 5$ ) comprised 75% SiO<sub>2</sub> (sd = 5%), 15% Al<sub>2</sub>O<sub>3</sub> (sd = 2%), 4% Fe<sub>2</sub>O<sub>3</sub> (sd = 2%), 2.4% K<sub>2</sub>O (sd = 0.2%) and 1.7% Na<sub>2</sub>O (sd = 0.4%) by weight. The clay fraction consists of hydroxy-interlayered vermiculite, smectite and kaolinite. The aluminum-hydroxy interlayers within the vermiculite represent a potential source/sink for labile aluminum (Bloom et al. 1977).

The dominant runoff mechanisms operating within the catchments consist of Horton overland flow from the open bedrock areas and shallow subsurface stormflow and saturation overland flow from the thin forested soil islands.

*Table 1.* Chemical and physical characteristics of the upland catchment soils. Numbers in parenthesis represent the coefficient of variation about the mean expressed as a percentage.

Soil Horizon	LFH	Ah1	Ah2	Ah3	C
N	11	9	5	1	3
Thickness cm	9.0 (58)	16.5 (47)	15.8 (61)	9.1	8.3 (49)
Sand %	—	32.9 (34)	27.6 (20)	22.0	46.0 (—) <sup>a</sup>
Silt %	—	51.4 (23)	63.6 (5)	70.0	51.0 (—)
Clay %	—	15.6 (36)	8.4 (37)	7.0	3.0 (—)
Bulk Density kg m <sup>-3</sup>	190 (41)	653 (100)	714 (32)	—	—
pH CaCl <sub>2</sub> <sup>1</sup>	3.35 (41)	3.46 (105)	4.12 (53)	4.06	4.87 (26)
H <sub>2</sub> O <sup>2</sup>	3.96 (52)	3.91 (120)	4.55 (78)	4.24	5.02 (26)
CEC meq 100 g <sup>-3</sup>	16.3 (21)	7.0 (49)	3.2 (83)	2.0	1.52 (60)
Base Sat % <sup>4</sup>	60.9 (34)	17.2 (53)	11.4 (47)	7.4	13.6 (46)
% Organic Carbon <sup>5</sup>	32 (27)	9.9 (63)	4.0 (49)	1.0	3.8 (82)

— not measured.

<sup>a</sup> Bulk density was only determined for one sample.

<sup>1,2</sup> Glass electrode determination on a 10 g soil: 20 mL 0.01 M CaCl<sub>2</sub> or distilled H<sub>2</sub>O slurry after a 20 min. agitation and 30 min. equilibration period.

<sup>3</sup> CEC calculated as the sum of exchangeable Ca + Mg + K meq 100 g<sup>-1</sup>. Soil extractions performed with 1 M NaCl followed by analysis of Ca, Mg and K by AAS

<sup>4</sup> Per cent base saturation calculated as:

$$\% \text{ Base Sat.} = \frac{\text{Ca} + \text{Mg} + \text{K}}{\text{Ca} + \text{Mg} + \text{K} + \text{Al}} * 100$$

\* All cations are exchangeable as operationally defined by extraction with 1 M NaCl followed by analysis of Ca, Mg, K and Al by AAS.

<sup>5</sup> UIC coulometric combustion furnace with electrometric titration.

Organic LFH and Ah soil horizons are highly permeable ( $K_{fs} > 1.0 \times 10^{-2}$  m sec<sup>-1</sup>), (Allan & Roulet 1994) and rapidly transmit water laterally when water tables rise into surface soils during rain and snowmelt events.

## Methods

### *Field sample collection*

Soil and runoff waters were collected from watersheds, designated as U1–U4 and U8, during the period 1987–1990. Water samples were also collected at the outlet of small subcatchments in the larger watersheds to characterize runoff from open lichen-bedrock surfaces and forested soil islands (Allan et

al. 1993). LFH soil solutions were collected from zero tension lysimeters (screened plexiglass boxes) that drained by gravity into collecting bottles. Soil water from Ah and C soil horizons was sampled using alundum plate tension lysimeters. Tension plates were cleaned before installation (Neary & Tomassini 1985), and left to equilibrate in the ground eight months prior to sampling.

### *Analytic techniques*

Analyses for  $\text{NO}_3^-$ ,  $\text{NH}_4^+$  (autoanalyzer colorimetry) and pH (glass electrode determination) in surface and soil waters were performed at ELA usually within 24 hours of collection. Cation ( $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Na}^+$ ,  $\text{K}^+$  and Fe) determinations were made on filtered samples by atomic absorption spectrophotometry,  $\text{SO}_4^{2-}$  and  $\text{Cl}^-$  by ion chromatography and Si by colorimetric detection after reaction with molybdate. Analyses were conducted at the Department of Fisheries and Oceans (DFO), Freshwater Institute (FWI), analytical laboratory. Total labile aluminum (TCVAI), and labile organic aluminum (OAI) were determined at ELA using a manual catechol-violet ion exchange procedure similar to that reported by LaZerte et al. (1988). Inorganic labile aluminum (IAI) was calculated as the difference between TCVAI and OAI. Inorganic aluminum speciation was determined with the chemical speciation program ALCHEMI (Schecher & Driscoll 1987). Thermodynamic calculations were corrected for the effects of temperature and ionic strength. Fluoride concentrations used for the speciation of inorganic aluminum in surface and soil waters were estimated from the following empirical relationship developed from ELA upland soil waters and bedrock and soil runoff waters (Allan et al. 1993):

$$F(\mu\text{g/l}) = \text{SC}(\mu\text{S @25 }^\circ\text{C}) * 1.26 - 8.31 \quad r^2 = 0.95, P \leq 0.01$$

where SC is specific conductance. Total aluminum (TAI) was measured by DC plasma emission spectrometry at the FWI metals laboratory.

Bulk soil chemistry was determined by the fusion with lithium tetraborate and subsequent analysis by X-ray fluorescence spectrometry. Clay mineral analysis involved size fractionation followed by X-ray diffraction analysis of six different treatments: 1) Ca-saturated at 54% relative humidity (RH); 2) Ca-saturated and glycolated; 3) K-saturated at 0% RH; 4) K-saturated at 54% RH; 5) K saturated at 300 °C; and 6) K-saturated at 550 °C. Analyses for bulk soil mineralogy and clay minerals were performed at the Soil Laboratory of the University of Western Ontario.

*Soil extractions and soil leaching experiments*

A series of laboratory soil extractions and leaching experiments were performed to: 1) quantify the size of the various pools of solid phase aluminum within the upland soil profiles; and 2) determine the source of dissolved aluminum from the various soil aluminum fractions under acidic leaching conditions. Soil samples were collected from the exposed faces of soil pits. All analyses were performed on the < 2 mm fraction of air dried soil. Various solid phase aluminum fractions within the upland soils were assessed with a sequential selective extraction procedure similar to that performed by Mulder et al. (1989a) and Dahlgren & Walker (1993). Two gram soil samples were used in all extraction and leaching experiments. The easily exchangeable fraction of aluminum was determined for each sample by extracting soils with 100 mL 1M KCl for 0.5 hour. Samples were filtered and the aluminum content of the filtrate determined. The KCl leached soils and filters were then extracted with 100 mL 0.1 M  $\text{Na}_4\text{P}_2\text{O}_7$  for 16 hours. Samples were filtered again and the filtrate analyzed. Results from the  $\text{Na}_4\text{P}_2\text{O}_7$  extraction are assumed to represent organically bound aluminum and minor amounts of non-crystalline hydrous aluminum hydroxides (interlayer aluminum and other relatively labile forms of surface precipitated aluminum, McKeague et al. 1971). The samples and filters were then extracted with 100 mL 0.2 M  $(\text{NH}_4)_2\text{C}_2\text{O}_4$  adjusted to pH 3.0 for 4 hours in the dark. Aluminum from this extraction represents amorphous aluminum hydroxides, short-range-order aluminosilicates such as allophane and imogolite, and a portion of the interlayer aluminum from 2:1 layer silicates (Schwertmann 1964, Dahlgren & Walker 1993). Samples were continuously shaken during all extractions. Aluminum concentrations for each stage of the extraction were corrected for residual aluminum left from the previous extraction and any evaporative loss that may have occurred during the filtration. Six replicate extractions from an Ah and a LFH horizon soil were performed to assess the reproducibility of the method. Aluminum concentrations in the filtrates were determined by atomic absorption at the Ontario Ministry of the Environment, (OME), Dorset research facility. Total soil aluminum was determined by X-ray fluorescence spectroscopy of a Li-tetraborate melt of the soil material at the University of Western Ontario, Department of Geology, soils laboratory.

The relative ease of dissolution of the various reactive aluminum soil fractions was assessed in a laboratory leaching experiment. Soils from each horizon of three upland soil profiles (T11-1, T11-2, T13-2), were leached for a total of 10, 30 and 50 days. During the three leaching cycles a 2-gram sample was leached every 24 hours with 100 mL of a pH 3.0 HCl solution in a capped centrifuge bottle at room temperature. Suspensions were shaken manually three times every 24 hours. Leaching solutions appeared to

reach equilibrium with the soil in < 2 hours. After a 24-hour equilibration period, suspensions were centrifuged at 2,000 rpm for 15 minutes. Eighty millilitres of the clear supernatant was poured off and replaced with 80 mL of fresh HCl solution. No attempt was made to keep the pH of the leaching solution constant and pH increased over the 24-hour period. Sub-samples of supernatant from each soil sample were pooled and submitted for analyses at 10, 30 and 50 days. Supernatants were kept frozen to prevent algal and fungal growth. At the end of each of the three leaching cycles, the leached soils were selectively extracted (as outlined above) and analyzed for the various fractions of solid phase aluminum. Analyses for aluminum, major ions, and Si in the HCl leachate solutions were performed at the OME Rexdale analytic laboratories (OME 1981). Fluoride concentrations were directly measured for HCl leachate solutions with an ion selective electrode after TISAB addition. Soil extracts were analyzed for aluminum at the OME Dorset research facility as outlined above. Six replicates of an Ah and a LFH horizon soil were leached over a 10-day period and the pooled supernatants were analyzed for aluminum, major ions and Si to assess reproducibility. Blanks were run simultaneously during all extraction and leaching trials.

#### *Bedrock surface leaching experiments*

A field leaching experiment was conducted to assess the potential removal of aluminum from natural bedrock surfaces. Eight  $\approx 1 \text{ m}^2$  plots were isolated with plywood diversion walls sealed with fibreglass to the underlying bedrock surface. The bedrock underlying seven of the plots consisted of a meta-granite with the following mineralogy: 35% Quartz, 35% Andesine and 30% Microcline. One plot (C2) was underlain by a tonalitic quartzo-feldspathic ortho gneiss with the following mineralogy: 35% quartz, 45% Andesine, 5% Microcline and 15% Biotite. Five of the bedrock plots contained surfaces covered with a crustose lichen cover (CC, C1–C4). Two plots (FC and F1) contained bedrock surfaces covered with fruticose lichen (*Cladina sp.*). One plot (M), contained a bedrock surface covered with the moss *Racomitrium microcarpon*.

All plots were initially leached with 6 L ( $\approx 6 \text{ mm}$ ) of distilled water and two plots, one which contained a fruticose lichen cover (FC) and another with a crustose lichen cover (CC), received three additional leachings with distilled water and served as references. There was no reference plot for the moss containing plot. The other six plots received 6 L each of pH 5.0, 4.0 and 3.0 HCl solutions consecutively after the initial distilled water rinse. Each addition was sprinkled on each plot over 1/2 hour and the runoff at the base of each plot was collected with a peristaltic pump. Runoff coefficients were determined by dividing the runoff volume by the area of the plot and

leachate solutions were analyzed in the same manner as soil and surface waters. Fluoride concentrations for distilled water and pH 5.0 and pH 4.0 leachates were determined with the same regression relationship used for soil and surface waters. Specific conductance values measured for pH 3.0 HCl leachates exceeded the range for which the conductance/fluoride relationship was established. It was decided to apply the maximum directly measured fluoride concentration for ELA upland waters ( $26 \mu\text{g L}^{-1}$ ) as a constant in aluminum speciation calculations for the pH 3.0 leachate solutions.

## Results and discussion

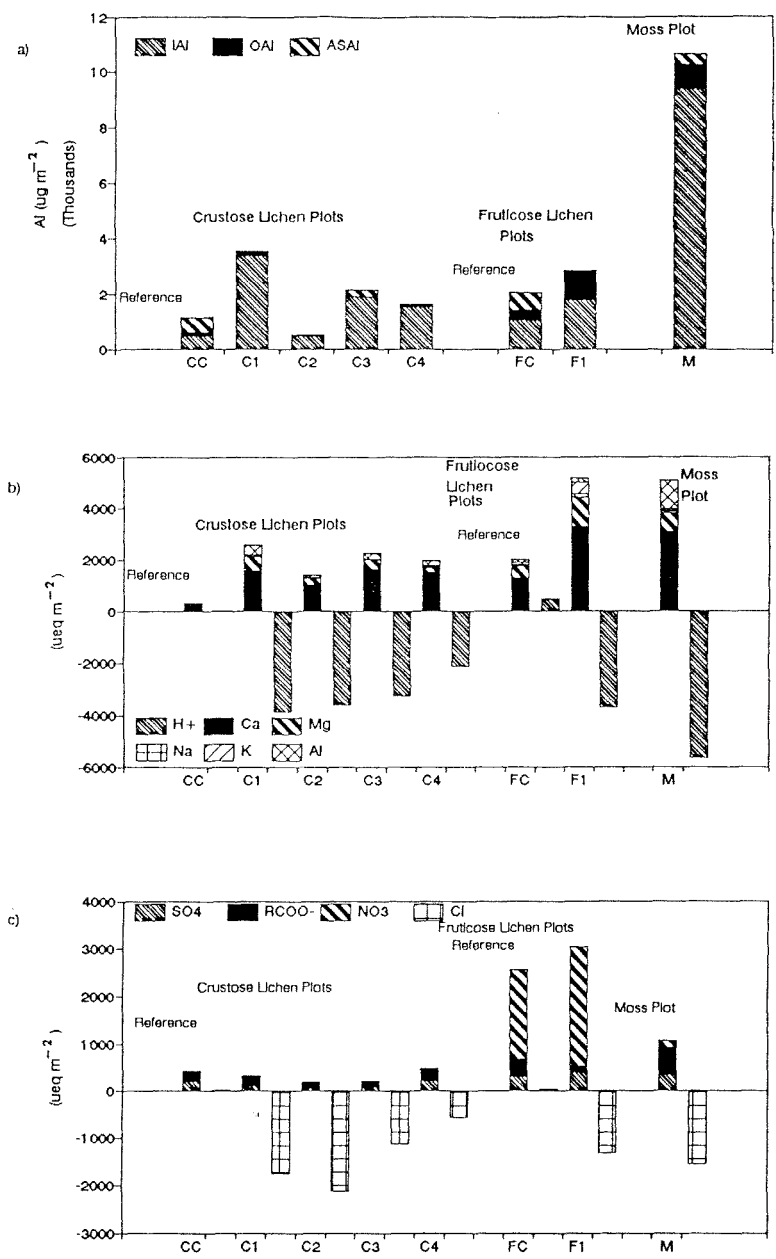
### *Removal of aluminum from natural bedrock surfaces*

The amount of aluminum mobilized from the crustose and fruticose lichen-covered bedrock surfaces ranged from 545 to  $3578 \mu\text{g m}^{-2}$  (Fig. 1a). Significantly more aluminum was removed from the moss-covered bedrock surface of plot M, ( $10,666 \mu\text{g m}^{-2}$ ) compared to that of the lichen-covered surfaces. This may be a result of a higher CEC of the moss surfaces as compared to lichen surfaces or, may be a function of the location of moss colonies in relation to forested soil deposits. Typically, colonies of *R. microcarpon* on dry granitic outcrops are located such that they receive prolonged seepage from upslope forest areas (Vitt 1991). *Racomitrium* colonies are exposed to prolonged soil island runoff that is characterized by high aluminum concentrations (Allan et al. 1993). This soil-derived aluminum may have been mobilized during the leaching experiment. Aluminum totals removed from the plot underlain by the ortho-gneiss bedrock (C2) were 15–20% of the totals removed from the metagranite plots with the same lichen cover (C1, C3 and C4) and only 46% that of the reference crustose lichen plot CC. This reflects differences in the amount of labile material on the various plot surfaces and the weathering susceptibility of the more resistant orthoclase feldspars as compared to the more easily weathered plagioclase feldspars (Brunskill et al. 1971).

Labile inorganic aluminum (IAI) comprised the majority of the aluminum mobilized from all the plots except the crustose lichen reference plot (CC) where acid soluble aluminum (polymeric and strong organically bound aluminum) comprised 46% of the aluminum removed. Appreciable quantities of labile aluminum organic complexes (OAI) were detected in leachates from the plots with moss (M,  $905 \mu\text{g m}^{-2}$ ) and fruticose lichen covers (FC,  $340 \mu\text{g m}^{-2}$  and F1,  $1085 \mu\text{g m}^{-2}$ ).

The amount of aluminum recovered from the second and third leaching solutions from the crustose lichen plots and the moss-covered plot tended to be lower than levels recorded from the first distilled water application (Fig. 2a).





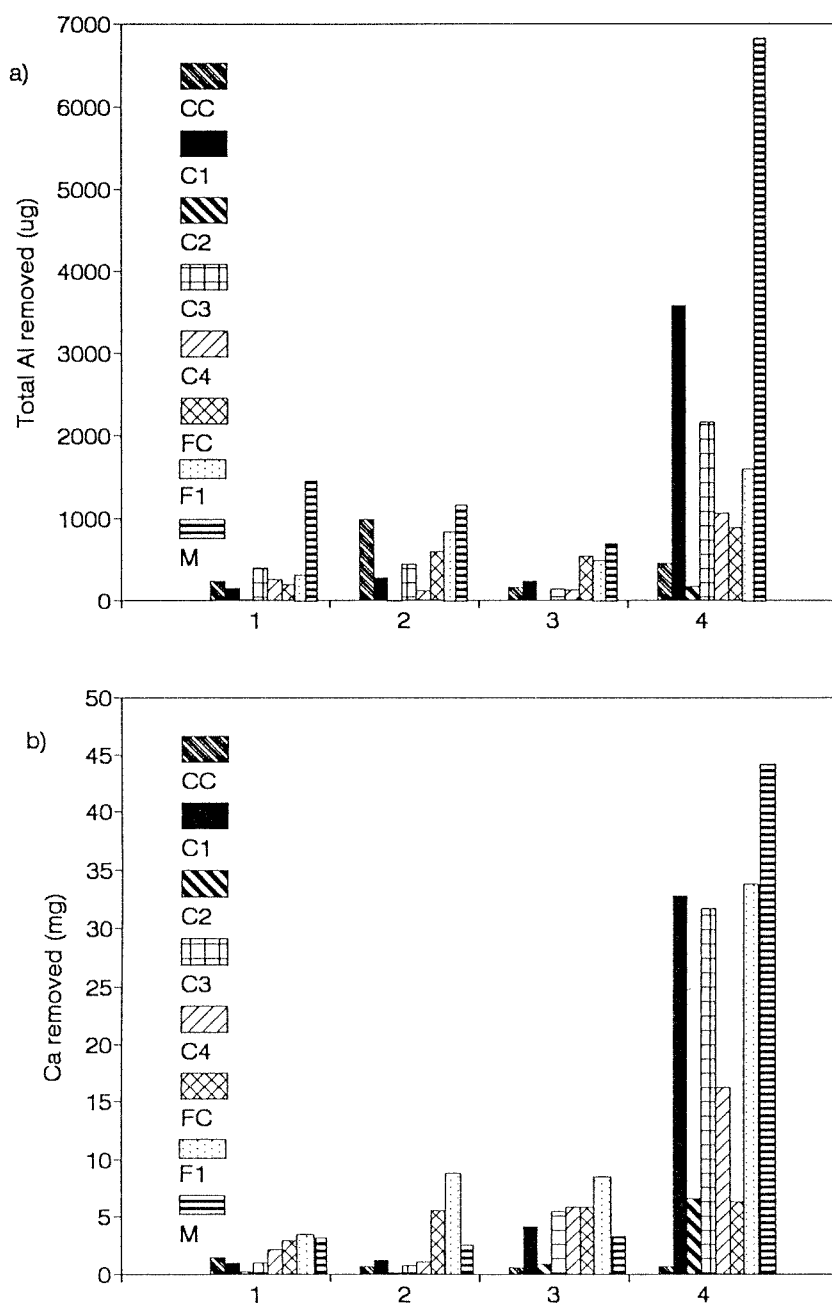
**Fig. 1.** A) Aluminum fractions ( $\mu\text{g m}^{-2}$ ) removed from natural bedrock surfaces. Plots CC-C4 represent crustose lichen covered surfaces. Plot M contained a moss covered bedrock surface and plots FC and F1 contained fruticose lichen covered surfaces. Plots CC and FC were references which received four applications of distilled water. All other plots were leached successively with pH 5.0, pH 4.0 and pH 3.0 HCl solutions after an initial distilled water rinse. B)  $\text{H}^+$  neutralization and cation export from the natural bedrock surfaces. C) Anion export from the natural bedrock surfaces.

Calcium leaching from these plots tended to increase with the application of the pH 4.0 leaching solutions, and calcium and aluminum removal increased dramatically with the application of the pH 3.0 leaching solutions (Fig. 2a and b). This indicates that most crustose lichen and moss covered surfaces contain a relatively small pool of easily solubilized aluminum at the pH of most rain events at ELA ( $> \text{pH } 4.0$ ). Aluminum removed during the initial distilled rinse (1–10% of the total for experimental plots) is attributed to the flushing of labile material from lichen-bedrock surfaces. This labile pool of material includes dry deposition, mineralization products and evaporates from previous runoff events. Cations leached from the fruticose lichen plots (FC and F1) tended to increase with each successive leaching solution application, reflecting increased hydrologic yields as the lichen colony is first wetted and then flushed.

The large increase in cation removal in response to the pH 3.0 leaching solution is attributed to the displacement of aluminum and other cations from mineral and organic exchange sites by the high levels of  $\text{H}^+$  in residual pH 4.0 HCl solutions and the final pH 3.0 leaching solution, as well as the congruent and incongruent dissolution of feldspars and mafic minerals on the bedrock surfaces. It is difficult to determine the relative importance of ion exchange reactions and chemical weathering. There is a strong linear relationship between  $\text{Al}^{3+}$  and pH (Fig. 3), which may indicate an ion exchange solubility control for  $\text{Al}^{3+}$ . Increasing contributions of cations from chemical weathering is indicated by changes in the relative proportions of cations removed as the acidity of the leaching solutions increased (Fig. 4).

Two distinct trends in the relative proportions of cations leached from the lichen-bedrock surfaces are evident. The relative proportion of  $\text{K}^+$  and  $\text{Na}^+$  in solution consistently declined after each subsequent leaching, and in all experimental plots, the proportion of the cation total comprised by  $\text{Ca}^{2+}$  tended to increase. No consistent trends in the relative proportions of  $\text{Al}^{n+}$  and  $\text{Mg}^{2+} + \text{Fe}^{2+}$  are evident. The decline in the relative proportions of  $\text{Na}^+$  and  $\text{K}^+$  in solution can be explained by the dissolution and removal of easily soluble K and Na salts during the first few leaching trials. The increasing proportion of  $\text{Ca}^{2+}$  in solution is evidence for the dissolution of  $\text{Ca}^{2+}$  rich plagioclase from the underlying metagranites.

The increased leaching of cations during the pH 3.0 addition was accompanied by a small concurrent increase in Si dissolution in plots C1, C4 and F1 (data not shown). Si dissolution did not increase in plots C2, C3 and M. In the plots where Si dissolution increased, the Ca:Si molar ratio were all  $\geq 9$  which is much higher than what would be expected from the congruent dissolution of plagioclase feldspars. This indicates that either ion exchange reactions are controlling cation solution concentrations or the underlying feldspars are dis-



*Fig. 2.* A) Aluminum removed from natural bedrock surfaces from applications of distilled water and HCl leaching solutions. B) Calcium removed from natural bedrock surfaces from applications of distilled water and HCl leaching solutions.

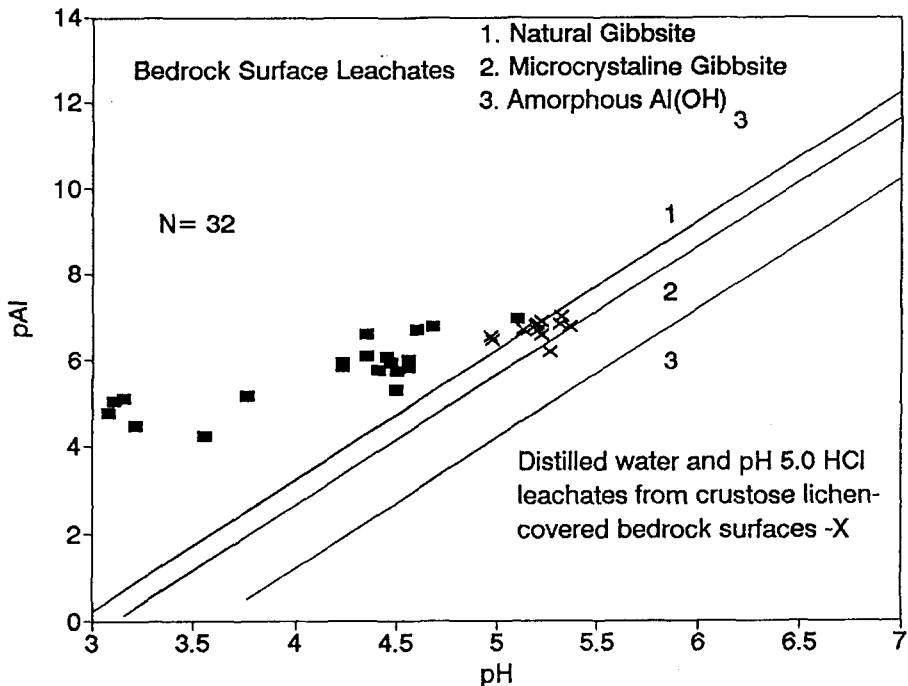


Fig. 3. Solubility diagram for bedrock HCl leachate solutions. The upper line represents equilibrium with natural gibbsite (May et al. 1979). The middle line represent equilibrium with microcrystalline gibbsite (Hem & Robertson 1967) and the lower line amorphous  $\text{Al}(\text{OH})_3$  (Stumm & Morgan 1981). The solubility for hydroxy interlayer aluminum falls between those for natural and microcrystalline gibbsite (Bloom et al. 1977).

solving incongruently. Nesbitt et al. (1991) reported that Si rich leached layers of varying thicknesses developed from incongruent dissolution on feldspars grains when exposed to HCl leaching solutions under laboratory conditions and Ca and Na depleted layers occurred on naturally weathered oligoclase outcrops in nearby areas of the Canadian Shield (Nesbitt unpublished data).

The neutralization of  $\text{H}^+$  from the HCl leaching solutions was largely accomplished through the mobilization of  $\text{Ca}^{2+}$  (28 to 88%), and to a lesser degree  $\text{Mg}^{2+}$  (8 to 31%, Fig. 1b). Aluminum was the second most important cation on a charge equivalent basis removed from the moss covered plot (M). Charge balance deviations for HCl bedrock leachates were all within 11% of cation totals, while distilled  $\text{H}_2\text{O}$  leachates from the reference plots exhibited strong cation surpluses, implying organic anions ( $\text{RCOO}^-$ ) were contributed from the lichen-covered surfaces (Fig. 1c). Several organic acids, in particular oxalic acid, are known to be produced by lichens (Wilson et al. 1981). Hydrogen ion was released from the bedrock surfaces of the reference plots (FC and CC) washed with distilled  $\text{H}_2\text{O}$ .

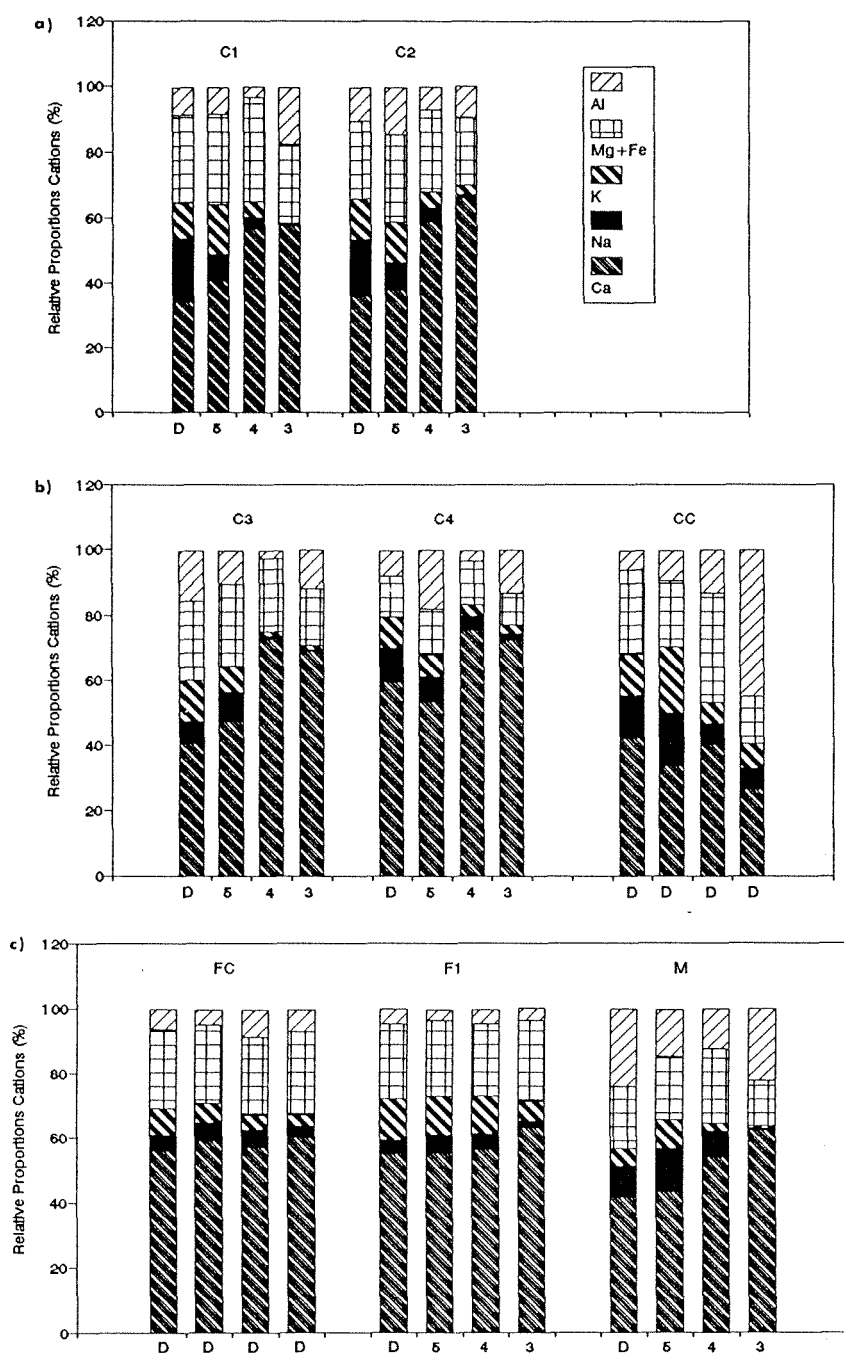


Fig. 4. Changes in the relative proportions of cations in lichen bedrock distilled water and HCl leaching solutions.

Large amounts of  $\text{NO}_3^-$  ( $> 1,885 \mu\text{eq m}^{-2}$ ), were mobilized from the fruticose lichen plots FC and F1. The increase in base cations, aluminum and  $\text{H}^+$  in distilled  $\text{H}_2\text{O}$  leachates from the two reference plots (CC and FC) was balanced by  $\text{NO}_3^-$  and to a lesser extent  $\text{RCOO}^-$  and  $\text{SO}_4^{2-}$ . The experimental plots retained 8% to 32% (555 to 2,137  $\mu\text{eq}$ ), of the  $\text{Cl}^-$  added in the HCl leaching solutions. Forty-nine to eighty-seven per cent of this  $\text{Cl}^-$  retention can be accounted for by the volume of the pH 3.0 leaching solution retained within the various plots. It is likely that the pH 3.0 HCl leaching solution also displaced earlier, less acidic leaching solutions from the lichen and moss covers of the various plots. This displacement would result in a higher retention of the pH 3.0 leaching solution than was evident by the reduced runoff volumes of the pH 3.0 treatment alone. Storage capacities measured for the various plots ranged from 3 to 9 mm. The displacement of 0.1 to 0.9 mm (4% to 30%) of the previous retained leaching solutions by the pH 3.0 solution is sufficient to account for the remaining  $\text{Cl}^-$  retained on the bedrock surfaces.

Leachates from moss and fruticose lichen covered surfaces and pH 4.0 and pH 3.0 leachates from crustose lichen covered surfaces were all undersaturated with respect to aluminum trihydroxide compounds (Fig. 3). Distilled  $\text{H}_2\text{O}$  and pH 5.0 HCl leachates from bedrock surfaces covered with crustose lichen appeared to be nearly saturated with respect to aluminum trihydroxide phases.

There are several possible explanations for the observed solubility behaviour. First,  $\text{Al}(\text{OH})_3$  minerals may be absent or in short-supply on the bedrock surfaces. As indicated earlier there is evidence that the initial leaching solutions may have depleted a limited pool of aluminum on the bedrock surfaces. In plots (C3, C4 and M) the removal of aluminum decreased by the third leaching despite increasing acidity of the leaching solutions (Fig. 2a). Secondly, short solution/surface contact times, may have resulted in runoff water being undersaturated with respect to an  $\text{Al}(\text{OH})_3$  mineral phase. The dissolution kinetics of primary aluminosilicate minerals, crystalline layer silicates, and gibbsite are exceedingly slow (Bloom 1983, Bloom & Erich 1987, May et al. 1986, Stumm & Furrer 1987). However, the solution/surface contact times during the experiments did approximate the transit time for overland flow produced during natural storm events (Allan & Roulet 1994). Finally, the nearly straight line relationship exhibited by the plotted data points in Fig. 3 could be interpreted as aluminum solubility regulation through a solid-phase humic adsorbent. The presence of significant quantities of OAl and organic acidity in reference plot leachate solutions (Fig. 1a and 1c), also implies that organic complexes influence the solubility of aluminum removed from these surfaces.

Table 2. Average pH, DOC, Si and Al concentrations in soil and runoff waters in the ELA upland catchments.

	pH	Si mg L <sup>-1</sup>	DOC mg L <sup>-1</sup>	IAI μg L <sup>-1</sup>	OAI μg L <sup>-1</sup>	TAI μg L <sup>-1</sup>
LFH	4.57	0.84	36.4	140	282	419
Ah1	4.37	2.70	41.3	487	781	1948
Ah2	4.68	3.64	18.9	203	373	823
Ah3	5.04	2.55	8.6	152	178	436
C	5.19	4.79	5.4	101	75	303
Soil Island Runoff	4.01	2.91	36.7	280	500	1080
Bedrock Runoff	4.66	1.37	17.2	94	150	340

The results from the reference plots indicate that organic acids would be mobilized from lichen-bedrock surfaces during natural runoff events and the dissolved aluminum chemistry would be dominated by labile inorganic and acid soluble forms. No significant relationship was found between DOC and the acid soluble aluminum fraction in natural lichen-bedrock runoff (data not shown), indicating this fraction comprises polymeric, microcrystalline and/or colloidal alumino-hydroxy species rather than strong aluminum-organic complexes.

#### *Aluminum solubility in natural runoff waters from lichen-bedrock surfaces*

Average aluminum chemistry and selected water quality characteristics of natural runoff from bedrock plots are presented in Table 2. Organic complexes comprise the largest fraction of labile aluminum in bedrock runoff waters (OAI:IAI; 1.6) which is much higher than the ratios in the reference plot leaching solutions (0.2 and 0.3). This probably results from bedrock surfaces being flushed by natural precipitation and throughfall solutions rather than distilled H<sub>2</sub>O and from natural runoff having a longer transit time through larger areas of fruticose lichen and moss colonies at the basin scale as compared to the plot experiments.

Average inorganic aluminum speciation for bedrock runoff was 37% Al<sup>3+</sup>, 28% aluminum hydroxides and 21% aluminum fluoride complexes. Bedrock runoff waters were often undersaturated with respect to a mineral Al(OH)<sub>3</sub> phase (Fig. 5), reflecting kinetic constraints and humic absorbent solubility controls discussed earlier. The solubility of natural gibbsite (May et al. 1979),

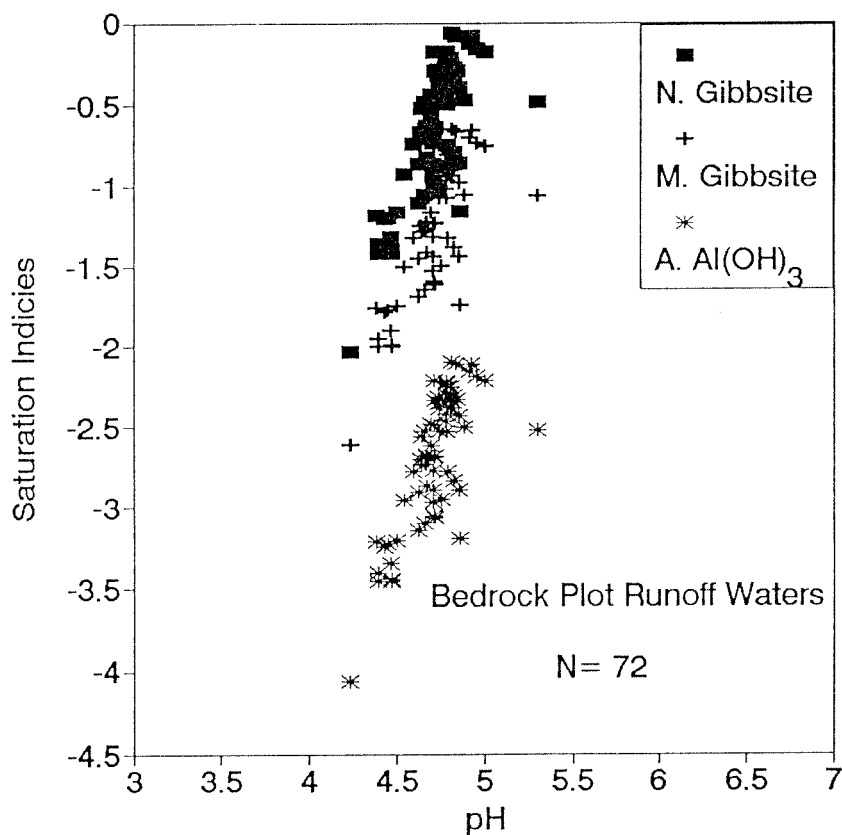


Fig. 5.  $\text{Al}(\text{OH})_3$  mineral saturation indices for natural runoff from lichen-bedrock surfaces. Positive SI values suggest that a solution is oversaturated with respect to the mineral in question, whereas negative values indicate undersaturation. Near zero values indicate an equilibrium condition.

appears to represent the upper solubility limit for dissolved aluminum in runoff from natural lichen-bedrock surfaces.

#### *Forest soil aluminum pools*

Reactive aluminum (exchangeable + organic + amorphous) comprises a relatively minor component of the total aluminum content of the soils from the forest islands (Table 3). Unreactive aluminum, which contains silicate-bound and hydroxy interlayer aluminum, comprised 71 to 96% of the total soil aluminum content.  $\text{Na}_4\text{P}_2\text{O}_7$  extractable aluminum was the largest component of the reactive pool, comprising 54 to 88% of free soil aluminum in LFH and Ah soil horizons. A comparison of pyrophosphate extractable aluminum and



Table 3. Soil aluminum pools in 3 silt loam soils from the Experimental Lakes Area, North-western Ontario.  $\pm$  values represent 1 SD. Extractable Aluminum ( $\text{mmol kg}^{-1}$ ).

Site	Depth (cm)	Horizon	KCl	$\text{Na}_4\text{P}_2\text{O}_7$	$(\text{NH}_4)_2\text{C}_2\text{O}_4$	Total Aluminum	% Reactive Aluminum
TL1-1	0-7	LFH	$6.7 \pm 0.9$	$58.4 \pm 4.7$	$19.2 \pm 2.9$	714	11.8
	7-15	Ah1	$28.2 \pm 2.8$	$188.8 \pm 13.2$	$28.3 \pm 4.0$	4137	5.9
	15-43	Ah2	$31.9 \pm 3.2$	$576.0 \pm 40.3$	$87.1 \pm 12.2$	4106	16.9
	43-58	Ah3	$15.0 \pm 1.5$	$559.9 \pm 39.2$	$234.9 \pm 32.9$	4756	17.0
TL1-2	0-8	LFH	$8.6 \pm 1.1$	$36.0 \pm 2.9$	$12.6 \pm 1.9$	213	26.9
	8-14	Ah1	$73.1 \pm 7.3$	$286.0 \pm 20.0$	$17.2 \pm 2.4$	3789	9.9
	14-33	Ah2	$52.2 \pm 5.2$	$172.5 \pm 12.1$	$4.5 \pm 0.6$	3229	7.1
TL3-2	0-5	LFH	$4.2 \pm 0.6$	$26.6 \pm 2.1$	$11.1 \pm 1.7$	146	28.8
	5-12	Ah1	$42.0 \pm 4.2$	$137.1 \pm 9.6$	$8.9 \pm 1.2$	3336	5.6
	12-16	Ah2	$45.4 \pm 4.5$	$70.4 \pm 4.9$	$14.6 \pm 2.0$	2974	4.4
TL2		C	$9.0 \pm 1.3$	$183.7 \pm 12.9$	$286.0 \pm 38.6$	4729	10.1

organic carbon content showed a range of 8–19  $\text{cmol aluminum kg}^{-1}$  organic carbon for LFH soils and 100 and 814  $\text{cmol aluminum kg}^{-1}$  organic carbon for Ah soils. Humic and fulvic acids have a range of carboxyl group contents ranging between 150–570 and 610–850  $\text{cmol kg}^{-1}$  carbon, respectively (Stevenson 1982). A comparison of pyrophosphate extractable aluminum with carboxyl content shows that in some instances aluminum concentrations derived from Ah horizon soils may exceed the amount of carboxyl sites, the primary metal-organic binding sites on soil humus. This may have occurred for the Ah2 and Ah3 samples from the TL1-1 soil profile (Table 1), and may indicate that the pyrophosphate extracted aluminum includes other forms of aluminum and thus overestimates organically bound aluminum for these two samples (Dahlgren & Walker 1993). The dominance of the reactive aluminum fraction by pyrophosphate extractable aluminum has been reported for sandy podzol soils in Europe (Mulder et al. 1989a) and northeastern North America (Driscoll et al. 1985, Dahlgren & Walker 1993).

Exchangeable soil aluminum (KCl extractable) in the Ah horizons was 2 to 11 times that of LFH horizon soils and comprised the second largest fraction of soil aluminum (22–35%), in Ah horizon soils from the TL1-2 and TL3-2 soil profiles. Ammonium oxalate-extractable aluminum formed the

second largest component of reactive soil aluminum in the Ah horizons of the TL1-1 profile and comprised the largest fraction of reactive soil aluminum (60%) in the C horizon from the TL2 site (Table 3). Total soil aluminum contents for the three profiles were relatively similar. The major difference between sites occurred in the deeper soil horizons of the TL1-1 (Ah2 and Ah3 soil horizons) and the TL2 (C horizon). There ammonium oxalate-extractable soil aluminum fractions became more important with depth. For the TL1-2 and TL3-2 sites, which are more representative of the shallow ( $\leq 30$  cm) soil cover found within the study catchments, organic and to a lesser degree exchangeable aluminum forms predominate. We cannot identify the specific solid phase aluminum form that the oxalate-extractable aluminum represents with our data. The X-ray diffraction analysis confirms the presence of substantial amounts of interlayer aluminum associated with the vermiculite clay fraction. However, the average ratio oxalate-extractable Al to Si is 2.1:1 (Al:Si ratios range from 7.8 to 0.8) indicating short range aluminosilicates such as allophane and imogilite (which can also be extracted by oxalate) may be present in the ELA upland soils (Dahlgren & Ugolini 1989, McKeague et al. 1971).

#### *Relative dissolution of soil aluminum compounds*

During the leaching experiment hydrogen ion was supplied at higher rates than those observed naturally at ELA:  $50 \text{ mmol H}^+ \text{ kg}^{-1} \text{ 24 hr}^{-1}$ , compared with  $0.2\text{--}0.4 \text{ mmol H}^+ \text{ kg}^{-1} \text{ yr}^{-1}$  from mass balance estimates (Allan et al. 1993). The pH 3.0 HCl solutions utilized in the leaching trials were  $\approx 0.9$  pH units lower than the minimum pH recorded for soil and runoff waters in the study catchments, but they were similar to the pH recorded for soil water in northwestern Europe (Mulder et al. 1989b).

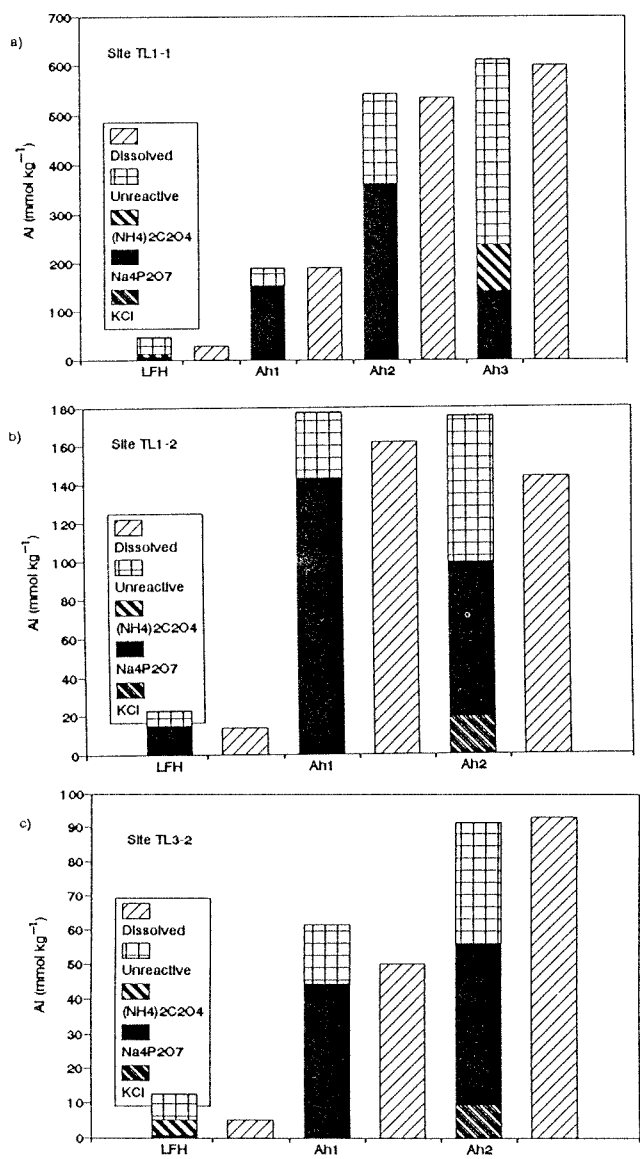
Results from the soil leaching experiments are presented in Table 4 and Fig. 6 and 7. Reactive soil aluminum comprised most of the aluminum removed from most soil horizons (Fig. 6). In several instances the aluminum extracted in the leaching solutions was in excess of the measured change in reactive aluminum of the leached soils. In these instances it was assumed unreactive aluminum contributed to dissolved aluminum totals in leachate solutions. Pyrophosphate-extractable aluminum accounted for the majority of the reactive soil aluminum solubilized. Significant removal of oxalate extractable aluminum only occurred from the LFH horizon of the TL3-2 soil profile and the Ah3 soil horizon of TL1-1 soil profile. The removal of exchangeable aluminum was only detected in the Ah2 horizons of the TL1-2 and TL3-2 soil profiles and was of secondary importance to organically bound aluminum removed from those horizons. In most instances exchangeable aluminum levels increased in LFH and Ah horizon soils following leaching

**Table 4.** Summary of aluminum removed ( $\pm$  values standard deviation) from catchment soils ( $\text{mg g}^{-1}$  soil) after 10, 30 and 50 days of leaching with pH 3.0 HCl solutions.

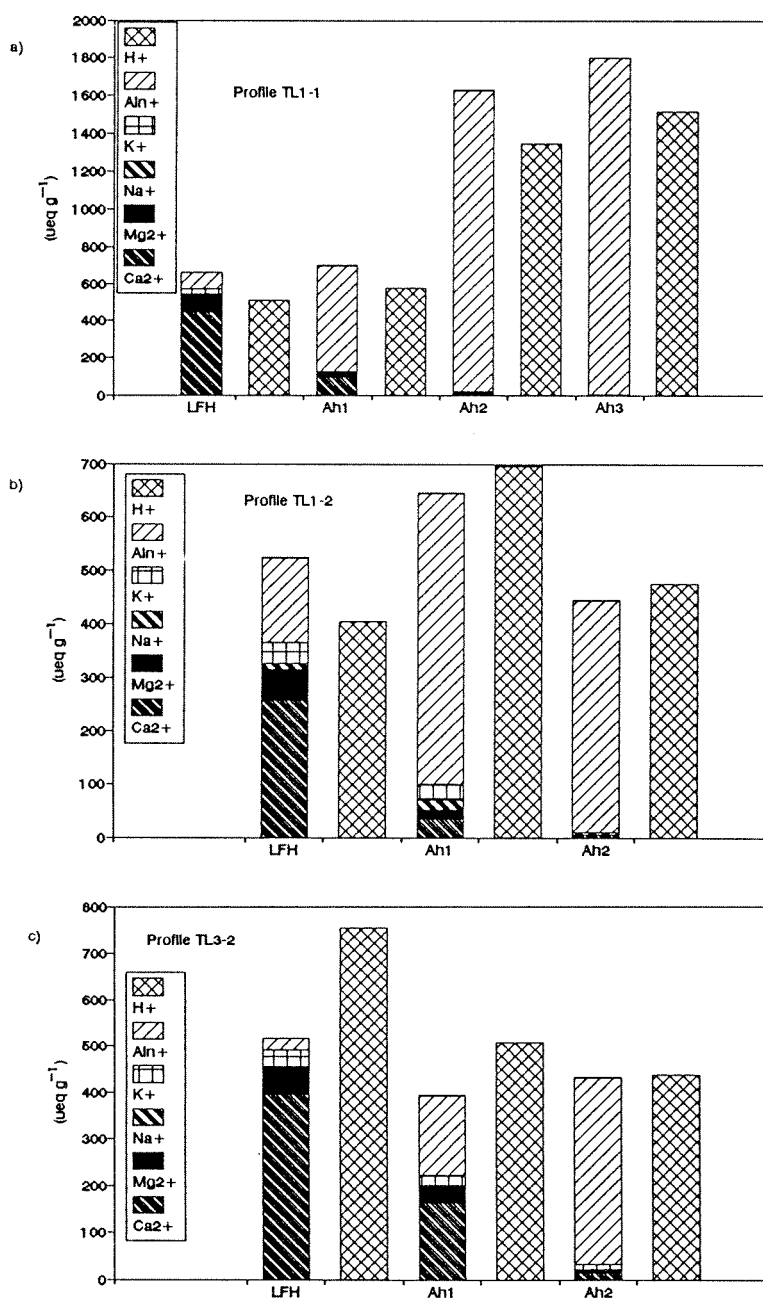
	10 Days	30 Days	50 Days
TL1-1			
LFH	$0.13 \pm 0.02$	$0.32 \pm 0.06$	$0.78 \pm 0.15$
Ah1	$1.23 \pm 0.05$	$3.88 \pm 0.16$	$5.13 \pm 0.21$
Ah2	$3.04 \pm 0.12$	$9.71 \pm 0.39$	$14.45 \pm 0.58$
Ah3	$3.20 \pm 0.13$	$10.57 \pm 0.42$	$16.18 \pm 0.65$
TL1-2			
LFH	$0.10 \pm 0.02$	$0.21 \pm 0.04$	$0.37 \pm 0.07$
Ah1	$1.12 \pm 0.04$	$4.22 \pm 0.17$	$4.36 \pm 0.17$
Ah2	$1.26 \pm 0.05$	$3.43 \pm 0.14$	$3.88 \pm 0.16$
TL3-2			
LFH	$0.10 \pm 0.02$	$0.14 \pm 0.03$	$0.19 \pm 0.04$
Ah1	$0.34 \pm 0.01$	$1.35 \pm 0.05$	$1.50 \pm 0.06$
Ah2	$0.99 \pm 0.04$	$2.51 \pm 0.10$	$3.12 \pm 0.12$

by HCl. Increases in aqueous aluminum activities in HCl leaching solutions resulted in increases of aluminum on the soil exchange matrix to maintain ion-exchange equilibrium. Percentages of total reactive soil aluminum removed after the 50 day leaching cycle ranged from 12 to 34% for LFH horizon soils and 63 to 83% for Ah2 and Ah3 horizons.

Aluminum was the dominant cation on a charge equivalent basis removed from all Ah horizons and generally the second most important cation removed from LFH horizons (Fig. 7). Calcium was the principal cation removed from LFH horizons and along with other base cations declined in importance with soil depth. Measurements obtained by the mapping of catchment soil deposits (Allan et al. 1994) and bulk density measurements indicate that Ah1 and Ah2 horizons comprise  $\approx 70\%$  of the soil mass in the study catchments. As well, Allan & Roulet (1993) identified the surface Ah horizons as the primary runoff pathways for lateral flow during storm runoff events. The results from the leaching experiment suggest that organically bound aluminum plays a major role in controlling the solubility of dissolved aluminum in soil and runoff waters within the study catchments.



**Fig. 6.** Summary of aluminum removed from three upland soil profiles after 50 days of leaching with pH 3.0 HCl. Dissolved aluminum represents aluminum removed in leaching solutions. KCl, Na<sub>4</sub>P<sub>2</sub>O<sub>7</sub> and (NH<sub>4</sub>)<sub>2</sub>C<sub>2</sub>O<sub>4</sub> aluminum represent exchangeable, organic and amorphous soil aluminum removed from HCl leached soils. Unreactive aluminum removed from HCl leached soils was assumed to equal dissolved aluminum totals in excess of reactive aluminum removed from soils. The unreactive + reactive aluminum totals exceed the dissolved aluminum total where the exchangeable aluminum totals measured for the 50 day leached soils exceeded exchangeable totals measured for the same soils prior to leaching. The increase in exchangeable Al on the leached soils was either solubilized from the unreactive or reactive Al soil fraction and does not contribute to the dissolved total.



*Fig. 7.* Neutralization of  $H^+$  in HCl soil leaching solutions and base cation solubilization from HCl leached soils. Note that the amounts of aluminum and other cations may exceed the amount of  $H^+$  neutralized as the data was not adjusted to the 'washing off' effect of the leaching solution.

The relative mobility of pyrophosphate extractable aluminum in relation to exchangeable and oxalate extractable soil fractions is similar to the results reported by Mulder et al. (1989a) for acidic sandy podzols. Contrasting Mulder's et al. (1989a) results, significant dissolution of unreactive aluminum occurred from all soil horizons in the present study. The difference is attributed to the higher  $H^+$  to soil ratio used in our study (2.5x) and differences in the physical and chemical characteristics of the soils. The ELA soils have a higher aluminum content and a finer texture than the sandy podzols investigated by Mulder et al (1989a).

The amount of unreactive aluminum removed during the 50-day leaching cycle increased with depth within each soil profile and was the largest component of soil aluminum removed from the TL1-1 LFH and Ah3 soil horizons (Fig. 7). The percentage of dissolved aluminum comprised of unreactive aluminum ranged between 35 and 75% of the dissolved total for LFH horizon and 19 and 61% for Ah horizon soils. The amount of Si removed from all soil horizons was extremely small (0.01–0.16 mg  $g^{-1}$ ) in relation to its elemental abundance. The molar ratio of dissolved Si:unreactive aluminum for all leachates was  $< 0.013$ . The minor amounts of Si in the leaching solutions indicates that the source of unreactive aluminum was from an Al-rich phase poor in Si or the incongruent dissolution of aluminosilicate minerals. No gibbsite was detected by X-ray diffraction in the ELA soils (K. Law 1992, personal communication). The absence of gibbsite in catchment soils may point to interlayer aluminum hydroxides from the vermiculate clay fraction as the most likely source of solubilized non-silicate bound unreactive aluminum. Previous investigations by Turner & Brydon (1965, 1967), Bloom et al. (1977), Dahlgren et al. (1989) and Dahlgren & Walker (1993) have all indicated that hydroxy-aluminum from expansible 2:1 layer silicates may control aluminum solubility in soil solutions. The percentage of total soil aluminum removed after the 50-day leaching cycle for LFH and most Ah horizon soils ranged from 2 to 8%. Aluminum removal was significantly higher ( $\approx 15\%$ ) from the TL1-1 Ah2 and Ah3 soil horizons.

The neutralization of  $H^+$  in soil leaching solutions was often accompanied by a more than equivalent increase in base cations and aluminum in solution (Fig. 7). The removal of base cations from the soil matrix is largely attributed to the replacement of cations on exchange sites with  $H^+$  and aluminum. Proton neutralization ranged from 550 to 700  $\mu eq\ g^{-1}$  for surface soil horizons. Proton neutralization increased substantially in the Ah2 and Ah3 soil horizons of the TL1-1 soil profile, with 1350 and 1550  $\mu eq\ g^{-1}$   $H^+$  having been neutralized. The increased proton neutralization that occurred in the deeper soil horizons was accompanied by increased dissolution of organically bound

and unreactive soil aluminum in the Ah2 soil horizon and unreactive and oxalate extractable aluminum in the Ah3 soil horizon.

All HCl leachates were undersaturated with respect to gibbsite and amorphous aluminum trihydroxide (Fig. 8). This result differs from those reported by Dahlgren & Walker (1993) for Spodosol Bs soil horizons from Maine, New Hampshire and Washington State. Despite pyrophosphate-extractable aluminum comprising the dominant reactive soil fraction for their soils, all three soils exhibited an aluminum trihydroxide equilibrium control between pH 3 and 5. The organic carbon contents of the ELA soils examined in this study are generally higher than the Bs horizon soils examined by Dahlgren & Walker (1993), and disequilibrium with aluminum trihydroxide may be expected given the quantities of organically bound soil aluminum mobilized. HCl leachates from the TL1-1 Ah3 soil horizon exhibited the highest solubilization of unreactive aluminum and oxalate extractable aluminum (Fig. 6) and plot closest to the natural gibbsite solubility line (Fig. 8). Although unreactive aluminum contributed the majority of the aluminum removed from this soil horizon,  $\approx 25\%$  of the aluminum in solution could be accounted for by organically bound aluminum removed from the leached soil. It is unclear how the multiphase mix of organic and interlayer soil aluminum may affect aluminum solubility, but it is reasonable to expect that some degree of disequilibrium with respect to  $\text{Al}(\text{OH})_3$  minerals to occur.

#### *Aluminum solubility in soil and surface waters*

Mean concentrations for aluminum and selected chemical species from soil waters and soil island and whole catchment runoff waters in the study catchments are presented in Table 2. Silica concentrations exhibited a minimum in LFH horizons and a maximum in C horizon soil waters, but there was no strong trend with soil depth. Runoff waters from the forested soil deposits were highly acidic and had high concentrations of aluminum and DOC, reflecting a mixture of LFH and Ah soil waters. Organically bound aluminum dominated the labile aluminum fraction in LFH, Ah and soil island runoff waters. Substantial quantities of acid soluble (ASAl) aluminum were detected in all soil and runoff waters and unlike bedrock runoff waters, a positive relationship between DOC and ASAl was evident (Fig. 9), indicating that strongly bound organic aluminum comprises an important component of acid soluble aluminum. Inorganic labile aluminum fractions in LFH and Ah soil and soil island runoff waters were dominated by  $\text{Al}^{3+}$  (48–52%), with fluoride (21–15%) and hydroxy complexes (22–13%) comprising smaller fractions. Soil waters from C horizon soils exhibited a very different inorganic aluminum speciation suite with hydroxy-aluminum complexes (67%) and aluminum fluoride complexes (24%) dominating the labile inorganic aluminum total.

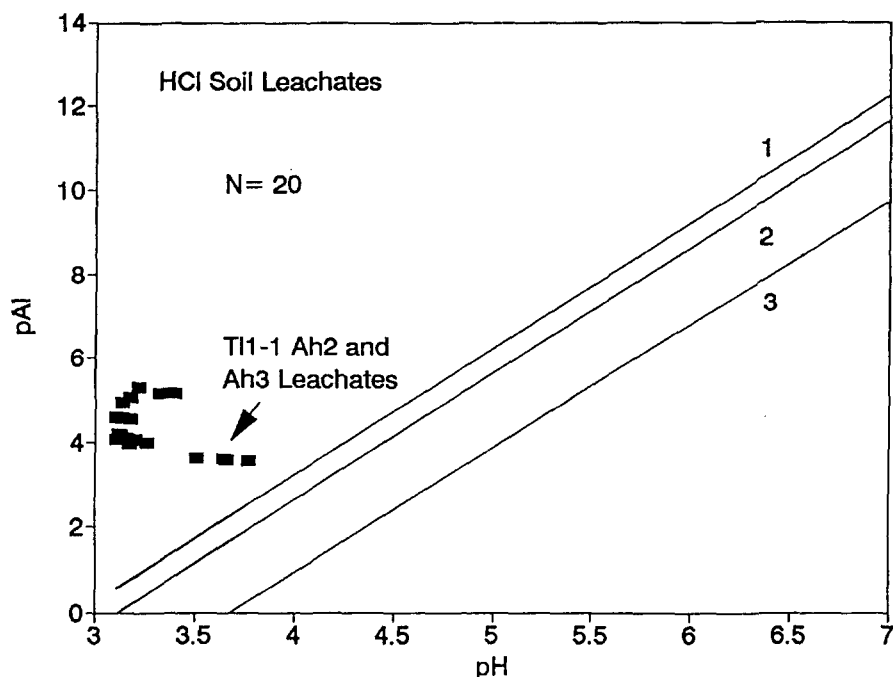


Fig. 8. Solubility diagram for HCl leachates of forest soils. See Figure 3 for an explanation of the solubility lines.

Aluminum sulphate complexes were a minor component (< 2%) of the labile inorganic aluminum total in all runoff and soil waters.

$\text{Al}(\text{OH})_3$  saturation indices for natural soil and soil runoff waters from the ELA upland catchments are presented in Fig. 10. It is apparent that LFH, Ah1 and Ah2 soil waters and forest runoff waters in the study catchments are often undersaturated with respect to  $\text{Al}(\text{OH})_3$  mineral solubilities. In contrast, soil waters from Ah3 and C horizons appear to be saturated with respect to an  $\text{Al}(\text{OH})_3$  solid phase (Fig. 10b). The solubility of aluminum in Ah3 and C horizon leachates is consistent with the increased proportion of oxalate extractable aluminum measured in the deeper soil horizons of the TL1-1 profile (Table 3) and the possible solubilization of unreactive (possibly interlayer) aluminum in lower Ah soil horizons (Fig. 6a).

Soil island runoff waters in the upland ELA study catchments are consistently undersaturated with respect to aluminum trihydroxide solid phases and during episodic runoff events saturation indices become increasingly undersaturated with time, rather than discharge, reaching a minimum during recession flows when runoff is almost entirely contributed from treed soil islands and  $\text{RCOO}^-$  and DOC levels reach their maximum (Allan 1993, Allan &



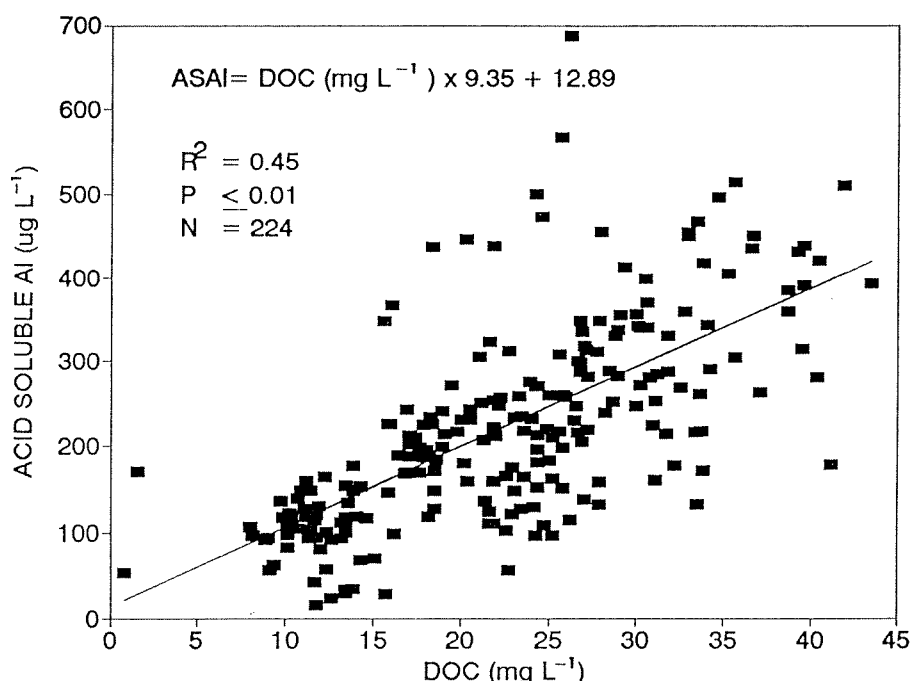


Fig. 9. Relationship between the acid soluble aluminum fraction (ASAl) and DOC in forest runoff waters in the study catchments.

Roulet 1994). Aluminum solubility for the upland ELA catchments appears to be dependent on the mixing ratio of runoff waters from lichen-bedrock runoff waters where kinetic constraints and organic controls are important, and runoff from the forested soil deposits where organic and interlayer solubility controls are important.

Cronan et al. (1986) developed a model to predict aqueous aluminum concentrations in organic rich waters based on the assumption that aqueous  $\text{Al}^{3+}$  concentrations are in equilibrium with aluminum on organic exchange sites. We cannot explicitly test the model with our data. However, an evaluation similar to that performed by Helmer et al. (1990) indicates discrepancies between model predictions and our data from upland organic rich LFH and Ah soil waters and runoff waters. Concentrations of  $\text{Al}^{3+}$  predicted by this model in the pH range 3.8–4.5 are generally higher ( $\text{pAl} = 5.4\text{--}3.8$ ) than the range observed for upland waters ( $\text{pAl} 6.5\text{--}4.88$ ). When values of  $\text{Al}^{3+}$  and pH from the present study are used to predict the organically bound aluminum fraction on soil exchange sites, negative values were obtained. Both, the solid phase humic absorbent model of Cronan et al. and aluminum trihydroxide

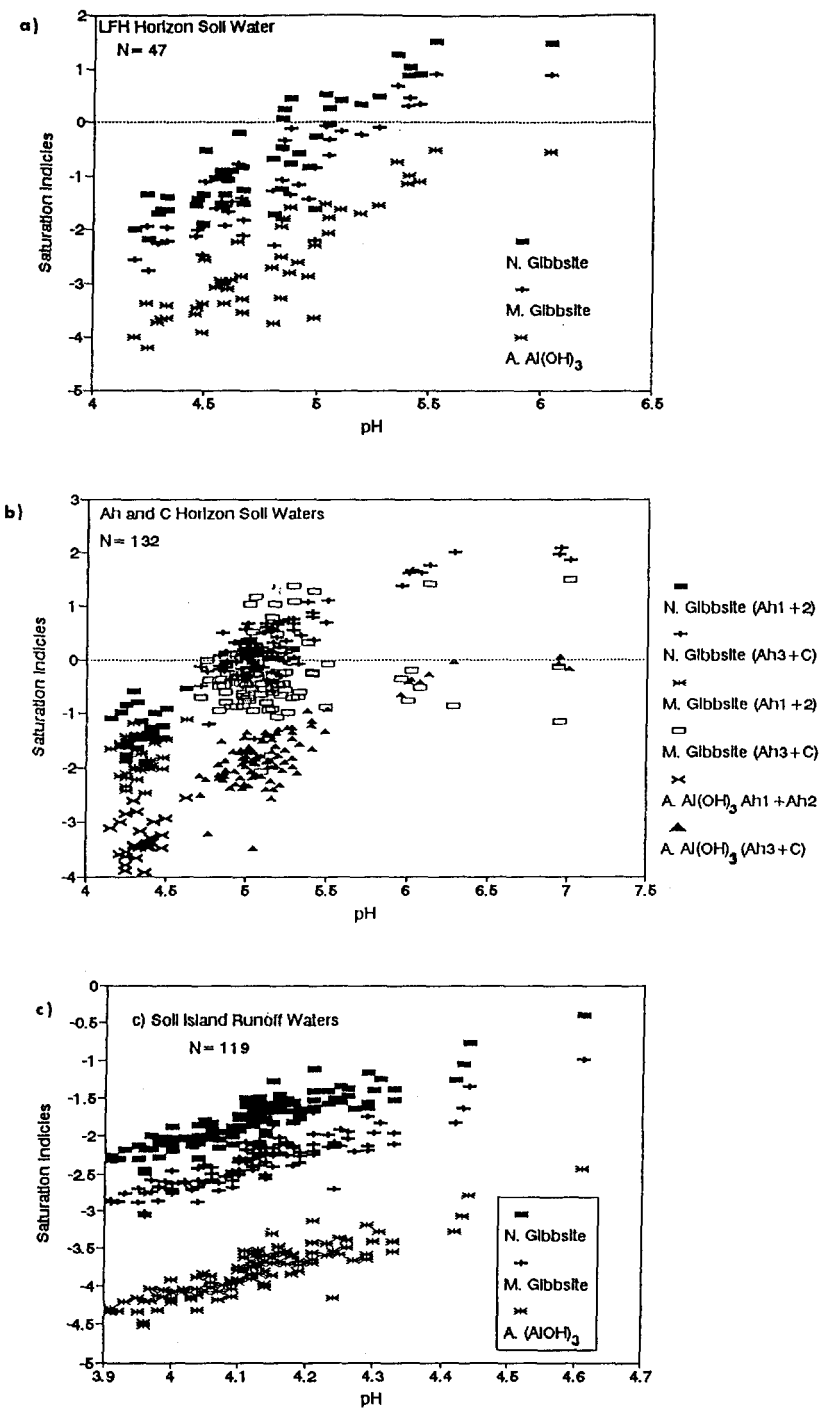


Fig. 10.  $\text{Al}(\text{OH})_3$  mineral saturation indices for a) LFH and b) Ah and C soil waters and natural soil island runoff waters.

mineral controls overpredict  $\text{Al}^{3+}$  concentrations in ELA upland soil and runoff waters.

The ELA upland aluminum solubility behaviour reflects both the nature of the soil cover and the hydrologic flow paths operating in the ELA upland catchments. The forested soil islands are located in topographic depression which receive runoff from upslope lichen-bedrock surfaces and soil islands (Allan et al. 1993). Runoff is routed laterally through surface LFH and Ah soil horizons as shallow subsurface stormflow and saturation overland flow (Allan & Roulet 1994). As a result, runoff waters are characterized by low pH's and high levels of organic acidity. The thin, patchy soils in the ELA catchments and the slow dissolution kinetics of the underlying and exposed granitic bedrock surfaces result in an extremely limited pool of easily solubilized aluminum. The high levels of organic acidity and organic binding ligands in ELA upland runoff combined with the limited pool of available aluminum result in acidic runoff with lower aluminum activities than runoff and soil waters from catchments for which the Cronan et al. model was validated.

## Summary

Results from the present study indicate several different physical and biogeochemical processes control aluminum solution chemistry in runoff and soil waters in Precambrian shield upland catchments. The heterogeneous nature of the upland landscape requires that sources of aluminum from both bedrock surfaces and soils be considered. Organic controls appear to be important on natural bedrock surfaces, moss and lichen covers providing surface exchange sites and aluminum complexing ligands. The reactive pool of aluminum on natural bedrock surfaces is limited and relatively short solvent/surface contact time results from a rapid generation and cessation of runoff from these areas. Moss covered surfaces which receive runoff from upslope soil deposits retain aluminum and other cations which are mobilized during subsequent runoff events.

Soil extraction and leaching experiments indicate pyrophosphate extractable aluminum (largely organically bound aluminum) comprises the largest component of reactive soil aluminum and is readily solubilized under acidic leaching conditions. Aluminum removal is limited from LFH soil horizons with base cation exchange reactions predominating.

The aluminum solubility displayed in soil and runoff waters coupled with the information from the soil extraction and leaching experiment shows that multiphase (organic/mineral) solid compounds and kinetic constraints (solution contact time and dissolution rates) will control aluminum solubility in these catchments. Aluminum trihydroxide solubility controls may exist in deeper soil waters but this is not reflected in runoff waters because of the

shallow flow paths operating in these systems. The neutralization of acid deposition in these environments will occur through base cation exchange reactions and the dissolution of soluble organically bound soil aluminum in surface LFH and Ah soil horizons. The large areal expanse and limited size of the labile aluminum pool on natural bedrock surfaces combined with the slow dissolution kinetics of primary aluminum-silicate minerals limits the ability of these systems to buffer strong acid inputs through the dissolution of soil aluminum as has been observed in other forested acid sensitive systems (Cronan & Schofield 1979).

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