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# Effect of basin physical characteristics on solute fluxes in nine alpine/subalpine basins, Colorado, USA†

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## Abstract:

Alpine/subalpine basins may exhibit substantial variability in solute fluxes despite many apparent similarities in basin characteristics. An evaluation of controls on spatial patterns in solute fluxes may allow development of predictive tools for assessing basin sensitivity to outside perturbations such as climate change or deposition of atmospheric pollutants. Relationships between basin physical characteristics, determined from geographical information system (GIS) tools, and solute fluxes and mineral weathering rates were explored for nine alpine/subalpine basins in Rocky Mountain National Park, Colorado, using correlation analyses for 1993 and 1994 data. Stream-water nitrate fluxes were correlated positively with basin characteristics associated with the talus environment; i.e., the fractional amounts of steep slopes ($\geq 30°$), unvegetated terrain and young debris (primarily Holocene till) in the basins, and were correlated negatively with fractional amounts of subalpine meadow terrain. Correlations with nitrate indicate the importance of the talus environment in promoting nitrate flux and the mitigating effect of areas with established vegetation, such as subalpine meadows. Total mineral weathering rates for the basins ranged from about 300 to 600 mol ha$^{-1}$ year$^{-1}$. Oligoclase weathering accounted for 30 to 73% of the total mineral weathering flux, and was positively correlated with the amount of old debris (primarily Pleistocene glacial till) in the basins. Although calcite is found in trace amounts in bedrock, calcite weathering accounted for up to 44% of the total mineral weathering flux. Calcite was strongly correlated with steep slope, unvegetated terrain, and young debris—probably because physical weathering in steep-gradient areas exposes fresh mineral surfaces that contain calcite for chemical weathering. Oligoclase and calcite weathering are the dominant sources of alkalinity in the basins. However, atmospherically deposited acids consume much of the alkalinity generated by weathering of calcite and other minerals in the talus environment. Published in 2001 by John Wiley & Sons, Ltd.

KEY WORDS solute flux; mineral weathering; mass balance; basin characteristics

## INTRODUCTION

Physical characteristics of watersheds may exert a substantial influence on basin hydrology and the rates and types of geochemical reactions occurring within a basin. Important physical characteristics in this regard might include rock type, amount and nature of soil, extent and type of vegetation, and basin size and relief. If basin physical characteristics affect hydrology and geochemistry, then variations in physical characteristics may determine the response of ecosystems to perturbations such as climate variability and deposition of atmospheric pollutants. In alpine and subalpine systems, differences in physical characteristics among basins may be extreme, and may lead to potentially large variations in aquatic chemistry and ecosystem behaviour.

To understand the potential hydrochemical response of mountain streams and lakes to perturbations, it is important to identify relationships between basin physical characteristics and surface-water chemistry. For

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example, if fluxes of solutes from weathering reactions depend on basin mineralogy and on water fluxes and flow paths, which in turn, depend on climate and the physical characteristics of the basins, then, to identify controls on solute release via weathering reactions, one could compare stream-water fluxes of weathering products (base cations, alkalinity and silica) to basin physical characteristics. Understanding controls on weathering rates is important because weathering reactions consume carbon dioxide ($CO_2$) and strong acids derived from acidic deposition; in addition, identifying controls on weathering rates may help improve global $CO_2$ budgets and models of basin response to acidic deposition or climate change.

Comparison of solute fluxes with basin characteristics also may be valuable for assessing the influence of basin characteristics on biogeochemical processes, such as nitrogen (N) cycling. In unperturbed natural ecosystems, little N is exported from basins via stream flow, because the ecosystems are usually N limited. In the late 1980s, it was noted that many streams in the eastern USA export N throughout the year (Stoddard, 1994). This characteristic indicates N saturation, a condition that occurs when the supply of nitrogen from the atmosphere exceeds the demands of biota within the watershed (Stoddard, 1994). Deleterious effects of excess N include alteration of species composition and acidification of aquatic ecosystems. Symptoms of N saturation have been documented recently in the Rocky Mountains, despite the fact that N deposition is much less than in the eastern USA (Baron and Bricker, 1987; Campbell *et al.*, 1995; Williams *et al.*, 1996). It has been hypothesized that certain physical characteristics of many alpine/subalpine basins in the Rocky Mountains, such as poorly developed soils and limited vegetation, may contribute to the sensitivity of the basins to N deposition (Clow and Sueker, 2000).

Several studies have documented relationships between surface-water chemistry and basin characteristics. In a regional synoptic study in the Sierra Mountains, California, lake alkalinity, sulphate and calcium were found to be positively related to the percentage of each basin underlain by volcanic or calcareous rocks (Melack *et al.*, 1985). In a survey of lakes in the Mount Zirkel Wilderness Area, Colorado (Turk and Campbell, 1987), and in a survey of lakes and streams in Yosemite National Park, California (Clow *et al.*, 1996), surface-water alkalinity was found to be positively related to the distribution of surficial materials. Studies in the eastern USA also have indicated that geological characteristics are important in determining surface-water alkalinity (Lynch and Dise, 1985; Newton *et al.*, 1987; Yuretich and Batchelder, 1988; Bricker and Rice, 1989; Puckett and Bricker, 1992). Recent studies in Rocky Mountain National Park have indicated that topography, vegetation and geology play important roles in stream-water chemistry and nitrogen export (Campbell *et al.*, 2000; Clow and Sueker, 2000).

Although these studies provide important information about the effect of geological characteristics on solute concentrations, no studies have directly compared a broad range of basin physical characteristics with annual fluxes of solutes in stream water. Doing so would permit an evaluation of how physical characteristics of drainage basins can influence solute budgets and weathering rates. These issues are important in the Rocky Mountains, in light of recent concern about the long-term effects of acidic deposition on ecosystems, including possible calcium depletion and nitrogen saturation in soils.

The purpose of this study was to identify physical characteristics that are important in determining rates of solute release from a suite of high-elevation basins in Rocky Mountain National Park, Colorado. Solute release rates (fluxes) were calculated using discharge and chemistry measurements made at gauging stations on nine streams in Rocky Mountain National Park, Colorado over a two-year period (1993–94). The physical characteristics of each basin were quantified using digitized geological, topographic and vegetation map information. Relationships between solute fluxes and physical characteristics were evaluated using correlation analyses.

## METHODS

### *Description of study area*

Rocky Mountain National Park (RMNP) is located in the Colorado Front Range about 100 km north-west of Denver, Colorado (Figure 1). Areas of the selected basins in RMNP range from 183 to 10 440 ha (Table I).

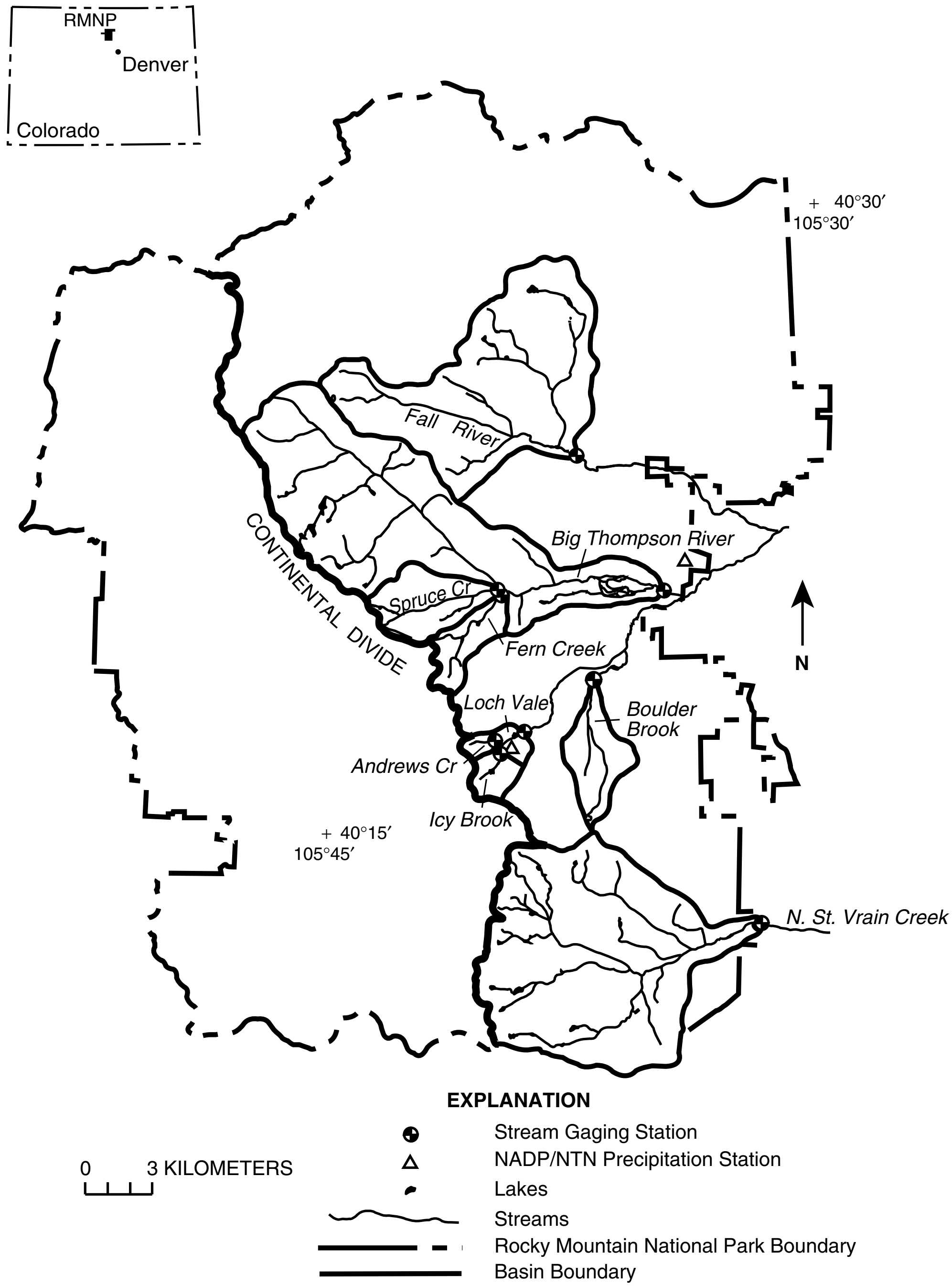


Figure 1. Site map

Gauge elevation ranges from 2450 to 3192 m and maximum elevation ranges from 3768 to 4345 m. Median basin slope ranges from 17 to 34°. Precipitation averages 60 to 100 cm annually, with about two-thirds of that falling as snow between October and April. Melting of the seasonal snowpack is the major hydrological event of the year, and about half the total annual runoff occurs in May and June (Sueker, 1996). Evapotranspiration

Table I. Physical characteristics of study basins and fractional areas of vegetation and geology classes

| Site | Topography | | | | Vegetation classes | | | | Geology classes | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Basin area (ha) | Average elevation (m) | Median slope | Steep slope[a] | Tundra | Unvegetated | Forest | Subalpine meadow | Granite | Gneiss | Young debris | Old debris |
| Andrews Creek | 183 | 3551 | 33° | 0·56 | 0·24 | 0·75 | 0·01 | 0·00 | 0·04 | 0·63 | 0·19 | 0·10 |
| Icy Brook | 326 | 3579 | 34° | 0·60 | 0·19 | 0·80 | 0·00 | 0·00 | 0·06 | 0·64 | 0·20 | 0·05 |
| Loch Vale | 661 | 3555 | 30° | 0·50 | 0·24 | 0·70 | 0·06 | 0·00 | 0·11 | 0·60 | 0·17 | 0·08 |
| Fern Creek | 780 | 3172 | 22° | 0·29 | 0·16 | 0·45 | 0·37 | 0·02 | 0·07 | 0·63 | 0·10 | 0·19 |
| Boulder Brook | 990 | 3517 | 17° | 0·02 | 0·34 | 0·28 | 0·32 | 0·06 | 0·31 | 0·06 | 0·01 | 0·62 |
| Spruce Creek | 1320 | 3262 | 22° | 0·29 | 0·30 | 0·45 | 0·23 | 0·02 | 0·34 | 0·34 | 0·11 | 0·20 |
| Fall River | 6280 | 3364 | 22° | 0·23 | 0·28 | 0·32 | 0·35 | 0·05 | 0·43 | 0·34 | 0·05 | 0·17 |
| North St Vrain | 8500 | 3435 | 17° | 0·15 | 0·18 | 0·36 | 0·42 | 0·04 | 0·34 | 0·15 | 0·10 | 0·39 |
| Big Thompson | 10 440 | 3195 | 20° | 0·21 | 0·23 | 0·31 | 0·41 | 0·05 | 0·47 | 0·34 | 0·05 | 0·13 |

[a] Steep slope refers to fraction of basin having slopes $\geq 30°$.

and sublimation rates have been determined for one of the basins, Loch Vale, which has been the site of intensive process-oriented research since the early 1980s (Baron, 1992). Evapotranspiration and sublimation in Loch Vale are estimated to account for approximately 40% of annual precipitation (Baron, 1992). Average daily air temperature in Loch Vale ranges from approximately $-6\,°C$ in January to $14\,°C$ in July.

Large valley glaciers scoured most of the basins during the late Pleistocene, creating cirques, arrettes, and u-shaped valleys, and leaving till deposits of varying thickness along the valley bottoms when they last retreated about 12 500 years ago (Madole, 1976). Late Holocene glacial activity resulted in glacial till, rock glacier and talus deposits in the cirques and along the valley sides (Madole, 1976). In this study, Pleistocene deposits are defined as 'old debris', and Holocene deposits are defined as 'young debris'.

Most soils in the basins have developed on Holocene and late Pleistocene till. Soils are generally poorly sorted, have minimal profile development, and are limited to tundra, forest and wet meadow areas, which account for 16–34%, 0–42% and 0–6% of the basin areas, respectively (Figure 2). Large portions of the basins (28–80%) are unvegetated and are composed mostly of talus and bedrock. Bedrock consists of biotite gneiss and Silver Plume granite, both Precambrian in age (Braddock and Cole, 1990). The mineralogy and chemistry of the two bedrock types are very similar, although relative mineral abundances vary (Mast, 1992). The dominant minerals in order of abundance include quartz, oligoclase ($An_{27}$ plagioclase), microcline (potassium feldspar), biotite and chlorite. Minor and accessory minerals include sillimanite, ilmenite, magnetite, cordierite, orthopyroxene, zircon and apatite (Braddock and Cole, 1990). Trace amounts of calcite occur along grain boundaries and along fractures and joints (Mast *et al.*, 1990; Mast, 1992). Clay mineralogy of Loch Vale soils includes a mixed-layer smectite–illite, kaolinite, detrital mica, chlorite, quartz and microcline (Mast *et al.*, 1990).

### *Determination of physical characteristics of drainage basins*

Basin physical characteristics were quantified using digital topographic, vegetation and geological map coverages provided by the National Park Service (Rocky Mountain National Park, unpublished data). Topographic coverages were derived from digitized US Geological Survey quadrangle sheets with a scale of 1 : 24 000. Information obtained from the topographic coverages included basin area, average elevation, median slope and fraction of slope $\geq 30°$. Vegetation coverages were determined from digitized aerial photographs. The main subunits identified on the vegetation coverages were non-vegetated area, forest, tundra and wet meadow. The non-vegetated area was mainly young surficial material (Holocene talus, till and rock glacier) and exposed bedrock. Geological coverages were constructed from a digitized geologic map with a scale

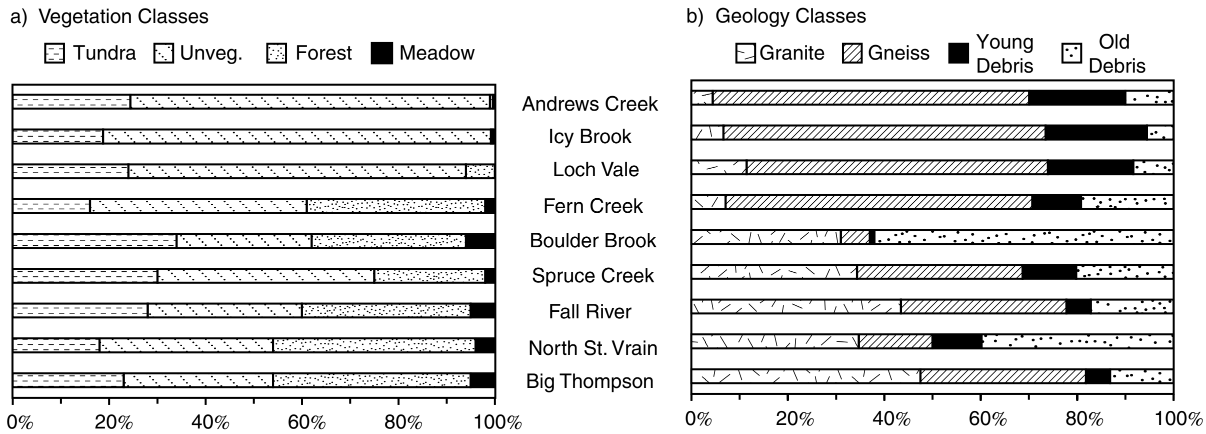


Figure 2. Fraction of basin area for (a) vegetation classes and (b) geology classes

of 1 : 50 000 (Braddock and Cole, 1990). Geological subunits included gneiss bedrock granite bedrock, and surficial material (till, rock glaciers and talus). Surficial material was further subdivided into young (Holocene) and old (Pleistocene and older).

*Flow measurements, sample collection and analyses*

Stream stage (water height) was measured continuously at gauges installed at the outlets of each of the nine study basins. Discharge was calculated from stage using equations developed from stage and discharge measurements made over a broad range of flows using current-meter and dye-dilution techniques according to standard methods (Rantz, 1982).

Stream-water samples were collected at the gauges approximately weekly from April through August, bi-weekly in September and October, and monthly to bi-monthly from November through March in 1993 and 1994. This sampling frequency reflected the rate of change in stream flow. Stream-water samples were collected in high-density polyethylene bottles that had been soaked in de-ionized (DI) water and triple rinsed with sample water prior to collection. Samples were split, and one portion was filtered through a 0·45-μm polycarbonate membrane within 24 h of collection. The filtered portion was split again, and one of the aliquots was acidified to pH 2 using concentrated high-purity nitric acid.

Alkalinity ($HCO_3$) and pH were measured on unfiltered samples at room temperature within one week of collection. Alkalinity was determined by Gran titration (Gran, 1952), and pH was measured using an electrode designed for low-ionic-strength water. Calcium (Ca), magnesium (Mg), sodium (Na) and silica ($SiO_2$) concentrations were determined by inductively coupled plasma atomic emission spectroscopy on filtered, acidified samples. Sulphate ($SO_4$), nitrate ($NO_3$) and chloride (Cl) were measured by ion chromotography on filtered samples. Accuracy of analyses generally was better than ±5% on the basis of repeated analyses of standard reference waters obtained from the US Geological Survey (Ludtke and Woodworth, 1997). Detailed discussions of discharge measurements; stream-water chemistry sampling and analysis methods; and precision, accuracy and detection limits of analyses are provided in Sueker (1996).

*Solute flux calculations*

Annual solute fluxes in precipitation were calculated by multiplying estimated annual precipitation amount for each basin with annual volume-weighted mean concentrations in precipitation. Precipitation amounts for individual basins were calculated using a Cl mass-balance technique as follows:

$$\text{amount}_{\text{precipitation}} = (\text{Cl concentration})_{\text{stream}}(\text{total annual runoff})_{\text{stream}}/(\text{Cl concentration})_{\text{precipitation}}$$

with the assumptions that precipitation was the only source of Cl and that Cl behaved conservatively. Precipitation solute concentrations were measured for samples collected from the Beaver Meadows (2490 m) and Loch Vale (3159 m) National Acid Deposition Program/National Trends Network (NADP/NTN) stations (Figure 1) (NADP/NTN, 1993 and 1994). A detailed description of the calculation of elevationally weighted solute fluxes from precipitation to the individual basins is provided in Sueker (1996).

Annual solute fluxes in stream water were calculated by multiplying the solute concentration for a given sample with the volume of water passing the stream gauge during the sampling period and summing the products for all of the sampling periods during the year. Sampling periods were defined as beginning halfway in time between the current sample and the previous sample and ending halfway in time between the current sample and the next sample. Stream flow was calculated for each sampling period using 15-min average discharge data and stage–discharge relationships developed for the outlets of each basin. The net efflux of solutes from each basin was determined by subtracting the precipitation influx from the stream flow efflux.

Separate definitions of water year were used for precipitation (1 October through 30 September) and stream-water flux (1 April through 31 March). These definitions allow us to account for precipitation when it is primarily contributing to stream flow. Most precipitation between 1 October and 31 March falls as snow and accumulates in snowpacks. Precipitation contributions to stream flow are negligible during the winter months, and stream flow at this time is due to draining of subsurface reservoirs that were recharged prior to winter (Sueker *et al.*, 2000). Melting of the annual snowpack, which typically begins in mid-April, and summer rains contribute to subsurface recharge and to stream flow throughout the summer and following winter.

*Mineral weathering calculations*

Mineral weathering rates were calculated using a mass-balance technique, an accounting system that can be used to estimate the amount of solutes that are derived from specific sources (Garrels and Mackenzie, 1967). A simple mass-balance equation for a watershed has the form

$$(\text{output}) - (\text{input}) = (\text{weathering} \pm \Delta\text{soil exchange pool} \pm \Delta\text{biomass})$$

where (output) is the flux of solutes leaving the basin in stream water or groundwater and (input) is the flux of solutes entering the basin via atmospheric deposition. Groundwater discharge from the study basins is likely to be negligible, because bedrock is hydrologically tight and soils are shallow at the basin outlets. In undisturbed ecosystems, annual changes in the soil exchange pool and in the biomass pool may be negligible, allowing the flux of solutes from mineral weathering to be calculated from the difference in output and input fluxes. The fluxes attributable to weathering of individual minerals then can be calculated if the stoichiometries of the dominant weathering reactions are known.

The assumption that biomass accumulation has a negligible effect on stream solute fluxes was evaluated by multiplying the biomass accumulation rate calculated for the Loch Vale forest (29 $\mu$mol m$^{-2}$ year$^{-1}$ base cations ($Ca + Mg + Na + K$) (Arthur and Fahey, 1993)) by the area of forest in each of the nine study basins. Biomass accumulation can account for a reduction in stream-water base cation concentrations of 0·0002 to 0·0418 $\mu$mol L$^{-1}$, compared with annual volume-weighted mean stream water cation concentrations of 51 to 138 $\mu$mol L$^{-1}$. The biomass sink is four to six orders of magnitude less than the 1994 annual stream cation flux and can be safely ignored.

Annual or longer term changes in the soil exchange pool are driven by changes in atmospheric deposition of strong acids (Lawrence *et al.*, 1997). Trends in precipitation fluxes of strong acid ions at the Loch Vale NADP/NTN site for the 1983 through 1997 time period were evaluated using the seasonal Kendall test; no significant trends were identified ($p \leq 0{\cdot}01$). Thus, the assumption that changes in the amount of solutes stored in the soil exchange pool have a negligible effect on stream solute fluxes appears reasonable.

Mineral weathering reactions in Loch Vale have been defined by Mast (1992) and Clow *et al.* (1997), who determined that the dominant weathering reactions include weathering of plagioclase to kaolinite, dissolution of calcite and pyrite, and conversion of biotite/chlorite to smectite/illite (Table II). Weathering reactions in the

Table II. Weathering reactions used in mass-balance calculations

Oligoclase to kaolinite

$$\underset{\text{oligoclase}}{Ca_{0\cdot27}Na_{0\cdot73}Al_{1\cdot27}Si_{2\cdot73}O_8} + 1\cdot27CO_2 + 4\cdot82H_2O \longrightarrow \underset{\text{kaolinite}}{0\cdot64Al_2Si_2O_5(OH)_4} + 0\cdot27Ca^{+2} + 0\cdot73Na^{+} + 1\cdot46H_4SiO_4 + 1\cdot27HCO_3^{-}$$

Biotite to mixed-layer smectite–illite

$$1\cdot15\underset{\text{biotite}}{(K_{0\cdot98}Mg_{1\cdot00}Fe_{1\cdot33}Ti_{0\cdot18}Al_{0\cdot33})(Al_{1\cdot35}Si_{2\cdot65})O_{10}(OH)_2} + 0\cdot10Ca^{+2} + 0\cdot49H_4SiO_4 + 1\cdot21O_2 + 2\cdot13CO_2 + (0\cdot73 + n)H_2O \longrightarrow$$

$$\underset{\text{smectite–illite}}{(K_{0\cdot32}Fe_{0\cdot25}Ca_{0\cdot10}Mg_{0\cdot39}Al_{1\cdot93}Si_{3\cdot54})O_{10}(OH)_2 \cdot nH_2O} + 0\cdot76Mg^{+2} + 0\cdot81K^{+} + 1\cdot28FeO(OH)_{(s)} + 2\cdot13HCO_3^{-} + 0\cdot21TiO_2$$

Chlorite to mixed-layer smectite–illite

$$\underset{\text{chlorite}}{(1\cdot39(Mg_{1\cdot81}Fe_{2\cdot72}Al_{1\cdot39})(Al_{1\cdot23}Si_{2\cdot77})(O_{10}(OH)_8} + 0\cdot10Ca^{+2} + 0\cdot10Ca^{+2} + 0\cdot32K^{+} + 0\cdot31H_4SiO_4 + 1\cdot78O_2 + 3\cdot74CO_{2+n}H_2O \longrightarrow$$

$$\underset{\text{smectite–illite}}{(K_{0\cdot32}Fe_{0\cdot25}Ca_{0\cdot10}Mg_{0\cdot39}Al_{1\cdot93}Si_{3\cdot54})O_{10}(OH)_2 \cdot nH_2O} + 2\cdot13Mg^{+2} + 3\cdot53FeO(OH)_{(s)} + 3\cdot74HCO_3^{-}$$

Microcline to kaolinite

$$\underset{\text{microcline}}{2KAlSi_3O_8} + 2CO_2 + 11H_2O \longrightarrow \underset{\text{kaolinite}}{Al_2Si_2O_5(OH)_4} + 2K^{+} + 4H_4SiO_4 + 2HCO_3^{-}$$

Calcite dissolution

$$\underset{\text{calcite}}{CaCO_3} + H_2O + CO_2 \longrightarrow Ca^{+2} + 2HCO_3^{-}$$

Pyrite dissolution

$$\underset{\text{pyrite}}{FeS_2} + 3\cdot5O_2 + H_2O \longrightarrow Fe^{+2} + 2SO_4^{-2} + 2H^{+}$$

other study watersheds are likely to be the same as in Loch Vale, because the same geological units and types of soil underlie them. Mineral weathering rates were calculated from the mineral weathering reactions using the net solute efflux from each basin and the method of Garrels and Mackenzie (1967). Solute influx from wet deposition was subtracted from solute efflux in stream water to obtain the net solute flux attributable to weathering. All of the Na in the net solute flux was assigned to weathering of oligoclase ($An_{27}$) to kaolinite. This also accounted for some of the Ca; remaining Ca was assigned to calcite dissolution. The Mg and K contents were attributed to weathering of biotite to a mixed-layer smectite clay containing approximately 30% illite layers. Any remaining K was assigned to weathering of microcline to kaolinite. As previously noted, chlorite partially replaces biotite in some of the altered rocks, and the mineral phase referred to here as biotite probably included some chlorite. In a laboratory dissolution experiment on a biotite separated from an alpine soil in Loch Vale (pH = 5·6, temperature = 20 °C), the stoichiometry of solute release was consistent with dissolution of biotite and chlorite in a 2 : 1 ratio (Clow, 1992). In the mass-balance calculations, it was assumed that biotite and chlorite weathered in a 2 : 1 ratio.

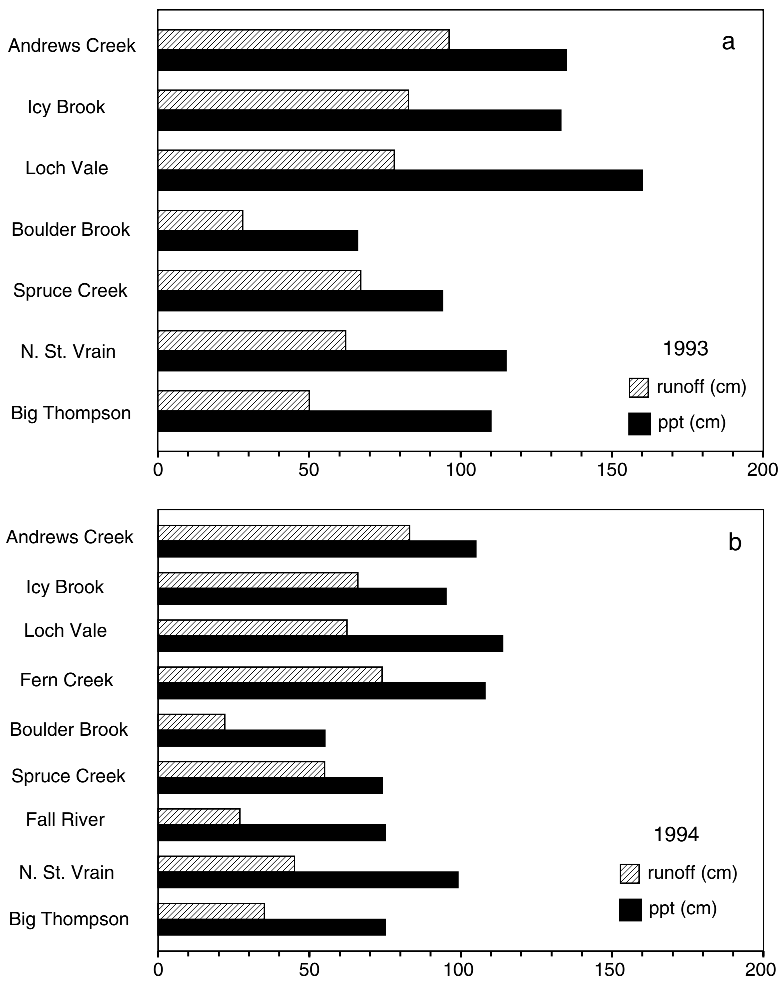


Figure 3. Precipitation and stream-water fluxes of water for (a) 1993 and (b) 1994

## RESULTS

### *Water and solute fluxes*

Estimated precipitation ranged from 66 to 160 cm in 1993 ($n = 7$) and 55 to 110 cm in 1994 ($n = 9$) (Figure 3). Runoff varied from 28 to 96 cm in 1993 and 22 to 83 cm in 1994. Losses from evapotranspiration (ET) and sublimation, defined in this study as the difference between precipitation and runoff, ranged from 27 to 82 cm (29 to 58%) in 1993 and 19 to 54 cm (21 to 64%) in 1994. Water losses were highest for basins with the greatest fraction of forested area.

Fluxes of solutes entering the basins via wet deposition were dominated by $NO_3$, H, $NH_4$ and $SO_4$ (Table III and Figure 4). Wet-deposition fluxes were higher in 1993 (300 to 770 mol $ha^{-1}$ $year^{-1}$) than in 1994 (290 to 580 mol $ha^{-1}$ $year^{-1}$), reflecting the greater amounts of precipitation that fell in 1993 (Figure 3). Differences in wet-deposition fluxes are due to differences in wet deposition amounts and elevation distributions between the basins. The potential influx of solutes from dry deposition is discussed in the sensitivity analysis section below.

Fluxes of solutes in stream water leaving the basins ranged from 1270 to 1750 mol $ha^{-1}$ $year^{-1}$ in 1993, and from 910 to 1470 mol $ha^{-1}$ $year^{-1}$ in 1994 (Table III and Figure 4). Stream-water fluxes of $HCO_3$, $SiO_2$, Ca and Na generally dominated, although fluxes of $NO_3$ and $SO_4$ were important in some of the smaller basins (Figure 4).

There were correlations among runoff, solute fluxes and solute flux ratios that may be linked to hydrological, biological or geochemical processes. For example, Na fluxes were correlated positively with $SiO_2$ and $HCO_3$ fluxes, probably because of a common source, such as weathering of oligoclase (Table IV). Other notable correlations include positive relations between runoff and Ca, $NO_3$ and $SO_4$ fluxes and between H fluxes and $NO_3$ and $SO_4$ fluxes.

Runoff had a positive correlation with the fraction of basin area having steep slopes, unvegetated terrain, and young debris ($p \leq 0{\cdot}01$) (Table V). Fluxes of Na, $HCO_3$ and $SiO_2$ were correlated positively with the fraction of basin area having old debris. Fluxes of $NO_3$ and Ca/Na flux ratios were correlated positively with fractional amounts of steep slopes, unvegetated terrain and young debris in the basins. Fluxes of $NO_3$ and Ca/Na flux ratios were correlated inversely with subalpine meadow. Fluxes of $SO_4$ and H exhibited correlations with basin characteristics that were similar to those of $NO_3$ and Ca/Na, although the correlations generally were not as strong, especially for H.

### *Mineral weathering rates*

Mass balance calculations indicate that solute fluxes from mineral weathering ranged from 370 to 600 mol $ha^{-1}$ $year^{-1}$ in 1993 and from 310 to 500 mol $ha^{-1}$ $year^{-1}$ in 1994. Most of the stream-water solutes derived from weathering are due to dissolution of oligoclase and calcite, which accounted for 59 to 76% of the mineral weathering products in stream water (Figure 5). Weathering of biotite/chlorite and pyrite is somewhat less important; these minerals accounted for 14 to 24% of the weathering-derived solutes. Dissolution of kaolinite or an amorphous aluminosilicate phase is required to achieve silica mass balance in most of the basins; contributions from this reaction were generally $\leq$ 10% of the total moles derived from mineral weathering. Weathering of microcline contributed a minor amount of solutes to stream water in 1993 ($<$ 2% of mineral weathering flux), but its contribution in 1994 was negligible.

The weathering rate of oligoclase was correlated positively with the fraction of basin areas underlain by old debris (Table V). Calcite and pyrite weathering rates were correlated positively with fractional amounts of steep slopes, unvegetated terrain and young debris in the basins. The calcite weathering rate was correlated negatively with the fraction of basin areas characterized as subalpine meadow.

### *Comparison of influx and efflux*

A comparison of precipitation solute influx and stream solute efflux provides insight into solute sources and sinks (Figure 6). Solutes that plot on the influx = efflux line are considered to be conservative. Solutes

Table III. 1993 and 1994 solute fluxes (mol $ha^{-1}$ $year^{-1}$) and water fluxes ($10^6$ $m^3$ and cm). Stream-flow solute flux (output) minus precipitation solute flux (input) equals net flux of solute from basin

| Year | Basin | Flux | Ca | Mg | Na | K | $SiO_2$ | $HCO_3$ | H | $NH_4$ | $NO_3$ | $SO_4$ | Cl | $H_2O$ ($10^6$ $m^3$) | $H_2O$ (cm) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1993 | Andrews Creek | Streamflow | 263 | 65 | 159 | 36 | 318 | 279 | 2 | 10 | 226 | 137 | 31 | 1·8 | 96 |
| | | Precipitation | 48 | 10 | 35 | 6 | 0 | 0 | 188 | 111 | 206 | 89 | 31 | 2·5 | 135 |
| | Icy Brook | Streamflow | 251 | 59 | 126 | 30 | 194 | 251 | 2 | 7 | 180 | 136 | 30 | 2·7 | 83 |
| | | Precipitation | 52 | 11 | 37 | 6 | 0 | 0 | 200 | 119 | 220 | 95 | 30 | 4·3 | 133 |
| | Loch Vale | Streamflow | 232 | 62 | 116 | 31 | 236 | 315 | 0 | 0 | 128 | 125 | 29 | 5·2 | 78 |
| | | Precipitation | 47 | 10 | 34 | 6 | 0 | 0 | 169 | 104 | 188 | 86 | 29 | 10·6 | 160 |
| | Boulder Brook | Streamflow | 105 | 42 | 214 | 20 | 455 | 398 | 0 | 0 | 3 | 39 | 13 | 2·8 | 28 |
| | | Precipitation | 20 | 4 | 15 | 3 | 0 | 0 | 76 | 51 | 84 | 38 | 13 | 6·5 | 66 |
| | Spruce Creek | Streamflow | 245 | 67 | 187 | 34 | 379 | 447 | 1 | 0 | 20 | 84 | 17 | 8·8 | 67 |
| | | Precipitation | 26 | 6 | 20 | 4 | 0 | 0 | 104 | 70 | 118 | 51 | 17 | 12·4 | 94 |
| | North St Vrain | Streamflow | 257 | 83 | 239 | 35 | 452 | 559 | 1 | 0 | 12 | 94 | 20 | 52·7 | 62 |
| | Creek | Precipitation | 29 | 7 | 23 | 4 | 0 | 0 | 124 | 79 | 138 | 60 | 20 | 97·8 | 115 |
| | Big Thompson | Streamflow | 204 | 85 | 190 | 38 | 317 | 448 | 1 | 0 | 10 | 85 | 20 | 52·2 | 50 |
| | River | Precipitation | 29 | 7 | 23 | 4 | 0 | 0 | 121 | 79 | 136 | 58 | 20 | 114·8 | 110 |
| 1994 | Andrews Creek | Streamflow | 210 | 54 | 131 | 26 | 244 | 203 | 2 | 6 | 188 | 101 | 21 | 1·5 | 83 |
| | | Precipitation | 29 | 6 | 23 | 6 | 0 | 0 | 134 | 106 | 141 | 65 | 21 | 1·9 | 105 |
| | Icy Brook | Streamflow | 192 | 46 | 96 | 20 | 122 | 188 | 2 | 8 | 123 | 94 | 19 | 2·2 | 66 |
| | | Precipitation | 27 | 6 | 21 | 5 | 0 | 0 | 121 | 96 | 128 | 59 | 19 | 3·1 | 95 |
| | Loch Vale | Streamflow | 186 | 51 | 97 | 24 | 197 | 257 | 0·0 | 0 | 97 | 89 | 23 | 4·1 | 62 |
| | | Precipitation | 32 | 7 | 25 | 6 | 0 | 0 | 144 | 115 | 153 | 70 | 23 | 7·5 | 114 |
| | Fern Creek | Streamflow | 233 | 78 | 175 | 30 | 333 | 422 | 1·3 | 0 | 79 | 99 | 22 | 5·8 | 74 |
| | | Precipitation | 32 | 7 | 24 | 6 | 0 | 0 | 134 | 115 | 149 | 67 | 22 | 8·4 | 108 |
| | Boulder Brook | Streamflow | 87 | 35 | 179 | 16 | 384 | 348 | 0·2 | 0 | 6 | 31 | 12 | 2·2 | 22 |
| | | Precipitation | 17 | 3 | 12 | 3 | 0 | 0 | 70 | 59 | 77 | 35 | 12 | 5·5 | 55 |
| | Spruce Creek | Streamflow | 185 | 52 | 141 | 22 | 280 | 342 | 0·9 | 0 | 55 | 65 | 16 | 7·3 | 55 |
| | | Precipitation | 23 | 5 | 17 | 4 | 0 | 0 | 94 | 81 | 105 | 47 | 16 | 9·8 | 74 |
| | Fall River | Streamflow | 120 | 52 | 112 | 24 | 204 | 328 | 0·3 | 0 | 15 | 42 | 13 | 17·0 | 27 |
| | | Precipitation | 19 | 4 | 14 | 3 | 0 | 0 | 81 | 68 | 88 | 40 | 13 | 47·1 | 75 |
| | North St Vrain | Streamflow | 186 | 62 | 167 | 22 | 341 | 423 | 0·6 | 0 | 33 | 71 | 22 | 38·3 | 45 |
| | Creek | Precipitation | 31 | 7 | 24 | 6 | 0 | 0 | 133 | 111 | 144 | 66 | 22 | 84·2 | 99 |
| | Big Thompson | Streamflow | 138 | 57 | 128 | 24 | 224 | 331 | 1 | 0 | 21 | 58 | 16 | 36·5 | 35 |
| | River | Precipitation | 23 | 5 | 17 | 4 | 0 | 0 | 97 | 83 | 108 | 49 | 16 | 78·3 | 75 |

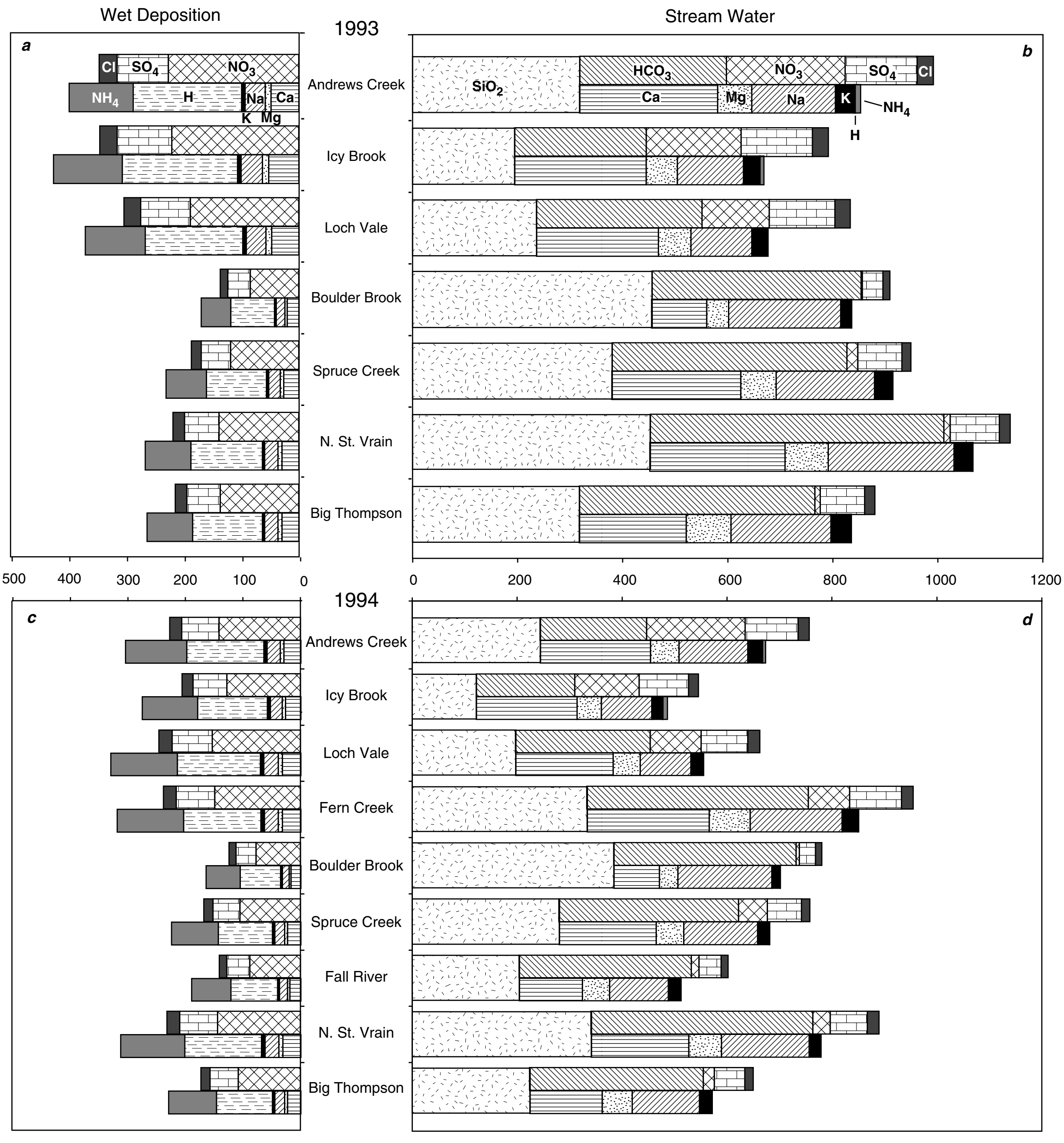


Figure 4. Fluxes of solutes (mol $ha^{-1}$ $year^{-1}$, indicated by length of bar) in (a) wet deposition in 1993, (b) stream water in 1993, (c) wet deposition in 1994 and (d) stream water in 1994

that plot below the line (influx > efflux) are consumed within the basin, and solutes that plot above the line (influx < efflux) are produced within the basin. With one exception (Boulder Brook), $SO_4$ plots slightly above the influx = efflux line. This indicates that movement of $SO_4$ is generally conservative, although a basin source, such as pyrite weathering, or an unaccounted atmospheric source, such as dry deposition of sulphur, is indicated for most basins. Hydrogen in wet deposition is consumed in the basin by weathering, exchange and biologic reactions. Ammonium is either consumed by biota or transformed into other inorganic or organic nitrogen compounds via microbially mediated reactions. In most basins, part of the atmospherically deposited $NO_3$ is consumed via biologic reactions, although the amount of consumption varies among basins. In one basin, $NO_3$ output exceeded input, indicating an unaccounted-for source of $NO_3$ or conversion of $NH_4$ to $NO_3$ via nitrification. Alkalinity, $SiO_2$ and base cations are generated within the basins predominantly by mineral weathering processes, although some of the base cations come from atmospheric deposition (wet and dry).

## DISCUSSION

Variations in solute fluxes and mineral weathering rates among the study basins reflect differences in hydrology and in the rates and types of geochemical and biological reactions occurring in the basins. The physical characteristics of the basins help determine basin hydrology and geochemistry. Water flow rates, for example, are high in areas with steep slopes, because water either moves directly across bedrock or passes quickly through highly permeable talus. Flow rates are much slower in areas that are shallowly sloping, which tend to have much finer grained and better developed soils. Sueker *et al.* (1999) estimated that the age of water exiting Boulder Brook basin was twice as old (*c*. 400 days) as water exiting Fern and Spruce Creek basins (*c*. 200) in August 1994. The differences in ages were attributed to differences in basin geomorphology, i.e., Fern and Spruce Creeks are much steeper and have more exposed bedrock and younger, shallower surficial debris compared with Boulder Brook (Table I). Biologic reactions also can be expected to be different in areas with steep slopes than in areas with shallow slopes, largely because of differences in vegetation, soil and hydrology. The following discussion presents interpretations about controls on spatial variations in solute fluxes and the role of specific environments on solute fluxes and mineral weathering rates.

### *Nitrogen fluxes*

Variations in N flux from the study basins are correlated with differences in the relative abundance of steep slopes, unvegetated terrain or young debris (Table V). The strong relationship between $NO_3$ flux and unvegetated terrain is shown in Figure 7. Any of these physical characteristics, which are derived from three separate GIS coverages (topography, vegetation and geology), may be useful predictors of the sensitivity of

Table IV. Spearman correlation coefficients for runoff and solute fluxes in streams in 1994

| | Runoff | Ca | Mg | Na | K | H | Alkalinity | $NO_3$ | $SO_4$ | Cl | $SiO_2$ | Ca/Na | SBC[†]/alkalinity |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Runoff | 1·00 | | | | | | | | | | | | |
| Ca | 0·95** | 1·00 | | | | | | | | | | | |
| Mg | 0·31 | 0·46 | 1·00 | | | | | | | | | | |
| Na | −0·20 | −0·09 | 0·31 | 1·00 | | | | | | | | | |
| K | 0·54 | 0·53 | 0·68 | −0·04 | 1·00 | | | | | | | | |
| H | 0·85* | 0·80* | 0·22 | −0·43 | 0·40 | 1·00 | | | | | | | |
| Alkalinity | −0·37 | −0·17 | 0·49 | 0·83* | −0·06 | −0·55 | 1·00 | | | | | | |
| $NO_3$ | 0·95** | 0·86* | 0·09 | −0·42 | 0·37 | 0·85* | −0·57 | 1·00 | | | | | |
| $SO_4$ | 0·98** | 0·98** | 0·37 | −0·18 | 0·54 | 0·83* | −0·32 | 0·93** | 1·00 | | | | |
| Cl | 0·69 | 0·77 | 0·44 | −0·16 | 0·46 | 0·47 | 0·00 | 0·67 | 0·76 | 1·00 | | | |
| $SiO_2$ | −0·27 | −0·15 | 0·29 | 0·98** | −0·14 | −0·50 | 0·85* | −0·45 | −0·23 | −0·16 | 1·00 | | |
| Ca/Na | 0·87* | 0·80* | −0·03 | −0·53 | 0·23 | 0·82* | −0·57 | 0·95** | 0·85* | 0·71 | −0·57 | 1·00 | |
| SBC/alkaline | 0·93** | 0·82* | 0·08 | −0·47 | 0·41 | 0·63 | −0·63 | 0·98** | 0·90** | 0·61 | 0·93** | −0·52 | 1·00 |

Numbers are *r*-values. * indicates $p \leq 0 \cdot 01$. ** indicates $p \leq 0 \cdot 001$. † SBC is sum of base cations.

Table V. Spearman correlation coefficients for relations between physical characteristics of basins and runoff, solute and mineral weathering fluxes in streams in 1994

| | Topography | | | Vegetation | | | | Geology | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Area (ha) | Average Elevation (m) | Steep slope | Tundra | Unvegetated | Forest | Subalpine meadow | Granite | Gneiss | Debris | Young debris | Old debris |
| Runoff | −0·73 | 0·20 | 0·83* | −0·48 | 0·88* | −0·48 | −0·84* | −0·80* | 0·85* | −0·05 | 0·83* | −0·55 |
| Solutes | | | | | | | | | | | | |
| Ca | −0·61 | 0·11 | 0·69 | −0·70 | 0·79 | −0·27 | −0·75 | −0·74 | 0·80* | 0·03 | 0·73 | −0·44 |
| Mg | 0·34 | −0·68 | −0·13 | −0·64 | −0·06 | 0·65 | 0·03 | 0·16 | 0·10 | −0·06 | −0·08 | 0·17 |
| Na | 0·23 | −0·50 | −0·64 | 0·10 | −0·52 | 0·50 | 0·52 | 0·06 | −0·51 | 0·78 | −0·54 | 0·88* |
| K | −0·15 | −0·41 | 0·30 | −0·38 | 0·22 | 0·15 | −0·31 | −0·16 | 0·47 | −0·43 | 0·12 | −0·30 |
| H | −0·58 | 0·20 | 0·81* | −0·55 | 0·78 | −0·47 | −0·69 | −0·63 | 0·90** | −0·35 | 0·76 | −0·75 |
| Alkalinity | 0·60 | −0·65 | −0·77 | −0·17 | −0·62 | 0·82* | 0·56 | 0·41 | −0·59 | 0·60 | −0·62 | 0·88* |
| $NO_3$ | −0·78 | 0·45 | 0·91** | −0·38 | 0·96** | −0·65 | −0·94** | −0·80* | 0·83* | −0·13 | 0·95** | −0·70 |
| $SO_4$ | −0·70 | 0·23 | 0·77 | −0·58 | 0·85* | −0·40 | −0·82* | −0·80* | 0·81* | −0·03 | 0·81* | −0·53 |
| Cl | −0·35 | 0·18 | 0·44 | −0·70 | 0·60 | −0·03 | −0·75 | −0·45 | 0·48 | −0·03 | 0·58 | −0·36 |
| $SiO_2$ | 0·30 | −0·43 | −0·70 | 0·12 | −0·54 | 0·53 | 0·54 | 0·12 | −0·61 | 0·82* | −0·54 | 0·92** |
| Ca/Na | −0·73 | 0·50 | 0·91** | −0·45 | 0·96** | −0·65 | −0·96** | −0·73 | 0·85* | −0·18 | 0·95** | −0·75 |
| SBC/Alkalinity | −0·77 | 0·40 | 0·93** | −0·37 | 0·93** | −0·67 | −0·62 | −0·75 | 0·89** | −0·23 | 0·92** | −0·77 |
| Minerals | | | | | | | | | | | | |
| Oligoclase | 0·35 | −0·57 | −0·69 | 0·01 | −0·59 | 0·57 | 0·15 | 0·16 | −0·55 | 0·70 | −0·60 | 0·88* |
| Calcite | −0·68 | 0·10 | 0·79* | −0·59 | 0·84* | −0·40 | −0·80* | −0·76 | 0·86* | −0·04 | 0·77* | −0·50 |
| Pyrite | −0·75 | 0·30 | 0·92** | −0·47 | 0·92** | −0·61 | −0·70 | −0·77 | 0·94** | −0·20 | 0·89** | −0·72 |
| Biotite | 0·40 | −0·70 | −0·18 | −0·67 | −0·12 | 0·70 | −0·43 | 0·23 | 0·05 | −0·16 | −0·16 | 0·17 |
| Chlorite | 0·44 | −0·75 | −0·19 | −0·65 | −0·12 | 0·71 | −0·42 | 0·26 | 0·02 | −0·10 | −0·15 | 0·22 |
| Kaolinte | 0·32 | −0·18 | −0·42 | 0·05 | −0·34 | 0·47 | 0·12 | 0·32 | −0·43 | 0·11 | −0·40 | 0·42 |
| Microcline | −0·21 | 0·10 | 0·21 | 0·26 | 0·10 | −0·21 | 0·31 | −0·10 | 0·16 | −0·26 | 0·05 | −0·21 |
| Total | −0·05 | −0·38 | 0·14 | −0·52 | 0·29 | 0·30 | −0·53 | −0·20 | 0·20 | 0·20 | 0·25 | 0·15 |

Numbers are $r$-values. * indicates $p \leq 0 \cdot 01$. ** indicates $p \leq 0 \cdot 001$.

ecosystems to N deposition. Areas in the basins where these physical characteristics overlap are coincident with the talus environment and are likely to be particularly sensitive to N deposition (Clow and Sueker, 2000).

The influence of the talus environment on elevating $NO_3$ concentrations in stream water has been noted previously by Clow and Sueker (2000) and by Campbell *et al*. (2000). Sparse vegetation and fast flow rates in the talus environment limit uptake of atmospherically deposited N ($NH_4$ and $NO_3$) by biota. In addition, the availability of atmospherically deposited $NH_4$, the presence of an active microbial population and a carbon-poor substrate are conducive to nitrification (conversion of $NH_4$ to $NO_3$) (Schlesinger, 1991; Campbell *et al*., 2000). Campbell *et al*. (2000) suggested that the large areal extent of talus deposits, along with their high concentrations of $NO_3$ and capacity to store groundwater, make talus the most likely source of $NO_3$ in stream flow in Loch Vale, especially during the growing season.

Other environments in the study basins also may play important roles in N cycling. Forests appear to be a significant sink of $NO_3$ in the subalpine zone, as indicated by extremely low $NO_3$ concentrations in soil

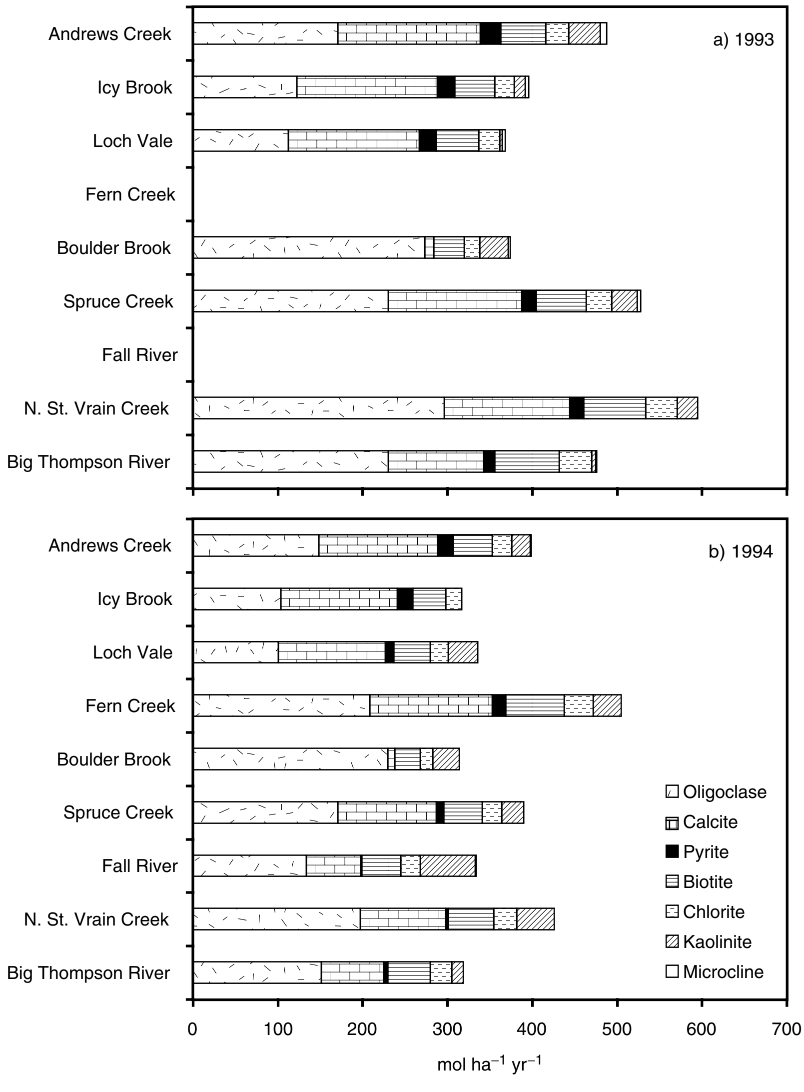


Figure 5. Mineral weathering rates for (a) 1993 and (b) 1994

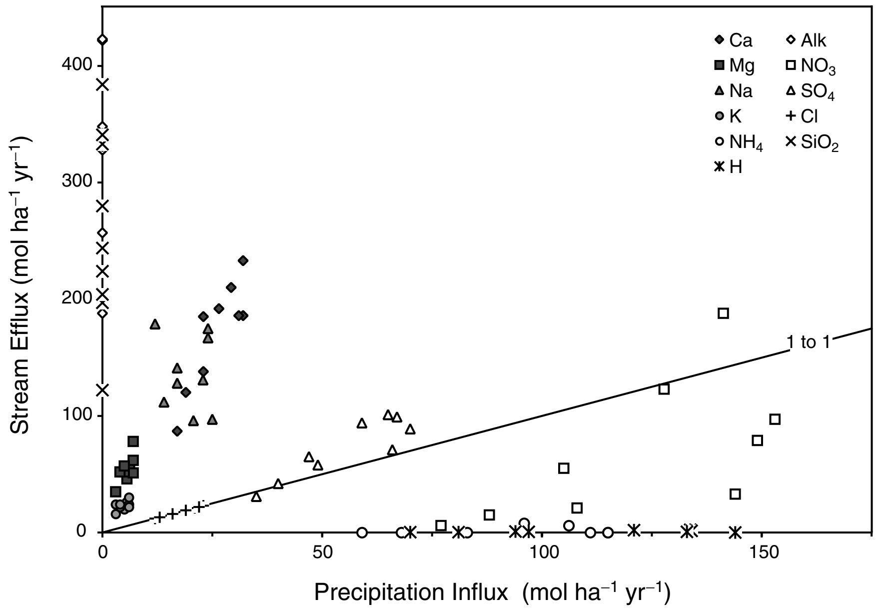


Figure 6. Precipitation influx and stream efflux of solutes for 1994

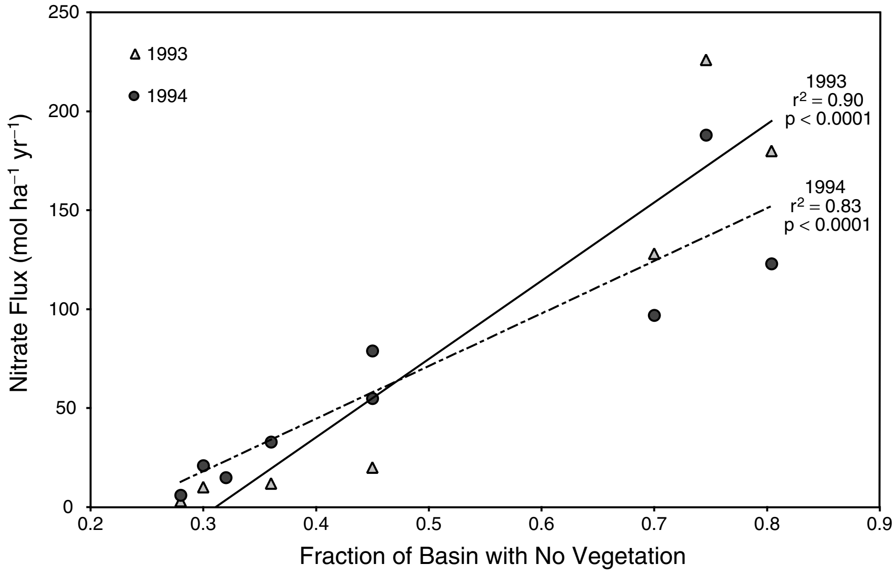


Figure 7. Comparison of nitrate fluxes and fraction of basin with no vegetation for 1993 and 1994

water during the growing season. High water consumption and N assimilation by forest plants, which limits runoff and solute export, might cause the lack of correlation of forest area with $NO_3$ flux.

Like the forest soils, subalpine meadow soils have relatively low $NO_3$ concentrations, probably owing to assimilation and denitrification in the anoxic meadow soils (Clow and Sueker, 2000). The negative relationship between the fractional amount of subalpine meadows in the basins and $NO_3$ export is somewhat surprising, given the small areal extent of the meadow environment. Subalpine meadows tend to occur along streams, and this proximity to surface water may allow the meadows to exert a relatively strong influence on stream-water $NO_3$ fluxes.

Minimal assimilation, potential mineralization and nitrification cause elevated $NO_3$ concentrations and possible nitrogen saturation in the tundra environment (Campbell *et al.*, 2000; Clow and Sueker, 2000). Despite the large areal extent in the study basins, the tundra environment appears to have little influence on $NO_3$ fluxes, as indicated by the lack of correlation between tundra and nitrate flux. This lack of correlation may result from a lack of hydrological connection between the upland tundra environment and the valley streams (Clow and Sueker, 2000).

Nitrogen saturation occurs when the supply of nitrogenous compounds from the atmosphere exceeds the demand for these compounds on the part of watershed plants and microbes (Stoddard, 1994). In the strictest sense, N saturation is occurring in these basins and other basins along the Colorado Front Range (Williams *et al.*, 1996; Campbell *et al.*, 2000). The results of this study indicate that the sensitivity of a basin to increased N deposition can be assessed by examining the basin's physical characteristics. Basins with more talus and bedrock and less established vegetation would be more susceptible to increases in N export and N saturation resulting from increased N deposition.

### *Mineral weathering*

Mineral weathering is the primary long-term source of acid-neutralizing capacity in natural ecosystems. It is important to understand controls on spatial variability in weathering rates, because those rates help determine the response of specific environments to perturbations, such as N deposition or climate change.

A strong non-linear positive correlation was identified between oligoclase weathering rates and the fractional amount of old debris in each of the basins (Figure 8 and Table V). This correlation probably is related to the mineralogical and hydrological characteristics of the environments where old debris occurs. Old debris consists of Pleistocene till, which tends to occur low in the basins in the forest environment, and Pleistocene colluvium, which tends to occur along ridge tops in the tundra environment. Preferential weathering causes readily dissolved minerals, such as calcite and pyrite, to become depleted from soils over time (Goldich, 1938). Minerals that weather more slowly, such as oligoclase, microcline and quartz, gradually become enriched in older soils. Thus, the correlation between oligoclase weathering rates and the fractional amount of old debris in the basins may be the result, in part, of a relatively high proportion of oligoclase in soils formed on old debris.

Hydrological characteristics of soils in the forest and tundra environments may also promote oligoclase weathering. Soils in these environments tend to be relatively deep and have shallow slopes compared with the immature and highly permeable material in the young debris. These factors increase hydrological residence time and water–rock interaction, which should in turn enhance weathering of all minerals present in the soils (albeit not equally for all minerals). Alkalinity, which is one of the main by-products of oligoclase weathering, also was correlated with old debris, indicating that old debris is an important source of buffering capacity in the basins.

The strong positive correlations between calcite and the fraction of each basin characterized by steep slopes, unvegetated terrain and young debris probably result from high rates of physical weathering in the talus environment. In the study basins, calcite is present in trace amounts in microfractures and between mineral grains in hydrothermally altered bedrock (Mast *et al.*, 1990). This calcite dissolves rapidly when exposed to water and becomes depleted from mineral surfaces over time. Physical weathering is active in the talus environment, because abundant ice and extremes in temperature promote freeze–thaw cycles. The physical weathering causes fresh mineral surfaces to be exposed periodically, renewing the supply of calcite available for weathering (Mast *et al.*, 1990).

Sulphate exports exceeded sulphate inputs in each of the seven basins monitored in 1993, and in eight of nine basins monitored in 1994. Pyrite weathering may contribute sulphate to the streams, although dry deposition could account for some of the excess sulphate (Grant and Lewis, 1982; Clow and Mast, 1995).

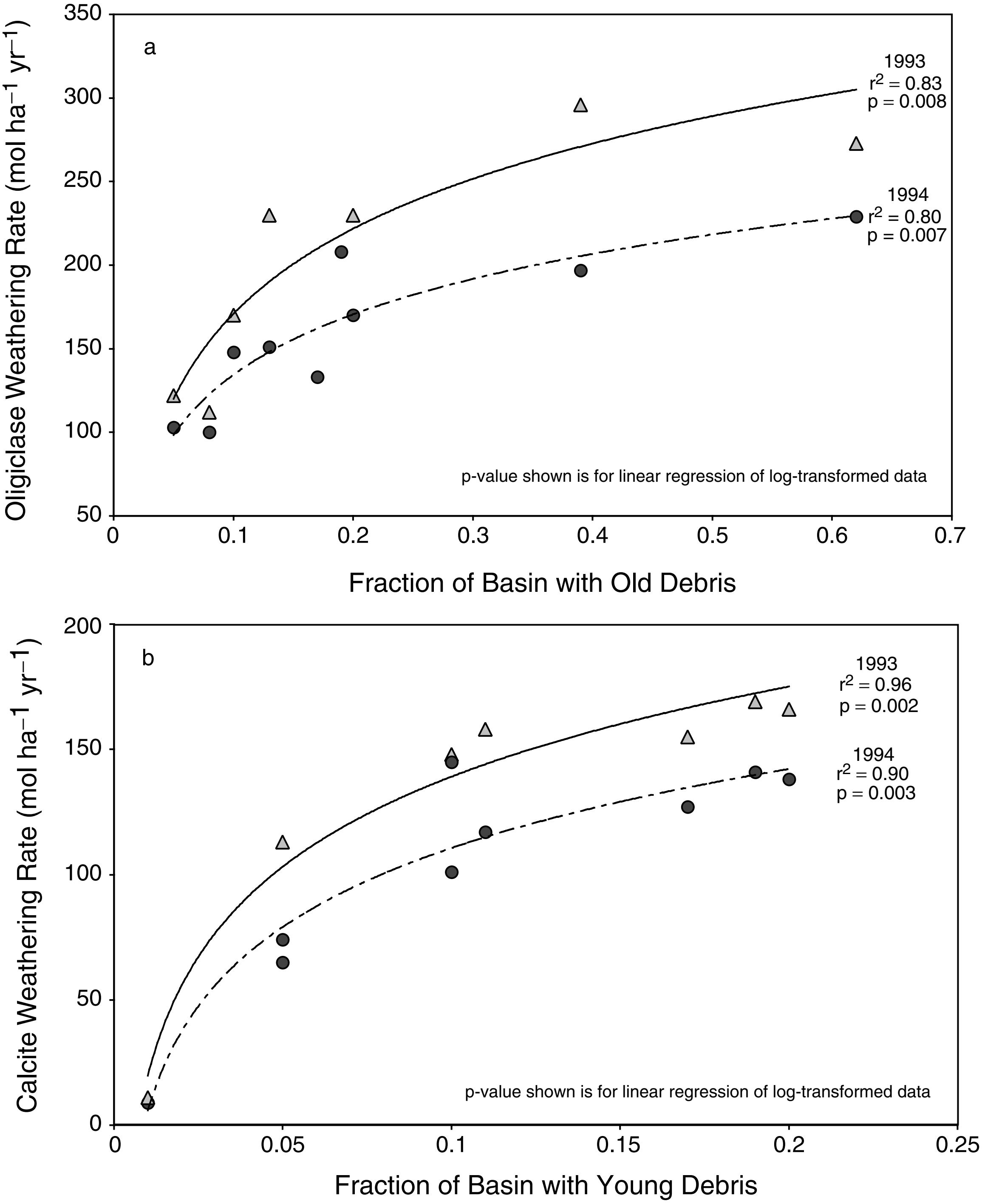


Figure 8. Comparison of (a) oligoclase weathering rate and fraction of basin with old debris and (b) calcite weathering rate and fraction of basin with young debris

Pyrite weathering rates were correlated with the same physical characteristics as calcite, except for the negative correlation between calcite and subalpine meadow. The physical weathering processes that appear to affect calcite weathering rates may affect pyrite weathering in a similar manner.

The positive correlation between the fractional amount of gneiss bedrock in the basins and calcite and pyrite weathering rates might be related to the chemical and mineralogical characteristics of the gneiss. Gneiss tends to be more heavily altered than granite, and thus is likely to contain more calcite and pyrite, which are believed to have formed during hydrothermal and metamorphic events (Mast *et al*., 1990).

### *Sensitivity analyses*

Sensitivity analyses were performed to determine the effect of uncertainties in solute influx and efflux estimates on the outcome of the mineral weathering mass-balance calculations. Uncertainties in the input values include precipitation amount, analytical error in the determination of solute concentrations and contributions from dry deposition. Uncertainties in the output values include stream-flow measurements, analytical error in the determination of solute concentrations, variability of stream-solute concentrations between sampling events, and groundwater flow.

Dry deposition is comprised of gases and particles that impact on natural surfaces in the absence of precipitation. Although adequate methods exist for estimating wet deposition fluxes to watersheds, measurement of dry deposition remains problematic (Edgerton *et al*., 1991). Grant and Lewis (1982) estimated dry deposition at a subalpine site approximately 20 km south of RMNP. Clow and Mast (1995) measured wet deposition and bulk deposition (wet + dry) in Loch Vale. Estimates of dry deposition based on these studies vary tremendously between solutes and between studies but typically range from about 10% to 60% of wet deposition for most solutes.

Precipitation amount is estimated using a chloride balance with the assumption that all chloride is contributed by wet deposition. Dry deposition of chloride may be about 20% of the wet deposition amount (Grant and Lewis, 1982; Clow and Mast, 1995), thus, wet deposition may be overestimated. If the ion ratios of solutes vary between wet deposition and dry deposition, then the solute influx estimates may be over- or underestimated, depending upon the difference in the wet and dry deposition ion ratios. Although Mast *et al*. (1990) found no evidence of chloride in sampled biotite, biotite may contain trace amounts of chloride. If biotite is assumed to contain 1% Cl, the contribution of chloride to surface waters from the dissolution of biotite would be only about 2% to 3% of the total chloride efflux (Sueker, 1996).

Estimated ET and sublimation losses for all nine of the study basins ranged from 19 to 82 cm (21 to 64%) over the two-year study period. Estimated losses for Loch Vale basin were 82 cm (51%) in 1993 and 51 cm (45%) in 1994. Although a rather simplistic Cl balance method was used to calculate evaporative losses, these estimates are in general agreement with other estimates of ET for Loch Vale basin. Baron (1992) and Baron *et al*. (2000) estimated ET and sublimation losses to be about 40% of total precipitation. Clow and Drever (1996) determined that ET losses ranged from 1·0 to 1·5 mm day$^{-1}$ during the summer. Meixner *et al*. (2000) estimated potential ET to be 0·66 mm day$^{-1}$ during the winter and 1·3 mm day$^{-1}$ during the summer, and potential sublimation to be 75% of potential ET.

The precision and accuracy of the analytical measurements of stream solute concentrations are less than $\pm$5·5% for base cations, silica and sulphate, $\pm$8·5% for nitrate and $\pm$12·5% for chloride (Sueker, 1996). The accuracy of stream-flow measurements is approximately $\pm$7% (Sueker, 1996). Stream-solute fluxes were estimated using solute data for discrete samples. However, solute concentrations vary diurnally as well as seasonally. Snowmelt is the main hydrological event on an annual basis. Daily sampling at Boulder Brook and Spruce Creek from mid-April through September 1993 indicated that seasonal variability was captured by the sampling scheme described above. To determine the effect of diurnal variability, diurnal sampling was conducted during high flow (late May) and recession flow (early September) in 1993 for Boulder Brook and Spruce Creek. Stream samples were collected every 2 h for a 48-h period. The relative standard deviation (standard deviation divided by the mean) was less than 10% for most solutes for both flow periods. The relative standard deviation for chloride was about 20% in May and 5% in September. Diurnal variability is greater than, but of a similar magnitude to, analytical error.

Water and solutes may be transported from the basins through groundwater flow. Groundwater flow through bedrock was assumed to be negligible. Groundwater outflow through glacial till material was estimated using Darcy's law (Fetter, 1994):

$$Q = A \times K \times \pi_e \times s$$

where $A$ is the cross-sectional area of the aquifer at the basin outlet, $K$ is the hydraulic conductivity, $\pi_e$ is the effective porosity of the aquifer matrix and $s$ is the slope of the water table. The widths of the contributing areas were measured from the geological map and depths of glacial till were estimated to range from about 10 to 20 m based on descriptions of the mapped till (Braddock and Cole, 1990). The till was assumed to be saturated the entire depth. Maximum hydraulic conductivity of the glacial till was assumed to $10^{-3}$ cm $s^{-1}$, and $\pi_e$ was assumed to be 0·3. The slope of the aquifer was set equal to the slope of the stream near the basin outlet. Based on these assumptions, Boulder Brook had the greatest groundwater flow equalling about 2% of the total annual stream flow, which is less than the measurement error for stream flow. Estimates of groundwater flow relative to stream flow for the other eight basins were 0·1% or less, and therefore, are negligible.

Mineral mass balance calculations were performed to determine the effects of varying input and output solute fluxes. To estimate the effect of dry deposition, solute inputs were increased by a factor of 1·4, based on a best estimate of the dry deposition rate for most solutes (Grant and Lewis, 1982; Clow and Mast, 1995). Mineral weathering fluxes decreased by 11 to 37 mol $ha^{-1}$ $year^{-1}$ (3 to 10%) for 1993 and by 6 to 23 mol $ha^{-1}$ $year^{-1}$ (2 to 7%) for 1994. To estimate the effects of groundwater flow, and analytical and stream flow measurement error, solute fluxes from the basins were varied by factors of 0·9 and 1·1. Mineral weathering fluxes decreased or increased in 1993 by 42 to 67 mol $ha^{-1}$ $year^{-1}$ (about 13%) and by 33 to 58 mol $ha^{-1}$ $year^{-1}$ (about 12%) for 1994 using factors of 0·9 and 1·1, respectively. Although the change in total mineral weathering fluxes varied from $-14$ to $+13$% depending upon the sensitivity scenario, the ratios of the mineral weathering rates for each basin did not vary significantly from the ratios determined using the initial assumptions. Therefore, there was no change in the statistical relationships between mineral weathering rates and basin physical characteristics and the initial interpretations of the physical meaning of the correlations remain unchanged.

## CONCLUSIONS

Stream-water fluxes of nitrate from nine alpine/subalpine basins were found to be strongly correlated with the fractional amounts of steep slopes ($\geq$ 30°), unvegetated terrain and young debris in the basins. These physical characteristics, which are derived from three separate GIS coverages (topography, vegetation and geology), are useful predictors of the sensitivity of an ecosystem to nitrogen deposition. Areas where these physical characteristics overlap, such as in the talus environment, are particularly sensitive. The sensitivity of the talus environment stems from hydrological and biological factors. Talus deposits typically have high permeability, which limits interactions between atmospherically deposited nitrogen and sulphur compounds and talus soils and microbiota. Lack of vegetation in the talus contributes to a carbon-poor environment that promotes mineralization and nitrification. Conversely, negative correlations between nitrate flux and subalpine meadows indicate that those areas are less sensitive to nitrogen deposition.

Fluxes of solutes derived from calcite weathering were correlated with steep slopes, unvegetated terrain and young debris in the basins. Although only trace amounts of calcite are found in bedrock, calcite dissolution is a substantial contributor of solutes. Physical weathering of bedrock in high-gradient areas exposes fresh, calcite-bearing mineral surfaces to chemical weathering. Alkalinity generated from calcite weathering in the talus environment neutralizes some of the acidity found there.

Oligoclase weathering is correlated with the fractional amount of old debris in the basins, probably because old debris promotes long residence times of water and because soils are enriched in silicate minerals. Alkalinity, which is one of the main by-products of oligoclase weathering, also was correlated with old debris, indicating that old debris (mostly Pliestocene glacial till) is an important source of buffering capacity in the basins.

Evaluation of basin physical characteristics provides a useful tool for determining the potential sensitivity of alpine/subalpine basins to increases in nitrogen or acidic deposition. Basins with substantial areas of steep, unvegetated terrain probably will be more sensitive than basins with shallower slopes and well-established vegetation.

## ACKNOWLEDGMENTS

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