

Base cation concentrations in subsurface flow from a forested hillslope: The role of flushing frequency

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Abstract. A 20-m-wide trench was excavated to bedrock on a hillslope at the Panola Mountain Research Watershed in the Piedmont region of Georgia to determine the effect of upslope drainage area from the soil and bedrock surfaces on the geochemical evolution of base cation concentrations in subsurface flow. Samples were collected from ten 2-m sections and five natural soil pipes during three winter rainstorms in 1996. Base cation concentrations in hillslope subsurface flow were generally highest early and late in the storm response when flow rates were low, but during peak flow, concentrations varied little. Base cation concentrations in matrix flow from the 10 trench sections were unrelated to the soil surface drainage area and weakly inversely related to the bedrock surface drainage area. Base cation concentrations in pipe flow were lower than those in matrix flow and were also consistent with the inverse relation to bedrock surface drainage area found in matrix flow. The left side of the trench, which has the highest bedrock surface drainage area, had consistently lower mean base cation concentrations than the right side of the trench, which has the lowest bedrock surface drainage area. During moderate size rain events of about 20–40 mm, subsurface flow occurred only on the left side of the trench. The greater volume of water that has flowed through the left side of the trench appears to have resulted in greater leaching of base cations from soils and therefore lower base cation concentrations in subsurface flow than in flow from the right side of the trench. Alternatively, a greater proportion of flow that bypasses the soil matrix may have occurred through the hillslope on the left side of the trench than on the right side. Flushing frequency links spatial hillslope water flux with the evolution of groundwater and soil chemistry.

1. Introduction

Chemical evolution is defined by the changes in concentrations of chemical constituents that occur as water moves along a flow path and interacts with the biological and geological media. Chemical evolution is complex in waters draining the hillslopes of small catchments because of the open-system conditions that are generally present in shallow, coarse-textured soils where transient groundwater flow (subsurface storm flow) is often the dominant hydrologic response. Because of the complexity in deriving chemical models of subsurface flow at the hillslope scale, there have been relatively few studies of chemical evolution on hillslopes [Bishop *et al.*, 1990; Wilson *et al.*, 1991]. Consequently, most studies and models of water chemistry have been derived at the catchment scale [Christo-

pherson *et al.*, 1982; Cosby *et al.*, 1985; Hooper *et al.*, 1990; Wolford *et al.*, 1996].

A common assumption in studies of spatial controls of base cations in drainage waters from hillslopes and small catchments is that concentrations increase with subsurface residence time, so that space can be substituted for time through consideration of the flow path length [Wilson *et al.*, 1991; Trudgill *et al.*, 1996; Wolock *et al.*, 1997]. Base cation concentrations increase with subsurface residence time because of the relatively slow kinetics of silicate mineral dissolution [Lasaga, 1984] and also because of diffusion from smaller pores with higher concentrations to larger, more hydrologically active pores with lower concentrations [Luxmoore and Ferrand, 1993]. As the mean subsurface path length of water movement increases, concentrations of base cations generally increase until a steady state or equilibrium concentration is reached. Biological uptake of nutrient base cations such as Ca^{2+} , Mg^{2+} , and K^+ may partly offset the trend of increasing concentration with increasing path length [Likens *et al.*, 1977; Taylor and Velbel, 1991]. Alternatively, if hillslopes, and thus subsurface residence times, are short, steady state concentrations may not be attained [Trudgill *et al.*, 1996].

During the past two decades, significant advances have been made in understanding the manner in which topography and other physical characteristics of the landscape affect runoff processes at the hillslope and small catchment scale [Beasley, 1976; Anderson and Burt, 1978; Beven and Kirkby, 1979; Beven and Wood, 1983; Burt and Butcher, 1985; Turton *et al.*, 1992; Woods and Rowe, 1996]. Several models have been developed

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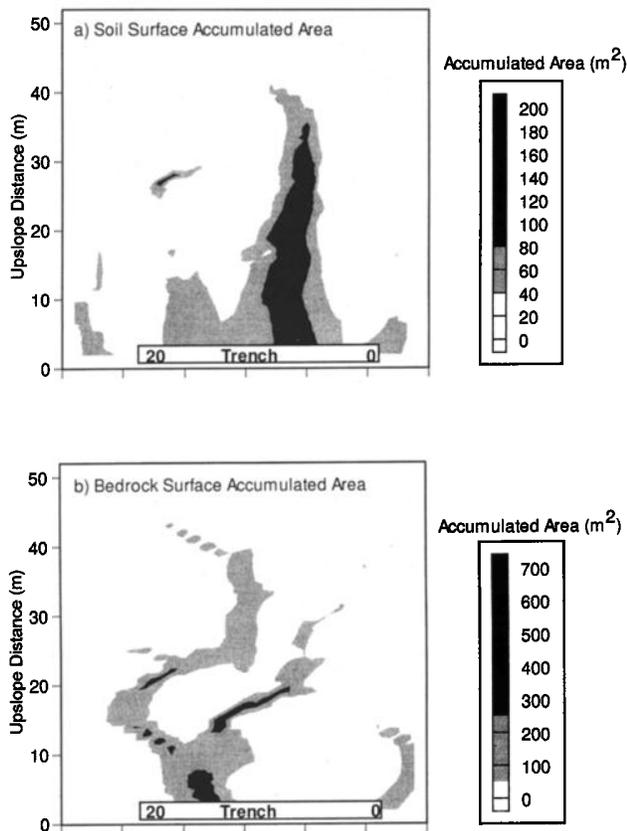


Figure 1. Modeled representation of the study hillslope above the trench showing regions of high accumulated area based on (a) the soil surface and (b) the bedrock surface.

that incorporate digital terrain analysis with variable source-area concepts to predict runoff [Beven and Kirkby, 1979; Bernier, 1985; Ormsbee and Khan, 1989; Grayson et al., 1992; Kubota and Sivapalan, 1995], among which TOPMODEL has been widely applied [Beven et al., 1995]. Fundamental to the spatial representation of saturated flux in TOPMODEL is the topographic index, $\ln(a/\tan\beta)$ [Kirkby, 1975], in which a is the upslope accumulated area and $\tan\beta$ is the local slope angle.

Spatial variability of the topographic index results in patterns of soil moisture and hydrologic flow paths across the landscape that have been linked to temporal and spatial patterns of water chemistry in small catchments [Wolock et al., 1989; Robson et al., 1992; Creed et al., 1996; Wolock et al., 1997]. Few studies to date have explored the relation between variable source-area concepts and water chemistry through digital terrain analysis, however, and this modeling approach has not yet been applied to the study of the chemical evolution of waters at the hillslope scale. The objective of this study, therefore, was to determine if a relation exists between topographically based spatial indices that infer flow path distributions at the hillslope scale and the concentrations of base cations in subsurface flow from that hillslope. Samples were collected during three winter rainstorms in 1996 from a hillslope trench at the Panola Mountain Research Watershed in the southern Piedmont region near Atlanta, Georgia. This study of water chemistry was closely linked with a study of hydrological processes at the same hillslope [McDonnell et al., 1996; Freer et al.,

1997], thereby providing detailed data on subsurface flow to relate to water chemistry.

Hydrological results from the study hillslope obtained during the winter of 1996 indicated that total flow volume and peak flow were significantly different among individual trenchface sections and were positively correlated with both $\ln(a/\tan\beta)$ and the drainage area calculated from a digital elevation model (DEM) of the soil-bedrock interface but were not significantly related to $\ln(a/\tan\beta)$ of the drainage area calculated from a DEM of the soil surface at this site (Figure 1) [Freer et al., 1997]. These hydrological results, when considered with results from previous studies of spatial controls of chemical evolution at the hillslope and watershed scale discussed previously, suggest that the base cation concentrations of hillslope groundwater at this site should be greatest in sections of the trench that have the greatest drainage area (and therefore inferring the greatest average subsurface flow path length) as determined from the DEM of the soil-bedrock interface.

2. Study Area

The study site is located in the Panola Mountain Research Watershed (PMRW), about 25 km southeast of Atlanta, Georgia, in the southern Piedmont province (Figure 2). The watershed is 93% forested, consisting of hickory, oak, tulip poplar, and loblolly pine [Carter, 1978], and the remaining 7% of the watershed includes exposed bedrock, of which a 3-ha outcrop in the southwestern corner of the watershed is the largest (Figure 2).

The study hillslope at PMRW is underlain by Panola Granite (of granodiorite composition) of Carboniferous age, described as a biotite-oligoclase-quartz-microcline granite [Atkins and Higgins, 1980]. The Panola Granite weathers to a red, clayey soil that is classified as an Ultisol. These soils are developed on both colluvium and residuum and grade to Inceptisols in the colluvium, in recent alluvium, or in eroded landscape positions [Huntington et al., 1993]. The soils at the study hillslope are developed on colluvium. Soil profiles at PMRW are generally about 0.5–1.5 m thick, overlying saprolite that ranges from 0 to 20 m thick. The mean depth to bedrock on the study hillslope was 0.65 m (mean depth to refusal with a soil corer from 288 holes at a 2-m grid interval). No saprolite was found on the hillslope above the trench, consistent with the colluvial origin of the soils. Kaolinite is the dominant secondary mineral in the watershed, and others include hydroxy-interlayered vermiculite, mixed layer mica/vermiculite, gibbsite, and goethite [Shanley, 1989].

The climate at PMRW is classified as humid, subtropical; mean annual temperature is 16.3°C, and mean annual precipitation is 1240 mm [National Oceanic and Atmospheric Administration, 1991]. Rainfall tends to be of longer duration and lower intensity, associated with the passage of fronts in the winter, and of shorter duration but higher intensity in the summer, associated with thunderstorms. Evapotranspiration is equal to about 70% of annual rainfall in the southern Piedmont [Carter and Stiles, 1983].

3. Methods

A trench 20 m in length was excavated to bedrock 30 m upslope from an ephemeral stream channel, opposite the 3-ha granite outcrop (Figure 2). The trench was divided into ten 2-m sections along the bedrock surface using PVC sheet that

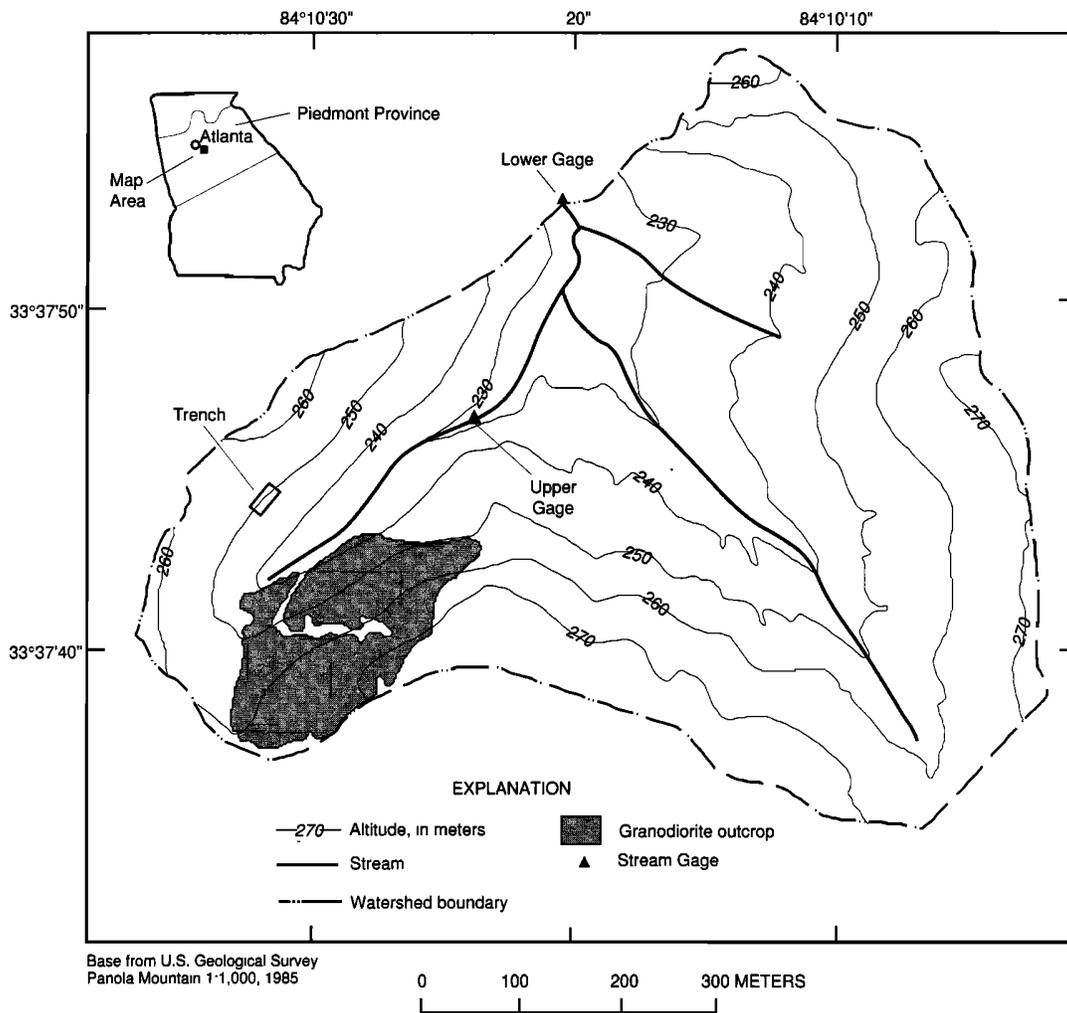


Figure 2. Map of the Panola Mountain Research Watershed showing the location of the hillslope trench.

funneled flow through PVC-lined garden hose. The trench was covered by a roof to prevent direct precipitation onto exposed bedrock. The 10 sections from which samples were collected are identified by the numbers 1, 3, 5, 7, 9, 11, 13, 15, 17, and 19, according to the distance in meters to the midpoint of each section from the right side of the trench as one faces upslope. The depth along the trench face varied from a few centimeters at section 19 to about 1.2 m at sections 13 and 15. Subsurface storm flow from these 10 sections appeared to emanate primarily from the soil matrix and will be referred to as matrix flow in this paper. No overland flow was observed to enter the trench from the upslope soil surface during any of the events for which samples were collected. Samples were also collected from five natural soil pipes on the trench face, and this storm flow will be referred to as pipe flow here. These pipes appear to be former root channels and have diameters that vary from about 10 to 60 mm. Trench outflow from each section and each soil pipe was collected at continuously recording tipping bucket gages.

Samples for chemical and isotopic analysis were collected in 250-ml polyethylene bottles from the tipping buckets when they spilled. Each sample for chemical analysis was passed through a 0.45- μm filter and acidified to a pH of 1–1.5 with HCl prior to analysis. Samples were shelf-stored prior to anal-

ysis of Ca^{2+} , Mg^{2+} , Na^+ , and K^+ by direct-coupled plasma emission spectroscopy. Samples of throughfall were collected at a location about 200 m downstream from the trench hillslope in a 50-mm-diameter PVC trough that drained into a polyethylene container. Soil water was collected at depths of 500–650 mm in 18 suction lysimeters on the trench hillslope through porous ceramic cups attached to PVC pipe. Soil lysimeters were pumped to a tension of 500 mm of water equivalent prior to sample collection. Soil water samples were used to establish a mean $\delta^{18}\text{O}$ value for preevent water on the trench hillslope.

Samples of subsurface flow, throughfall, and soil water were analyzed for $\delta^{18}\text{O}$ by mass spectrometry and reported in per mil units (‰) relative to Vienna standard mean ocean water (VSMOW). These isotopic measurements were then used to separate subsurface flow into event and preevent components using a two-component model similar to that described in numerous studies [Sklash *et al.*, 1976; Pearce *et al.*, 1986]. A sample of throughfall collected for the entire storm was assumed to represent the event component, and the mean $\delta^{18}\text{O}$ value of all lysimeters collected 1–3 days before the storm was assumed to represent the preevent component.

A DEM of the hillslope above the trench was developed from a 2 \times 2 m survey grid. A subsurface DEM of the soil-

Table 1. Characteristics of the Three Rain Events During the Winter of 1996 in Which Subsurface Storm Flow Samples Were Collected From the Hillslope Trench

Rainstorm	Precipitation Amount, mm	7-Day Antecedent Rainfall, mm	14-Day Antecedent Rainfall, mm
February 2	62	115	161
March 6	96	10	10
March 27	26	9	39

bedrock surface of the hillslope above the trench was developed by kriging from depth-to-bedrock data from a soil corer at the same grid scale. The multidirectional flow algorithm of Quinn *et al.* [1991] was used to calculate the drainage area for both the soil-bedrock interface (BR_{area}) and the soil surface (SS_{area}).

Samples of subsurface flow were collected during three rainstorms in the winter of 1996 (Table 1). Rainfall during the February 2 storm was 62 mm, and the storm occurred under wet antecedent conditions. Flow was measured in only five of the ten trench sections (1, 3, 13, 15, and 17) and five pipe flow collectors during this storm. Nevertheless, subsurface flow was observed across the entire trench face during this storm, and samples were collected from six trench sections (1, 3, 5, 13, 15, 17). The storm on March 6 was the largest of the three at 96 mm and occurred under relatively dry antecedent conditions. All of the ten trench sections and all five pipe flow collectors produced flow and were sampled during this storm. The 26-mm March 27 storm resulted in subsurface flow at only five trench sections (11, 13, 15, 17, and 19) and no pipe flow. In addition to the three rainstorms described above, the flow response of the trench to three storms in the succeeding winter of 1996–1997 is also discussed in this paper. Finally, the number and size of all rainfall events at PMRW from October 1985 through January 1997 was compiled to provide a frame of reference for the three 1996 winter rainstorms.

4. Results

4.1. Temporal Variability of Base Cation Concentrations

The sum of the base cation concentrations (SBC) in subsurface flow at the trench face was generally greatest for the first sample collected after the initiation of flow and was relatively invariant during the period of highest flow rates (Figure 3). For example, the SBC changed only slightly during the events of February 2 and March 6 as the flow rate at section 15 increased more than an order of magnitude. The SBC at the other trench sections changed similarly during the highest flow. The SBC increased at some of the sections late in the event of March 6, when flow rates were low and declining (Figures 3b and 3c), but a similar pattern was not observed during the February 2 or March 27 events (Figures 3a and 3d). The temporal variability of base cation concentrations was generally greater for the rain events of March 6 and 27 under dry antecedent conditions than for the February 2 event under wet antecedent conditions. The coefficient of variation of the mean SBC concentration for all sections sampled during the February 2 event was 21.0%, about twice that of the mean value of the coefficient of variation for each section, indicating that spatial variability was about twice that of temporal variability during this event (Table 2). The same two measures were about equal for the March 6 event and showed greater spatial variability (30.7%) than

temporal variability (24.2%) for the March 27 event. Generally, the temporal variability of the SBC concentrations at all sampled trench sections for each event decreased in the order March 27 > March 6 > February 2.

4.2. Isotopic Hydrograph Separations

The difference in $\delta^{18}O$ values between throughfall and soil water was 4.4‰ for the February 2 storm but was less than 0.5‰ for the other two storms, so an adequate hydrograph separation could be obtained only for February 2. During this storm, little or no event water was present in subsurface flow (Table 3). The greatest proportion of event water was 9.1% for a sample collected from trench section 1, and several negative values were recorded because $\delta^{18}O$ values of subsurface flow reached lower values than that of the preevent soil water.

4.3. Spatial Variability of Base Cation Concentrations

A principal objective of this study was to examine the relations between the concentrations of base cations in subsurface flow from the trench and the upslope drainage area a , as determined from the DEM. The local slope angle β varied little among the trench sections and therefore was not included in any of the relations developed here. The hydrological results summarized previously have shown that the flow rate from each trench section was significantly related to BR_{area} for the March 6 storm [Freer *et al.*, 1997]. The mean SBC was inversely related to BR_{area} ($p = 0.055$, determined by linear regression; Figure 4a) for the March 6 storm, whereas the mean SBC was unrelated to BR_{area} ($p > 0.10$) for the storms of February 2 and March 27. Additionally, the mean SBC was unrelated to SS_{area} ($p > 0.10$) for all storms. The mean SBC concentration was used to represent flow from each trench section in this analysis because of the relatively small temporal variations that were measured. The inverse relation of the mean SBC to $\ln BR_{area}$ for the March 6 event explains about 39% ($r^2 = 0.39$) of the variability in the mean SBC of the trench sections. The strength of this inverse relation is largely determined by Ca^{2+} and K^+ concentrations, which are also inversely related to $\ln BR_{area}$ ($p = 0.055$ and 0.039 , respectively; Figures 4b and 4c). In contrast, Na^+ and Mg^{2+} concentrations are unrelated to $\ln BR_{area}$ ($p > 0.10$). The strength of the relations for SBC and Ca^{2+} are dependent on the point with the greatest value of $\ln BR_{area}$ (section 15).

4.4. Comparison of Left-Side and Right-Side of Trench

During the March 27 storm, only sections 11–19 on the left side of the trench provided flow at the trench face. These observations of a partial flow response of the trench during small to moderate size rain events in winter have since been confirmed by a 24-mm rainstorm on December 13, 1996, that induced flow at sections 13–19 only, whereas a larger 56-mm rainstorm on January 9, 1997, resulted in flow at all the trench sections. The left side of the trench includes sections 15 and 17, which have BR_{area} of 735 and 201 m^2 , respectively, the largest of any of the trench sections. Section 13 has a BR_{area} of 93 m^2 , the fourth highest of any section, whereas sections 11 and 19 have relatively low BR_{area} of 24.0 and 19.9 m^2 , respectively. Overall, the BR_{area} is 1073 m^2 for sections 11–19 on the left side of the trench, which flow during moderate-size and greater rainstorms, compared to 259 m^2 for sections 1–9 on the right side of the trench, which flow only during large storms. In contrast, the SS_{area} for the left and right halves of the trench are similar to each other at 516 and 633 m^2 , respectively. A

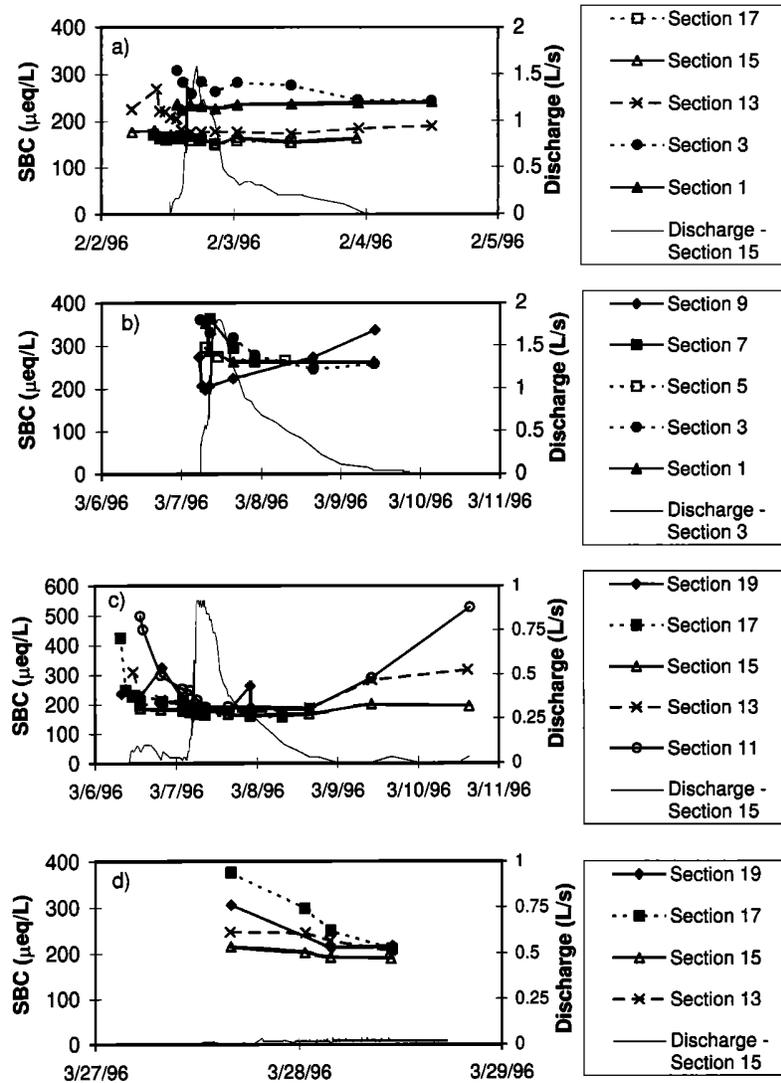


Figure 3. The sum of the base cation concentrations (SBC) and discharge in subsurface flow at the hillslope trench during three rainstorms in the winter of 1996: (a) SBC from samples collected at sections 1, 3, 13, 15, and 17 and discharge at section 15 during the February 2 storm; (b) SBC from samples collected at sections 1, 3, 5, 7, and 9 and discharge from section 3 during the March 6 storm; (c) SBC from samples collected at sections 11, 13, 15, 17, and 19 and discharge at section 15 during the March 6 storm; and (d) SBC from samples collected at section 13, 15, and 17 and discharge at section 15 during the March 27 storm.

spillover effect may provide flow to sections that are adjacent to those with high drainage area, because the surface of the water table at these high-flow sections appeared to exceed the height of the drainage area boundaries used for calculations of BR_{area} . Additionally, errors inherent in calculations of drainage area at a 2×2 m grid scale may limit the certainty of conclusions derived from examining relations between base cation concentrations and BR_{area} at this fine grid scale.

During the two rain events of February 2 and March 6 for which samples were collected on both sides of the trench, the mean concentration of each base cation on the high-flow left side of the trench is consistently less ($p < 0.05$, as determined by analysis of variance (ANOVA)) than the mean concentration on the low-flow right side of the trench (Figure 5), except for Ca^{2+} concentrations during the March 6 storm (which were strongly influenced by samples with high Ca^{2+} concentrations during the early and late stages of flow). If sections 9 and 11

near the middle of the trench are not considered because of possible mixing between the two halves, these differences in base cation concentrations among the two sides of the trench become even larger, and the differences in Ca^{2+} concentrations for the March 6 storm become statistically significant.

4.5. Pipe Flow

Samples of pipe flow were collected at four locations on the trench face during the February 2 and March 6 storms. The mean coefficient of variation of the SBC for pipe flow samples was 24.0% during the February 2 storm and 15.5% during the March 6 storm, compared to values of 11.2 and 19.7%, respectively, for matrix flow from the trench sections. The mean concentration of each base cation in pipe flow was less than that of matrix flow ($p < 0.05$, as determined by ANOVA) in trench flow during both storms (Figure 6), except for Mg^{2+} during the February 2 storm. Additionally, mean base cation

Table 2. Mean Sum of Base Cation Concentrations and Coefficients of Variation at Each Trench Section for the Three Rain Events That Were Sampled in 1996

Trench Sections	February 2		March 6		March 27	
	Mean	Coefficient of Variation	Mean	Coefficient of Variation	Mean	Coefficient of Variation
1	233.2	14.4	281.1	13.1
3	271.0	7.8	298.2	15.3
5	193.1	26.7	275.3	5.4
7	312.5	10.9
9	244.8	20.8
11	303.8	42.2	463.7	57.5
13	190.3	9.5	223.0	22.8	300.9	6.3
15	165.5	5.1	183.3	10.3	314.8	3.9
17	160.6	3.8	213.2	36.2	239.3	30.0
19	219.0	19.7	225.6	23.5
Mean	202.3	11.2	255.4	19.7	308.9	24.2
Coefficient of Variation	21.0		17.5		30.7	

Base cation concentrations measured in microequivalents per liter.

concentrations at each pipe flow site were generally less than that of the matrix flow from trench sections encompassing each pipe flow collector. During the March 6 storm the two pipe flow sites with the highest values of $\ln BR_{area}$ (6.3 and 5.73) had the lowest mean values of SBC (164.8 and 155.3, respectively), whereas the two pipe flow sites with the lowest values of $\ln BR_{area}$ (3.32 and 3.46) had the highest mean values of SBC (218.1 and 183.8, respectively). These data are consistent with the inverse relation between $\ln BR_{area}$ and mean SBC for matrix flow during this storm.

5. Discussion

5.1. Temporal Variability

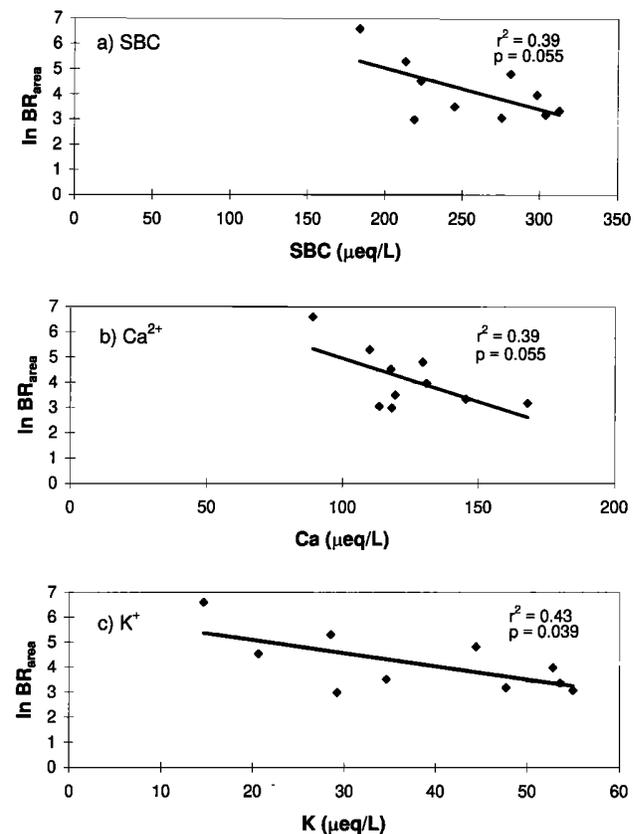
The base cation concentrations of groundwater from the study hillslope are notable for the lack of significant variation through the periods of greatest flow at all trench sections (Figure 3). These results stand in sharp contrast to those reported from a subwatershed of Walker Branch in Tennessee in which base cation concentrations increased with subsurface flow rate and then declined as flow decreased [Luxmoore *et al.*, 1990; Wilson *et al.*, 1991; Luxmoore and Ferrand, 1993]. They hypothesized that "high supply" solutes such as base cations maintained a diffusion gradient between high-concentration

immobile water in micropores and low-concentration mobile water in mesopores. At the time of peak flow the average subsurface path length of water transport reached its highest value coinciding with the greatest concentrations of the high supply solutes. The results from this study do not support a similar path length–supply mechanism at this hillslope in the Georgia Piedmont.

Table 3. The Percent Event Water From $\delta^{18}O$ Values of Subsurface Flow at the Hillslope Trench During the Rainstorm of February 2, 1996

Trench Section	Mean	Maximum	Minimum
1	2.9	9.1	0
Pipe 2.059	1.2	1.6	0.9
3	-1.9	4.8	-6.6
5	-2.3	-0.9	-5.2
Pipe 5.081	2.2	4.3	-1.8
Pipe 8.079	0.2	3.2	-1.8
13	-2.1	2.5	-5.7
Pipe 13.09	3.3	6.6	0
Pipe 14.07	0.2	4.8	-5.2
15	-1.7	1.1	-5.5
17	-4.2	1.8	-10.2

A two-component mixing model was applied, on the basis of the $\delta^{18}O$ of throughfall (-9.61) and preevent soil water (-5.21).

**Figure 4.** Volume-weighted mean base cation concentrations as a function of $\ln BR_{area}$ for each trench section during the March 6 rain storm: (a) sum of the base cations, (b) Ca^{2+} , and (c) K^+ .

Our results suggest that subsurface flow is generally well mixed on this hillslope. Under wet antecedent conditions (February 2), temporal variations in base cation concentrations were lower than under the drier antecedent conditions that were present prior to the other two storms (March 6 and 27), consistent with results for Cl^- transport in subsurface waters from a nearby hillslope at PMRW [Peters and Radcliffe, 1997]. The higher concentrations that were measured near the time of flow initiation at some trench sections on March 6 and 27 suggest either that water with a greater subsurface residence time may have resided further downslope and been eluted early in the storms or that accumulations of soluble salts were initially flushed from the soil early in the runoff period. A similar short-lived increase in base cation concentrations has been observed in studies of surface waters soon after the onset of rainfall [Miller and Drever, 1977; Peters, 1994; Elsenbeer et al., 1995; Anderson et al., 1997]. Alternatively, some drainage from networks of finer pores close to the trench face with greater base cation concentrations may have occurred early in the storm response before the larger-pore size networks began to deliver large volumes of subsurface flow from farther upslope. This latter mechanism is also consistent with the increasing base cation concentrations observed at some trench sections late in the storm response on March 6 (Figures 3b and 3c). The

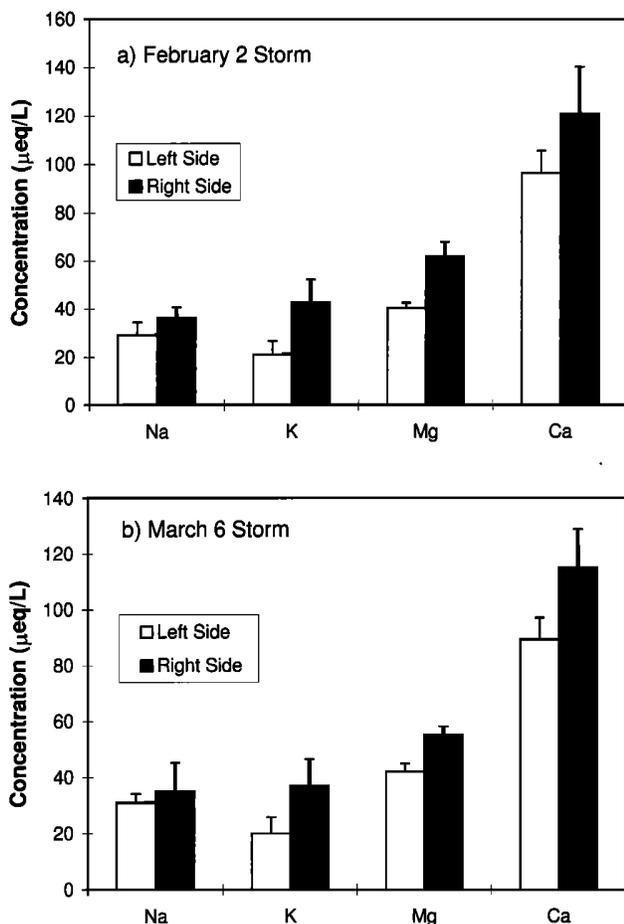


Figure 5. Volume-weighted mean and standard error of Na^+ , K^+ , Mg^{2+} , and Ca^{2+} concentrations in subsurface flow from the left and right sides of the trench for the rainstorms of (a) February 2 and (b) March 6.

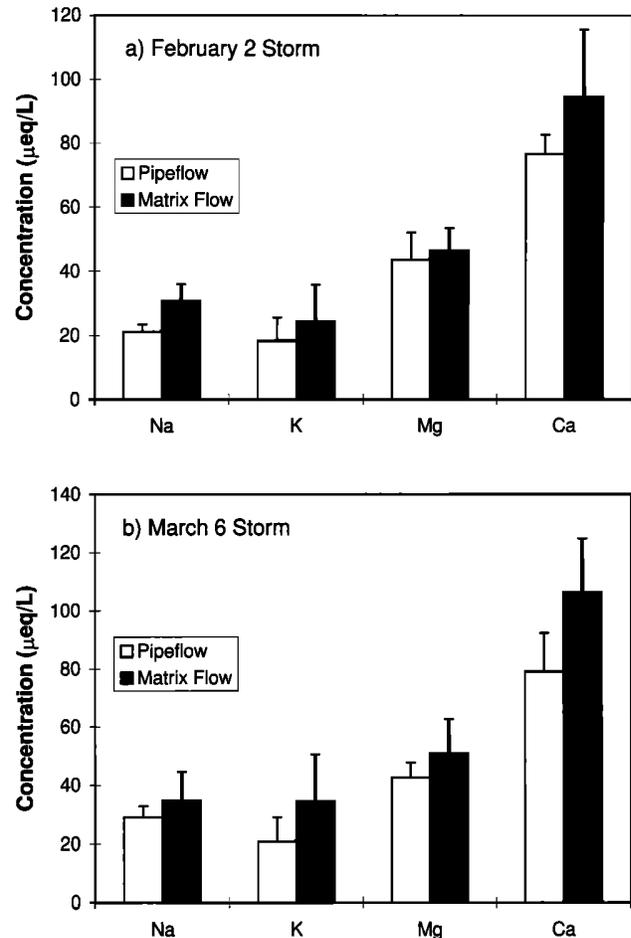


Figure 6. Volume-weighted mean and standard error of Na^+ , K^+ , Mg^{2+} , and Ca^{2+} concentrations in matrix flow and pipe flow for the rainstorms of (a) February 2 and (b) March 6.

lack of significant short-lived increases in base cation concentrations at any of the trench sections at the beginning of the February 2 event under wet antecedent conditions is similar to the results reported by Anderson et al. [1997] for sprinkler experiments at a zero-order catchment in Oregon. Wet antecedent conditions do not favor the release of soluble salts early in a storm, because hillslope waters are more thoroughly mixed among different pore sizes under wet conditions than under dry conditions.

5.2. Spatial Variability

The spatial variability of base cation concentrations across the trench face was not related to the SS_{area} , consistent with the absence of any relation between the soil surface drainage area and the subsurface flow rate [Freer et al., 1997]. Instead, the BR_{area} accounted for a significant amount of the variability in flow rates across the trench face (Figure 1) [Freer et al., 1997]. The spatial variability of base cation concentrations in hillslope subsurface flow indicated a consistent, albeit not statistically strong, inverse relation to the BR_{area} . Although the inverse relations are not strong, they are consistent for each base cation for every storm that was sampled, increasing the likelihood that the relation reflects the dominant processes operating on the hillslope. Additionally, the base cation con-

centrations are consistently and significantly lower on the left side of the trench with high BR_{area} than on the right side of the trench with low BR_{area} . The volume of pipe flow was also greatest on the left side of the trench with the greatest BR_{area} , suggesting a possible relation to soil pipe development. We propose that the chemical evolution of waters at the hillslope scale is related to the dominant hydrological flow patterns, which in turn are affected by the shape of the impermeable bedrock surface on which transient subsurface flow develops.

The initial hypothesis—that the sections of subsurface flow with the greatest drainage area would have the highest base cation concentrations because they were draining flowpaths with the greatest average path length—is not supported by these results. The discussion that follows examines several alternative hypotheses that may explain the study results.

5.3. Why Does the Side of the Trench With the Greatest Bedrock Surface Drainage Area Have the Lowest Base Cation Concentrations?

Three hypotheses are offered that may partly explain the results of this study. The side of the trench with the greatest BR_{area} may (1) receive more event water, (2) have a more highly developed macropore and pipe flow network, or (3) have flushed more water through the base of the hillslope historically.

These data do not indicate that a greater proportion of event water is present in subsurface flow that drains sections with greater BR_{area} . The subsurface flow hydrograph separations with ^{18}O indicated that little or no event water was present in any of the subsurface flow samples collected during the February 2 storm (Table 3). So little event water flowed from either side of the trench during this storm. Because adequate hydrograph separations could not be obtained for the March 6 and 27 storms, however, the relative proportion of event water delivered in subsurface flow could not be determined under the drier antecedent conditions present prior to these events.

The possibility of a greater degree of bypass flow in the hillslope soil that drains the left side of the trench could not be adequately evaluated with the results of this study. The two areas of pipe flow that provided the greatest flow at the trench face were both located on the left side of the trench, and samples of this flow generally had lower base cation concentrations than matrix flow from the trench sections. A two-component model using $\delta^{18}O$ data from pipe flow samples for the February 2 event, however, indicated that this pipe flow was dominated by preevent water, consistent with a recent study of the isotopic composition of pipe flow at Plynlimon, Wales [Sklash *et al.*, 1996]. None of the pipe flow samples had more than 6.6% event water (Table 3). The pipe flow sites that were sampled at the trench face had lower base cation concentrations than the matrix flow but did not have a significantly greater proportion of event water. No measurements were made upslope of the trench to determine if a greater amount of pipe flow occurred throughout the hillslope that drained the left side of the trench than in the hillslope that drained the right side of the trench. This hypothesis, therefore, can be neither confirmed nor refuted and remains a possibility.

The results from the winter of 1996, confirmed by data from the succeeding winter, indicate that the amount of rainfall necessary to initiate subsurface flow throughout the hillslope in the winter seems to be greater than 25 mm but less than 56 mm. These results are similar to those reported by McDonnell [1990] in which a rainfall threshold was necessary for signifi-

cant hillslope contributions to channel storm flow. This triggering amount of rainfall probably varies depending on antecedent moisture conditions and other factors such as rainfall intensity and duration. In the growing season, when dry conditions generally prevail, the amount of rainfall necessary to induce flow at the trench is even greater. For example, on November 2, 1996, near the end of the growing season, a rain event of 27 mm resulted in a small volume of flow at only one of the trench sections.

A compilation of rainfall amounts from more than 1000 events from October 1985 through January 1997 at PMRW indicates that 4330 mm of precipitation fell during events of <20 mm, 3950 mm fell during events of 20–40 mm, and 5890 mm fell during events >40 mm. Assuming the events of <20 mm resulted in no hillslope subsurface flow, the events of 20–40 mm resulted in flow at the present location of the left half of the hillslope trench only, and the events of >40 mm resulted in flow throughout the current trench location, then about 28% of the total rainfall resulted in flow from the area of high BR_{area} only. All of the precipitation in the events of 20–40 mm would have remained in the area of low BR_{area} as soil moisture (assuming insignificant deep seepage losses through the granodiorite bedrock) and been available for evapotranspiration but would not have eluted base cations from hillslope soils. Thus these 20- to 40-mm rain events would likely have resulted in some flow from the high BR_{area} part of the trench hillslope and little or no flow from the low BR_{area} part of the trench hillslope, and therefore, the elution of a much greater mass of base cations from these high BR_{area} soils. Years of more frequent flushing of this part of the hillslope has likely resulted in fewer base cations available for leaching from the biogeochemical matrix of this part of the hillslope (soil exchange sites, primary and secondary minerals, and organic matter). This hypothesis is also consistent with the results of studies of solutional denudation on hillslopes in which greater dissolution rates were found in hillslope hollows than in spurs [Crabtree and Burt, 1983; Burt *et al.*, 1984].

5.4. Importance of Scale

The principal finding of this study that an inverse relation exists between drainage area and base cation concentrations is the opposite of the relation found in a set of nested catchments in the Catskill Mountains of New York, where base cation concentrations in base flow stream water increased as the mean $\ln(a/\tan \beta)$ increased in nested catchments with drainage areas of 0.2–3 km² [Wolock *et al.*, 1997]. These increases in base cation concentrations were attributed to increases in subsurface residence time as watershed size increased. We suggest that a transition may occur from an inverse relation of base cation concentrations to the topographic index to a positive relation as the scale increases from a 0.01 km² hillslope to a 0.2- to 3-km² catchment. An insufficient number of studies that relate water chemistry to digital elevation modeled parameters currently exist to make a definitive statement here, but these relations warrant further study in other catchments at varying scales. A pertinent factor that may explain the differences between the results of this study and those of Wolock *et al.* [1997] is that the Panola Mountain hillslope has only transient saturated subsurface flow, whereas the Catskill catchments had perennial flow. The effect of parts of hillslopes that are flushed more than others may matter less at the catchment scale, where the subsurface residence time of groundwater in the

alluvial area determines the base cation concentrations of stream water.

5.5. Chemical Evolution of Water at the Hillslope Scale

A common assumption in studies of the chemical evolution of waters is that the time-dependent release of solutes such as base cations can be substituted for space to understand and predict concentration changes along a flow path [Plummer *et al.*, 1983; Trudgill *et al.*, 1996]. The results of this study, however, indicate that this simple assumption has less validity for subsurface water chemistry on a hillslope with ephemeral saturated flow. If the delivery of waters from the study hillslope to areas downslope is considered, a rainstorm of 25 mm would deliver waters of relatively low base cation concentrations, but these waters would be derived from the areas of greatest drainage area with the greatest average flow path length. In a larger rainstorm, sufficient to cause flow throughout the hillslope, the average flow path length would likely be shorter because of contributions from areas of low BR_{area} , but base cation concentrations would actually be higher because of contributions of subsurface flow from areas of low Br_{area} . Although the simplified model of the geochemical evolution of waters on a hillslope [Trudgill *et al.*, 1996] may be valid if the possibility existed to track one parcel of water downslope, in reality the mixing of waters from areas with varying amounts of upslope drainage area dominates, and the simple time-for-space substitution does not adequately describe the chemical evolution of water at this hillslope in the Georgia Piedmont.

6. Summary and Implications

The results of this study have shown the amount of variability in the base cation concentrations of ephemeral subsurface flow through time and space across a section of a hillslope. Overall, temporal variations in base cation concentrations were small, particularly through the period of greatest flow. Temporal variations in base cation concentrations were greater under dry antecedent conditions than wet antecedent conditions, reflecting better mixing of hillslope waters when conditions are wet. These results are not consistent with the path length–supply hypothesis offered to explain variations in the chemistry of subsurface flow at the Walker Branch Watershed.

The variations in base cation concentrations across the trench face were unrelated to the SS_{area} and were weakly inversely related to the BR_{area} . Mean concentrations of each base cation on the left side of the trench with high BR_{area} were consistently lower than those on the right side of the trench with low BR_{area} for two rainstorms. A tendency for subsurface flow to occur only on the left side of the trench during rain events of 20–40 mm was noted. Historically, this side of the trench hillslope has likely been flushed more frequently and with greater volumes of water than the right side of the trench, resulting in the leaching of a greater mass of base cations from the soils that deliver water to the left side of the trench. This hypothesis suggests a coevolution of soil and water chemistry on hillslopes controlled by the extent to which subsurface flow is affected by the upslope distribution of the impermeable surface. The extent of development of a network of macropores and pipe flow capable of bypassing the soil matrix may also affect the chemistry of subsurface flow.

This flushing frequency hypothesis has implications for many aspects of biogeochemistry. Soils in the area of high BR_{area} are predicted to have lower base saturation values and higher

exchangeable acidity than those in areas with low BR_{area} , which has implications for the study of mechanisms causing spatial variation in soil chemistry. Topographically driven spatial variations in the leaching of nutrient base cations such as Ca^{2+} that are necessary for the growth of vegetation may also have current and future effects on tree growth and the spatial distribution of species. Finally, differences in the degree of chemical weathering in soil minerals may also be related to flushing frequency.

The validity of the flushing frequency hypothesis should be tested more definitively to determine if variations in soil chemistry and mineralogy in this Piedmont hillslope are consistent with the hypothesis. Furthermore, the hypothesis should also be tested at other sites to determine if upslope drainage area from digital elevation models is a potential tool for predicting variations in groundwater chemistry in other landscapes and climatic settings. Relations between the chemistry of subsurface flow and upslope drainage area may be stronger in hillslopes of greater length (>50 m) than the one in this study.

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