

HYDROLOGIC PATHWAY CONTRIBUTIONS TO STREAM FLUXES OF WEATHERING PRODUCTS AT THE PANOLA MOUNTAIN RESEARCH WATERSHED, GEORGIA

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Abstract. Short-term weathering rates (chemical denudation) were derived from an analysis of fluxes of the primary weathering products in precipitation and streamwater. Rainfall, streamflow (runoff), and related water quality have been monitored at the Panola Mountain Research Watershed since 1985. Regression relations of stream solute concentration of major ions including weathering products [sodium (Na), magnesium (Mg), calcium (Ca) and silica (H_4SiO_4)] were derived from weekly and storm-based sampling from October 1986 through September 1998; run-off, seasonality, and hydrologic state were the primary independent variables. The regression relations explained from 74 to 90 percent of the variations in solute concentration. Chloride (Cl) fluxes for the study period were used to estimate dry atmospheric deposition (DAD) by subtracting the precipitation flux from the stream flux; net Cl flux varied from years of net retention during dry years to less than three times more Cl exported during wet years. On average, DAD was 56 percent of the total atmospheric deposition, which also was assumed for the other solutes; average annual net cation and H_4SiO_4 fluxes were 50.6 and 85.9 millimole per square meter (mmol m^{-2}), respectively. The annual cumulative density functions of solute flux as a function of runoff were evaluated and compared among solutes to evaluate relative changes in solute sources during stormflows. Stream flux of weathering solutes is primarily associated with ground-water discharge. During stormflow, Ca and Mg contributions increase relative to Na and H_4SiO_4 , particularly during wet years when the contribution is 10 percent of the annual flux. The higher Ca and Mg contributions to the stream during stormflow are consistent with increased contribution from shallow soil horizons where these solutes dominate.

INTRODUCTION

Chemical denudation and, in some cases, the rates of mineral weathering have been estimated from mass balance for forested small catchments (Johnson et al. 1968; Paces 1985, 1986; Velbel 1985; April et al. 1986; Peters et al. 2006). Weathering rates for some minerals, e.g. feldspar, have been attributed to hydrologic controls (Velbel 1993; White et al. 2001), whereas the weathering rates of other minerals, e.g.

biotite, have been attributed to kinetic controls (White et al. 2002). These studies evaluate fluxes, which typically are bounded by atmospheric deposition inputs and streamwater outputs (Bluth and Kump 1994; Oliva et al. 2003), changes in soil solution and mineral and elemental depletion/enrichment in soils and bedrock (White et al. 2001, 2002), or a combination of fluxes and changes in solutions and solid phases (Paces 1985, 1986; April et al. 1986; Velbel 1985, 1993; Huntington et al. 2000). Solid phase chemical and mineralogical changes reflect long-term weathering whereas soil solution and input-output fluxes reflect both short and long-term weathering, but are sensitive to short-term “readjustments” of exchangeable ions caused by changes in the composition of atmospheric deposition (Paces 1985, 1986; Huntington 2000). Temporal and spatial variations in hydrologic conditions affect fluxes, and therefore, interpretation of short-term chemical denudation rates. Can hydrochemical characteristics and variations in streamwater and soil solutions allude to processes, i.e., solute sources and transport controlling the short-term chemical denudation rates?

A weathering profile at the Panola Mountain Research Watershed (PMRW), the site of the study herein, shows large changes in mineral and elemental composition with depth to ~ 9.5 meter (4.5 meter soil and 5 meter bedrock), which reflects long-term weathering of the underlying Panola Granite (White et al. 2001, 2002). The chemistry of surface-horizon soil solutions differs significantly from the solid phase chemistry and reflects typical biogeochemical cycling by the forest and cation exchange in the soil (Peters and Ratcliffe 1998; White et al. 2001). The surface soil solutions are enriched in calcium (Ca), magnesium (Mg), and potassium (K) compared with soil solutions lower in the profile (Hooper et al. 1990; Peters and Ratcliffe 1998). In contrast, dissolved silica (H_4SiO_4) and sodium (Na) are minimally affected by biogeochemical cycling and ion exchange, and their concentrations increase progressively with depth below the land surface and also increase with residence time in ground water (Peters and Ratcliffe 1998; Burns et al. 2003).

Base cations (Ca, Mg, and sodium Na) and H_4SiO_4 concentrations dilute as runoff increases during rainstorms at PMRW (Peters 1994). Hooper et al. (1990) showed the general dominance of a ground-water source, which was augmented by hillslope water when the watershed was wet and by shallow soil water when the watershed was dry. A

follow up end-member mixing analysis by Hooper (2001) showed a pronounced temporal change in the end-member solute composition. Hooper (2001) concluded that the hillslope end member, which represents ~85 percent of the watershed (Freer et al. 2002), is not chemically expressed in the stream and that the stream chemical dynamics largely reflect the relative contribution of different parts of the riparian area, and not the workings of the catchment as a whole.

Streamwater sources change during rainstorms. Hydrologic processes at PMRW are nonlinear during rainstorms, but maximum ground-water levels, maximum soil moisture content, and stormflow water yields are linearly related to each other above a wetness threshold (Peters et al. 2003; Tromp-van Meerveld and McDonnell 2006). The general relations among streamflow, soil moisture, and water table response are attributed to variable source areas, particularly ground-water contributions from a riparian zone aquifer ≤ 5 m thick that expands as the watershed becomes wetter, and subsurface translatory flow during rainstorms (Hewlett and Hibbert 1967).

Perturbations to the long-term chemical/weathering evolution of the watershed have likely occurred due to agricultural land abandonment in the early 1900s (Huntington et al. 2000) and to changes in atmospheric deposition since 1900. In particular, increases in “acid rain” [pH of rainfall at PMRW averages in the low 4s (Peters et al. 2002)]; sulfate (SO_4^{2-}) mobilization causes leaching of cations, particularly Ca, from soil exchange sites (Huntington et al. 2000). In the long run, this process should approach a steady state with respect to inputs and outputs of SO_4^{2-} . For PMRW, the chemical readjustment of the watershed to SO_4^{2-} inputs will be slow because the soils in the Southeast strongly adsorb SO_4^{2-} (Shanley 1992). PMRW is currently displaying considerable sulfate mobilization during rainstorms despite an annual retention of 80 to 90 percent of the SO_4^{2-} (Huntington et al. 1994).

The objective of this paper is to present annual chemical denudation results and those of a preliminary investigation of relative changes in mobility and hydrologic pathway contributions of base cations and H_4SiO_4 with respect to runoff and general wetness condition. The analysis focuses on stream base cation and H_4SiO_4 concentrations and relative cumulative flux distributions.

SITE DESCRIPTION

The PMRW is a 0.41 square kilometer relatively undisturbed forested watershed in the Panola Mountain State Conservation Park, in the Piedmont Province of Georgia, USA ($84^\circ 10' \text{W}$, $33^\circ 37' \text{N}$; Fig. 1) located 25 kilometers southeast of Atlanta. Climate is humid continental to subtropical. A long growing season, warm temperatures, and many sunny days result in high rates of evapotranspiration (ET), particularly during summer. Air temperature averages 15.2°C annually and the average monthly temperatures range from 5.5°C during January to 25.2°C during July. During WY1986–WY2001 (WY1986, October 1, 1985 through September 30, 1986),

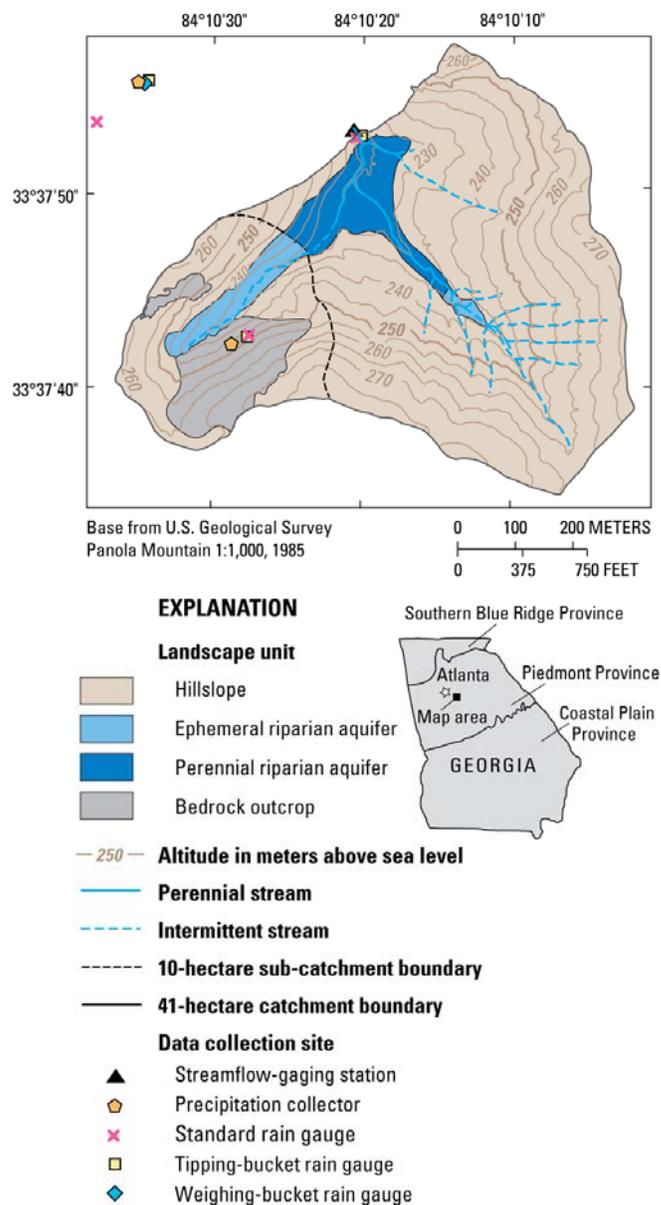


Figure 1. Location of the Panola Mountain Research Watershed, Georgia.

annual precipitation averaged 1,220 mm and ranged from ~760 to 1,580 mm; less than 1 percent of the precipitation occurred as snow; annual runoff averaged 377 mm and ranged from ~150 to 700 millimeter (mm); and annual water yield averaged 30 percent and ranged from 16 percent to 50 percent (Peters et al. 2003). Winter frontal systems provide long, typically low intensity rainstorms in contrast to short intense convective thunderstorms in spring and summer from April through September.

The PMRW is covered with a mixed deciduous/coniferous forest; the oldest deciduous trees are ~130 years old and the oldest coniferous trees are ~70 years old (Cappellato 1991). The dominant bedrock at PMRW is the 320-million-year-old Panola Granite, a biotite-oligoclase-quartz microcline granodiorite, which contains pods of amphibolitic gneiss, particularly at lower elevation (Higgins et al. 1988).

The results presented herein were for samples collected at a compound V-notch weir at the basin outlet. Discharge at the gauge was determined from a stage-discharge rating and stage measurements recorded by a datalogger using a potentiometer and a float-counterweight system. Weekly manual samples (965) were augmented by samples (1,922) collected during rainstorms using a stage-activated automatic sampler (Peters 1994). The analysis herein focuses on data collected from WY1986–WY1998.

Rainfall quality was measured for samples collected weekly using Aerochem Metrics Model 301 wet/dry precipitation collectors following National Atmospheric Deposition Program/National Trends Network protocols (Dossett and Bowersox 1999). In addition to the measured volume of the rainfall sample, 1-minute (min) rainfall totals measured to the nearest 0.25 mm were recorded for each of several tipping-bucket rain gauges (Fig. 1).

Streamwater and precipitation samples were analyzed in the laboratory for pH, specific conductance, and major solutes. The samples were refrigerated upon receipt in the laboratory until the time of analysis. The major solutes, including Na, Ca, Mg, and K were determined by ion chromatography before 1992 and by direct current plasma since 1992; Cl and SO₄ were determined by ion chromatography.

Flux computation

Solute loadings in precipitation were computed by multiplying the solute concentration by the volume of the sample divided by the collection area.

A composite method was used to estimate stream solute fluxes. The composite method combines elements of the typically used regression-model method and period-weighting approach (Aulenbach and Hooper 2006). The regression-model component estimates short-term variations in solute concentrations between sample observations based on known relations with continuous variables such as discharge and season. The residual flux portion of the flux uses a period-weighted approach to correct the regression model to the actual sample concentration by adjusting the model concentration by the residual concentration at the time of sampling and applying the error between sampling times in a piecewise linear fashion. The concentration–discharge relation is modeled using a hyperbolic function (Johnson et al., 1969). This functional form fits the data in this study well. In the hyperbolic model, the best discharge averaging-period, i.e., preceding the time of sample collection, was 15 min for Na, Cl, and H₄SiO₄; 30 min for Mg; and 12 hours for Ca. Seasonal variations in concentration were modeled using sine and cosine functions. One year and half-year periods were used for sine and cosine terms to fit asymmetrical annual cycles.

Streamwater concentrations of Ca, Mg, Na, and H₄SiO₄ are strongly correlated with discharge [or runoff, expressed in mm per day (mm d⁻¹)] and the regression models explain most of the concentration variation with 74, 78, 89, and 90 percent of the variation explained, respectively. Furthermore, there was no apparent change in the relation between concentration and runoff from year to year (Fig. 2). Potassium was not included in the detailed analysis; K is very active in forest biogeochemical cycling (Likens et al. 1994), K concentrations were low compared to the other base cations, and were not highly correlated with runoff nor did the regression model explain much of the concentration variation (32 percent). The concentration-runoff relation is strongest for Na and H₄SiO₄, and the relation is more curvilinear, i.e., concentration versus base-10 logarithm of runoff, for Ca and Mg. Calcium and Mg concentrations are relatively larger at higher runoffs than can be explained by the dilution of ground water, i.e., the mixing of two components, dilute “new” water with “old” ground water (Hooper et al. 1990). The relative Ca increase with increasing flow suggests that Ca is mobilized from another source. This increase in Ca and Mg can be explained by the mobility of SO₄. The relation between Ca and SO₄ is not highly significant, but shows a general pattern of decreasing Ca with increasing SO₄ through a minimum at SO₄ of ~40 micro-equivalents per liter (μeq l⁻¹) followed by an increase in Ca and SO₄ (Fig. 3A). This result is consistent with the hypothesis that cations are depleted from exchange sites in the upper soil horizons due to the mobility of SO₄, which occurs during rainstorms (Fig. 3B). The highest stream Ca concentration at the lowest runoff and concurrent lowest SO₄ concentration are consistent with high ground-water contributions.

The interannual cumulative probability distribution of water flux varied markedly among years (Fig. 4). During a dry year (WY1986), most of the water was transported during base-flow periods with only less than 20 percent being transported during rainstorms, i.e., higher runoff; precipitation was 760 mm and runoff was 150 mm. In contrast, during a wet year (WY1990), ~60 percent of the water was transported during base flow; precipitation was 1,330 mm and runoff was 550 mm. Maximum runoff during base-flow periods was higher during the wet WY than during the dry WY (~2 compared to 0.4 mm d⁻¹). Also, the maximum base flow, which occurs during the winter dormant season, was much lower during WY1986 (0.5–0.6 mm d⁻¹) than WY1990 (~1.8 mm d⁻¹), and there were fewer major rainstorms in WY1986 (Fig. 5).

Cumulative H₄SiO₄ (and Na) and Ca fluxes were markedly different for the two WYs reflecting the effect of stormflow and associated change in hydrological pathway contributions on solute transport (Fig. 6). The similarity and dominance of base flow in water transport during the WY1986 suggests that most of the Ca, Na, and H₄SiO₄ flux was contributed by ground water. During WY1990, however, there is a noticeable shift in the response at higher runoff.

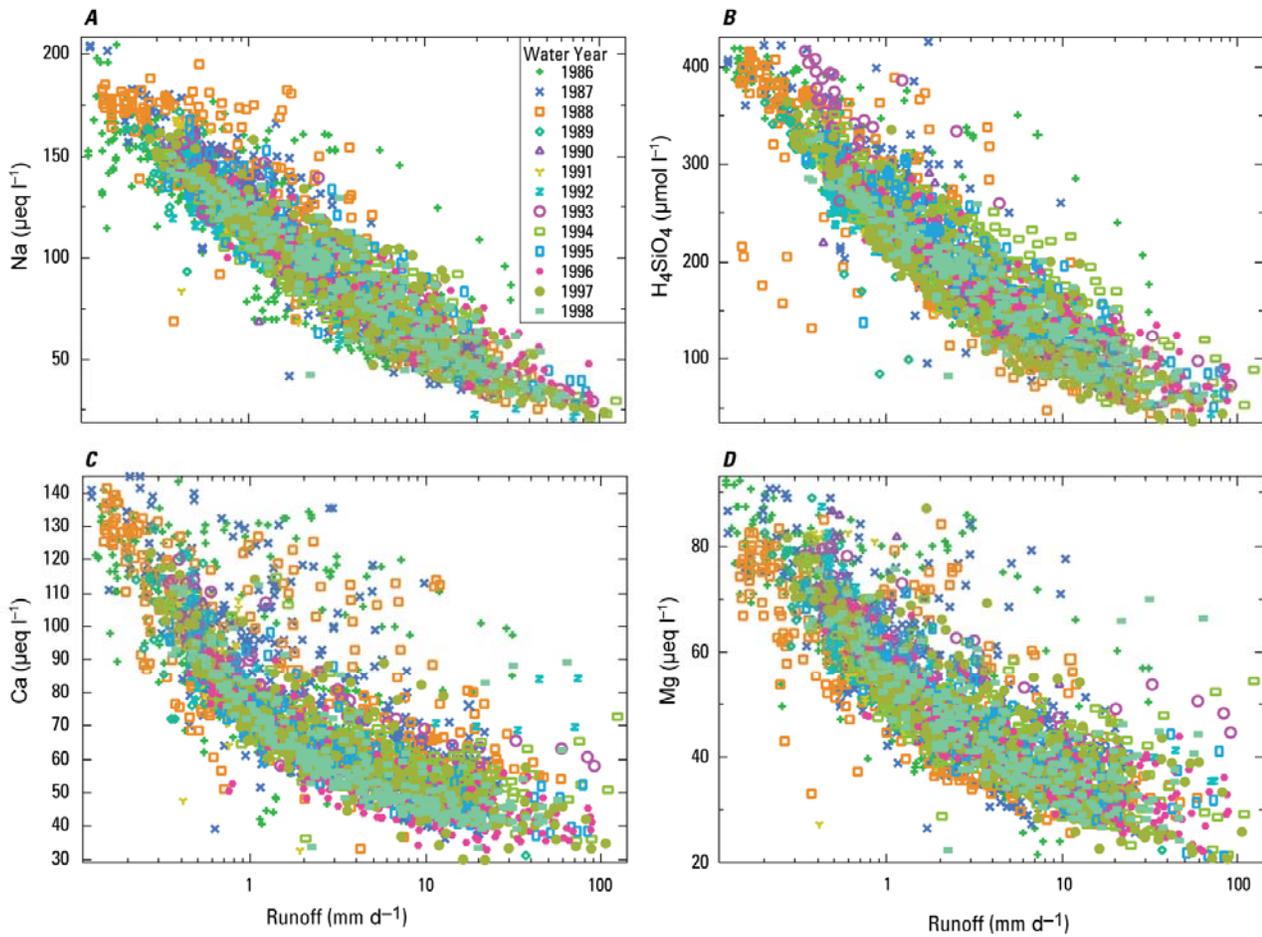


Figure 2. Relation between (A) Na, (B) H₄SiO₄, (C) Ca, and (D) Mg concentration and runoff subdivided by water for WY1986 through WY1998.

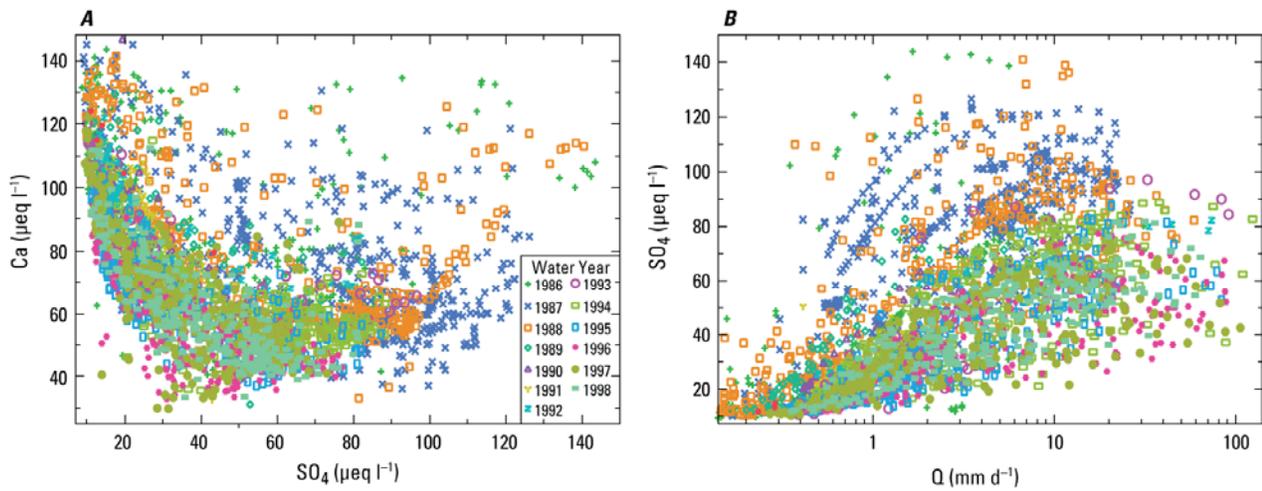


Figure 3. Relations between (A) Ca and SO₄ concentration, and (B) SO₄ concentration and runoff subdivided by water for WY1986–WY1998.

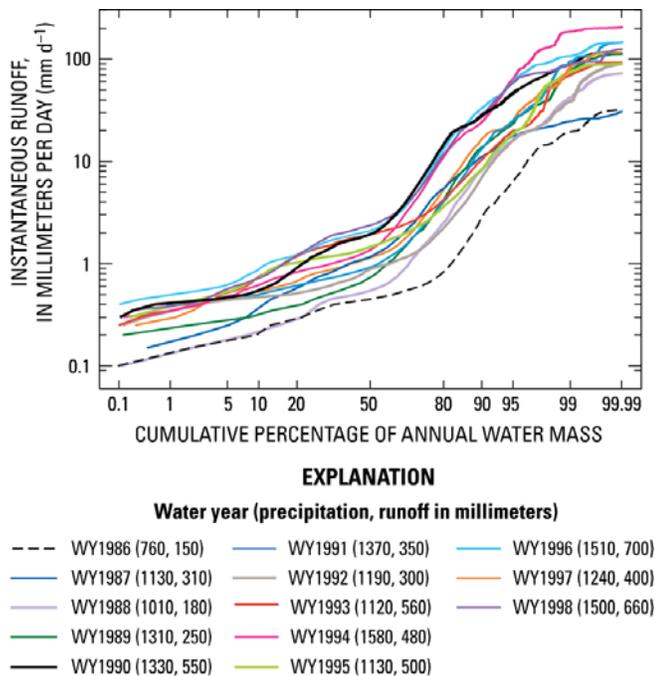


Figure 4. Cumulative distribution of annual water flux with respect to runoff for WY1985–WY1998.

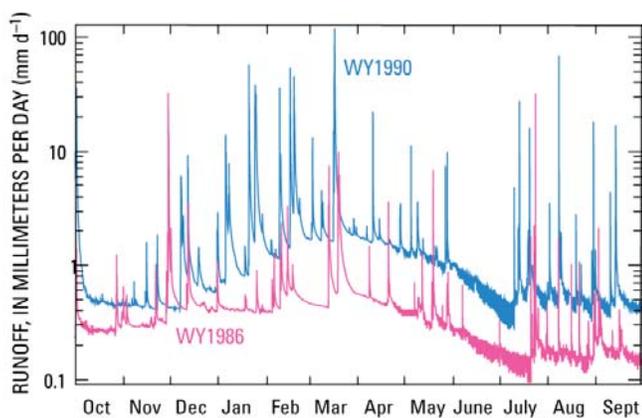


Figure 5. Runoff hydrographs at PMRW during WY1986 and WY1990.

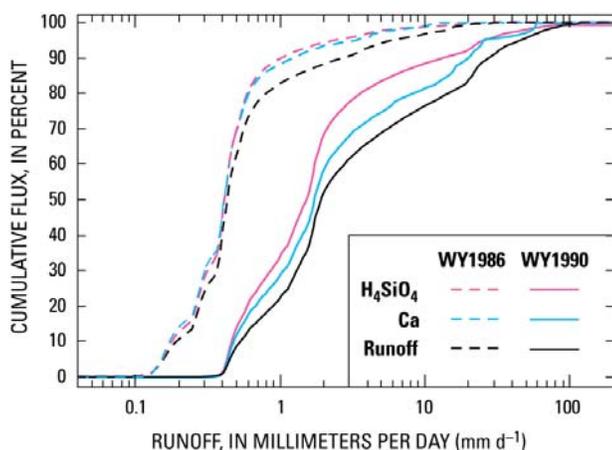


Figure 6. Cumulative density functions of stream Ca and H_4SiO_4 flux, and runoff during WY1986 and WY1990.

Comparing the differences in the constituent flux distributions across runoff alludes to hydrochemical processes. By subtracting the Ca from the H_4SiO_4 flux from the percentage cumulative distribution, the observed H_4SiO_4 excess indicates that the Ca is derived from a different source than H_4SiO_4 . The maximum difference for the wet year is ~10 percent at high runoff (Fig. 7). Because H_4SiO_4 is derived from weathering and is highly correlated with residence time, ground water is the primary and likely the only source. Likewise, subtracting Na from H_4SiO_4 flux, very small differences are noted in either the wet or dry WYs, consistent with a ground-water source for Na and H_4SiO_4 . The 10-percent H_4SiO_4 –Ca difference is attributed to the mobilization of Ca during rainstorms from either cation exchange sites in the upper soil horizons or possibly enriched soil solutions due to biogeochemical cycling by the forest. In addition, maximum H_4SiO_4 –Ca flux difference varied from year to year, but it was highly correlated with annual runoff (Fig. 8). These relations suggest the importance of hydrological processes in solute transport. Ground-water discharge is the sole contributor to runoff during base flow, but as the watershed wets up during rainstorms and runoff increases, some of the runoff is hypothesized to be derived from flow through the unsaturated zone, particularly the areas adjacent to the stream channel (Hooper et al. 1990; Hooper 2001; Peters et al. 2003; Burns et al. 2003; Tromp van Meerveld and McDonnell 2006).

The solute composition of soil solutions and streamwater support this result (Fig. 9). Soil solutions are relatively more enriched in Ca in the upper soil horizons and depleted in H_4SiO_4 (Fig. 9A), which is consistent with the relation between H_4SiO_4 and residence time reported for ground water at PMRW (Burns et al. 2003). Soil solutions become more Na and H_4SiO_4 rich with increasing depth and presumably residence time. In contrast, streamwater is more Na and H_4SiO_4 rich during base flow, and as observed with the flux estimates, Ca and Mg are relatively more enriched at higher runoff (Fig. 9B).

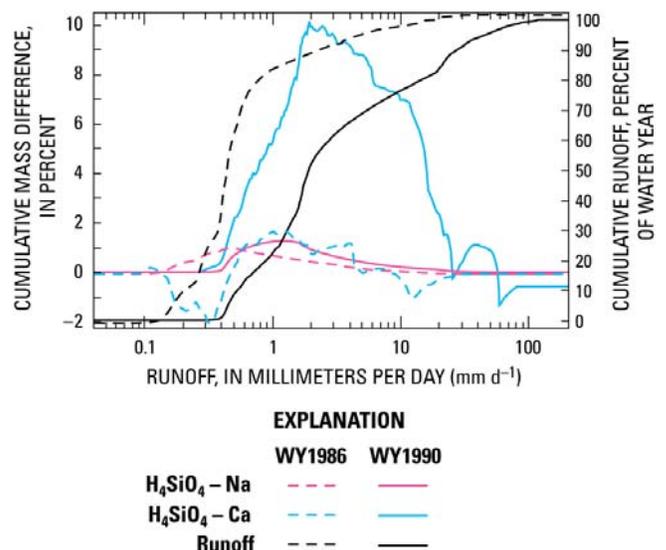


Figure 7. Cumulative density functions of the differences between fluxes of H_4SiO_4 and Na, and H_4SiO_4 and Ca, and runoff during WY1986 and WY1990.

Annual solute fluxes

The annual stream Cl flux (O, output) varied markedly and when compared to the annual precipitation Cl flux (I, input) ranged from years with net retention ($I/O = 1.13$) to years much higher output than input ($I/O = 0.28$). These differences are attributed to variations in the mobilization of wet and dry atmospheric Cl deposition, which is the main source of Cl to the watershed (Peters and Ratcliffe 1998). Assuming that the Cl is conservative and mobile with no internal watershed source, dry Cl deposition, on average, was 56 percent of the total deposition for WY1986–WY1998, i.e., the net flux was zero for the study period. The 56 percent dry deposition estimate was used to compute the dry deposition of cations, SO_4 and H_4SiO_4 (Table 1). Chemical denudation, on average, accounts for net cation and H_4SiO_4 fluxes of 50.6 and 85.9 mmol m^{-2} . These solute fluxes are comparable to those reported for other temperate streams underlain by granitoid rocks (Bluth and Kump 1994; Oliva et al. 2003).

Table 1. Average annual solute fluxes during WY1986–WY1998 at PMRW; atmospheric deposition includes both wet and dry deposition.

Solute	Flux (mmol m^{-2} , kilograms per hectare)		
	Atmospheric deposition	Stream	Net
Ca	4.7 (1.9)	14.4 (5.8)	9.7 (3.9)
Mg	1.6 (0.4)	10.5 (2.5)	8.8 (2.1)
Na	15.5 (3.6)	40.7 (9.4)	25.3 (5.8)
K	2.7 (1.0)	9.5 (3.7)	6.8 (2.7)
Cations	24.5 (6.9)	75.1 (21.4)	50.6 (14.5)
H_4SiO_4 (as Si)	0 (0)	85.9 (24.0)	85.9 (24.0)
Cl	16.7 (5.9)	16.7 (5.9)	0 (0)
SO_4	45.8 (44.0)	8.6 (8.3)	-37.2 (-35.7)

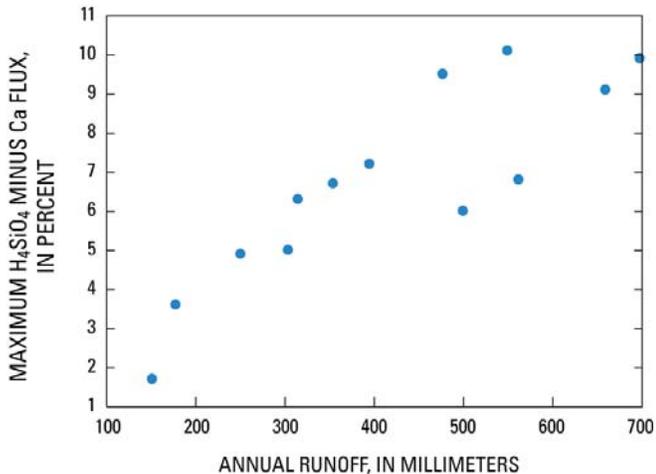
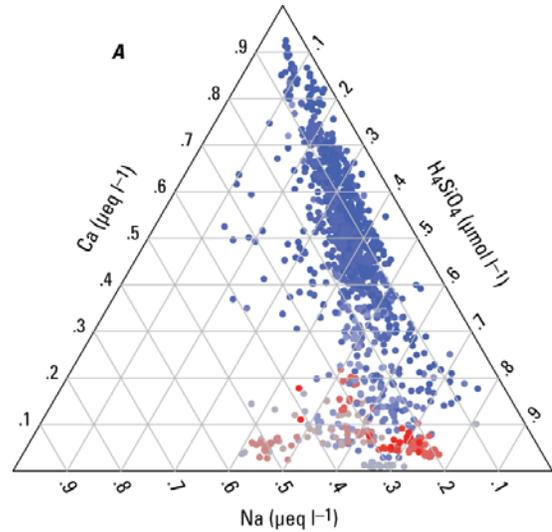
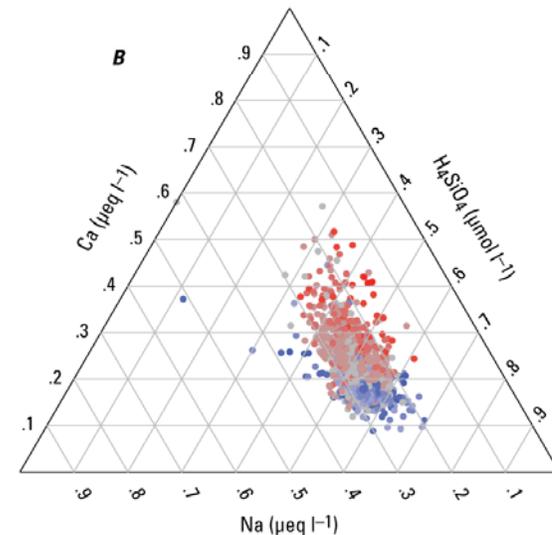
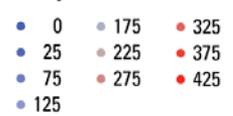


Figure 8. Maximum differences in the cumulative density functions between fluxes of H_4SiO_4 and Na, and H_4SiO_4 and Ca, and annual runoff during WY1986–WY1998.



EXPLANATION

Depth, in centimeters



EXPLANATION

Log10 (Runoff, in millimeters)



Figure 9. Ternary plot of Ca, Na, and H_4SiO_4 concentrations in (A) soil solution and (B) streamwater. The soil solution analyses are shaded by depth of the sampler below land surface. The streamwater analyses are shaded by the base10 logarithm of the instantaneous runoff.

CONCLUSIONS

Precipitation and stream fluxes of the primary weathering products (sodium, calcium, magnesium and silica) were evaluated from October 1985 through September 1998 at the relatively undisturbed, small (0.41 square kilometers) forested Panola Mountain Research Watershed (PMRW), Georgia. Rainfall, streamflow (runoff), and related water quality have been monitored at PMRW since 1985. Regression relations of stream solute concentrations were derived from weekly and storm-based sampling. Runoff, seasonality, and hydrologic state were the primary independent variables. These relations were statistically significant and explained from 74 to 90 percent of the variations in solute concentration.

Streamwater solute fluxes were evaluated with respect to annual precipitation and runoff characteristics, including water fluxes and water yield. Stream solute fluxes were computed from the concentration predicted by the regression relations and runoff. Precipitation fluxes were computed from the weekly water-quality samples and measured precipitation. In addition, annual precipitation chloride (Cl) flux was subtracted from the stream Cl flux to estimate dry deposition assuming that there is no internal source of Cl and that Cl is mobile and conservative. Dry Cl deposition, on average, contributes 56 percent to the total atmospheric deposition, which also was applied to the other solutes. The average net annual cation and silica fluxes were 50.6 and 85.9 mmol m⁻², respectively.

The cumulative density functions (CDF) of solute and runoff flux as a function of runoff varied markedly among years and displayed a decrease in the relative contribution of base flow to annual flux during wet years. While streamwater flux of weathering solutes is primarily associated with base flow ground-water discharge, calcium and magnesium displayed a relatively higher during rainstorms particularly during wet years, e.g. 10 percent of the annual flux. Also, the maximum silica-minus-calcium CDF difference was positively correlated with annual runoff. The source is hypothesized to be mobilization from shallow soil horizons where these solutes dominate.

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