

Quantifying contributions to storm runoff through end-member mixing analysis and hydrologic measurements at the Panola Mountain Research Watershed (Georgia, USA)

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Abstract:

The geographic sources and hydrologic flow paths of stormflow in small catchments are not well understood because of limitations in sampling methods and insufficient resolution of potential end members. To address these limitations, an extensive hydrologic dataset was collected at a 10 ha catchment at Panola Mountain Research Watershed near Atlanta, GA, to quantify the contribution of three geographic sources of stormflow. Samples of stream water, runoff from an outcrop, and hillslope subsurface stormflow were collected during two rainstorms in the winter of 1996, and an end-member mixing analysis model that included five solutes was developed. Runoff from the outcrop, which occupies about one-third of the catchment area, contributed 50–55% of the peak streamflow during the 2 February rainstorm, and 80–85% of the peak streamflow during the 6–7 March rainstorm; it also contributed about 50% to total streamflow during the dry winter conditions that preceded the 6–7 March storm. Riparian groundwater runoff was the largest component of stream runoff (80–100%) early during rising streamflow and throughout stream recession, and contributed about 50% to total stream runoff during the 2 February storm, which was preceded by wet winter conditions. Hillslope runoff contributed 25–30% to peak stream runoff and 15–18% to total stream runoff during both storms. The temporal response of the three runoff components showed general agreement with hydrologic measurements from the catchment during each storm. Estimates of recharge from the outcrop to the riparian aquifer that were independent of model calculations indicated that storage in the riparian aquifer could account for the volume of rain that fell on the outcrop but did not contribute to stream runoff. The results of this study generally indicate that improvements in the ability of mixing models to describe the hydrologic response accurately in forested catchments may depend on better identification, and detailed spatial and temporal characterization of the mobile waters from the principal hydrologic source areas that contribute to stream runoff. Copyright © 2001 John Wiley & Sons, Ltd.

KEY WORDS stormflow; end-member mixing analysis; mixing model; riparian groundwater; Georgia, bedrock outcrop; hillslope runoff; runoff model

INTRODUCTION

Many studies of small catchments have used hydrograph separation techniques to identify the principal source components of stormflow (see reviews in Bonell (1993), Buttle (1994), and Genereux and Hooper (1998)). Separation techniques generally use isotope (Sklash *et al.*, 1976; Pearce *et al.*, 1986) or chemical tracers

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(Caine, 1989; Eshelman *et al.*, 1993) to solve a mass balance expression for the relative proportions of stream runoff derived from: (1) precipitation (sometimes referred to as new water or event water), and (2) water stored in the catchment prior to the onset of a hydrologic event (sometimes referred to as old water or pre-event water). The tracers in these two components of runoff are assumed to mix conservatively in the catchment during the event to provide an accurate representation of stream runoff, an assumption that is sometimes violated (Pilgrim *et al.*, 1979). Applications of a two-component modelling approach to small, forested catchments generally have found that the pre-event component dominates stream runoff during high flow (Buttle, 1994; Genereux and Hooper, 1998). The pre-event and event water are considered time-source components because they provide a temporal separation of stream runoff (Sklash *et al.*, 1976; Genereux and Hooper, 1998). DeWalle *et al.* (1988) found that inclusion of a third time-source component—soil water—was necessary to account for variations in ^{18}O values in a Pennsylvania stream during rainstorms. Subsequent stormflow models have been developed using mixing diagrams, resulting in a geographic source separation of streamflow into three runoff components (Christophersen *et al.*, 1990; Hooper *et al.*, 1990; Mulholland, 1993; Ogunkoya and Jenkins, 1993).

Despite the wide application of tracer-based, multi-component mixing models to describe the runoff response to rainfall and snowmelt, little work has been done to systematize the varied observations among catchments. A review of data from more than 90 storms that were analysed through a two-component modelling approach indicated that peak flow in forested and agricultural catchments has a greater proportion of pre-event water than peak flow in urban catchments, and that peak flow resulting from rainfall has a greater proportion of pre-event water than peak flow resulting from snowmelt (Buttle, 1994). Within a catchment, the proportion of pre-event water in peak flow was found to decrease as rainfall intensity and amount increased (Hill and Waddington, 1993; Brown *et al.*, 1999), and was found to increase as antecedent soil moisture increased (Burns and McDonnell, 1998). Additional studies are needed in a wide variety of catchment environments, however, to confirm these findings. In particular, an overrepresentation of mixing model studies from forested catchments in northern temperate climates and few studies in sub-tropical and tropical environments has been noted (Bonell, 1993).

Many studies that have developed three-component models to describe catchment runoff have used throughfall, soil water, and groundwater as the three runoff components (DeWalle *et al.*, 1988; Bazemore *et al.*, 1994; Rice and Hornberger, 1998). Although this approach recognizes the importance of soil water as a runoff component, it has generally failed to provide insight into the geographic distribution of hydrologic source areas in a catchment. Of particular interest in many catchments, yet little explored to date, is the interaction between mobile waters on the hillslope and groundwater stored in the riparian area (Robson *et al.*, 1992; Peters and Ratcliffe, 1998; McGlynn *et al.*, 1999).

The Panola Mountain Research Watershed (PMRW), a 41 ha forested catchment in the Piedmont region of Georgia, has been the site of several studies of storm runoff (McDonnell *et al.*, 1996; Freer *et al.*, 1997) and stream chemistry during rainstorms (Shanley and Peters, 1988; Hooper *et al.*, 1990; Peters, 1994; Peters and Ratcliffe, 1998; Peters *et al.*, 1998). The response of the stream to rainfall in the catchment is affected strongly by a 3.6 ha bedrock outcrop in the headwaters that provides rapid runoff during storms (Shanley and Peters, 1988). Some studies have concluded that runoff from this outcrop has little direct effect on stream chemistry (Hooper *et al.*, 1990; Shanley and Peters, 1993), whereas others have discerned a large direct effect (Shanley and Peters, 1988; Peters and Ratcliffe, 1998). This apparent discrepancy probably results, in part, from temporal and seasonal variations in runoff, and from differences in the spatial scale at which these studies were conducted. Additionally, the effects of direct runoff from the outcrop on stream chemistry may depend on the combined effects of the size and intensity of the storm, and the antecedent soil moisture conditions. The recent addition of a hillslope trench at PMRW (Burns *et al.*, 1998) has allowed the collection of mobile subsurface flow during rainstorms. The chemistry of this subsurface flow is distinct from groundwater in the stream riparian area (Hooper *et al.*, 1998), thus providing an opportunity to examine the relative role of these two geographic source areas in stream runoff during rainstorms. In this study, we describe the results of a three-component model of storm runoff derived by end-member mixing analysis (EMMA) during two

rainstorms in the winter of 1996. We address three questions about the response of winter runoff in this catchment. (1) What is the relative importance to stream runoff of direct runoff from the outcrop compared to hillslope and riparian groundwater? (2) What can the results from these two winter storms indicate about how runoff processes vary with storm size, rainfall intensity, and antecedent wetness conditions? (3) Are the EMMA modelling results consistent with physical hydrologic measurements in the catchment?

STUDY SITE

The PMRW is about 25 km southeast of Atlanta, GA, in the southern Piedmont province (Figure 1). The forested watershed is dominated by hickory, oak, tulip poplar, and loblolly pine (Carter, 1978). The 10 ha upper catchment at Panola is underlain by the Panola Granite, which is a biotite–oligoclase–quartz–microcline granite (Crawford *et al.*, 1995). The 41 ha research catchment downstream from the 10 ha sub-catchment is underlain by the Clairmont Formation, a mélangé of amphibolite, granite, gneiss, and other rock types

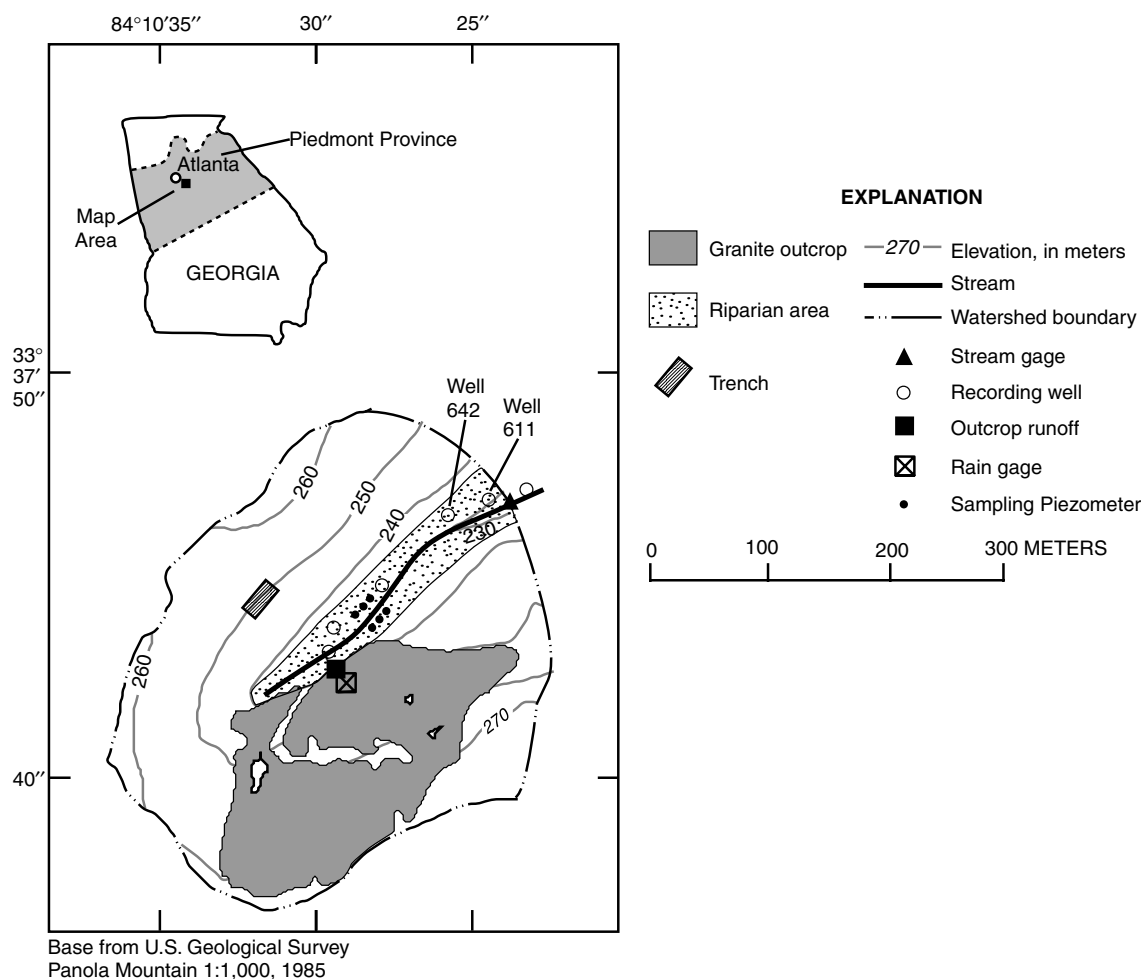


Figure 1. Map of 10 ha catchment at PMRW, Georgia, showing locations of the sampling and monitoring sites, riparian area, and outcrop

(Crawford *et al.*, 1995). A 3.6 ha outcrop of the Panola Granite is present in the southwest corner of the catchment and its lowermost terminus is 1 to 2 m from the stream channel (Figure 1). The Panola Granite weathers to a red, clayey soil that is classified as an Ultisol. The Ultisols are developed on alluvium and colluvium, and grade to Inceptisols in the colluvium, in recent alluvium, or in eroded landscape positions (Huntington *et al.*, 1993). Soil profiles generally are 0.5 to 1.5 m thick overlying saprolite, which ranges from 0 to 2 m thick on the hillslopes to as much as 6 m thick in the riparian area.

The climate is humid and subtropical with a mean annual air temperature of 16.3 °C and mean annual precipitation of 1240 mm (NOAA, 1991). Rainfall tends to be of long duration and low intensity in winter, when it is associated with the passage of fronts, and of short duration but high intensity in summer, when it is associated with thunderstorms. Stream runoff at PMRW has a stronger seasonal pattern than rainfall—the highest flows occur during the dormant season (November through April), and the lowest occur during the growing season (May through October). Soils have greater moisture content and riparian groundwater levels are higher during the dormant season than during the growing season. For example, the mean volumetric soil-moisture content during water year 1996, based on time-domain reflectometry measurements at a midslope location at 40 cm depth, was 0.30 during the dormant season and 0.24 during the growing season (N.E. Peters, unpublished data, volumetric soil moisture based on calibration of Ledieu *et al.* (1986)). The annual wetting–drying cycle at PMRW is strong enough that the hydrologic response to rainstorms may be different in the winter than summer; for this reason, all discussion of antecedent conditions in this paper is prefaced with the word ‘winter’ to highlight this difference.

Stream runoff at the 10 ha study catchment is ephemeral, and the duration of stream runoff following a rainstorm is greatest in winter and least in the summer. Evapotranspiration is about 67% of annual rainfall, and annual stream yield from the 41 ha catchment varied from 8 to 50% of precipitation during 1986–99 (Peters *et al.*, 2000).

METHODS

Samples of stream water, runoff from the outcrop, subsurface stormflow from the hillslope trench, and riparian groundwater were collected for chemical analysis during two rainstorms in the winter of 1996. Physical measurements during these rainstorms included: stream runoff rate, rainfall amount and intensity, runoff rate from the hillslope trench, and riparian water table levels.

Field measurements

Stream water samples were collected during storms by an automated sampler/data logger system similar to the one described by Peters (1994), whose intake line was located about 5 m upstream from the stream gauge at the outlet of the 10 ha catchment (Figure 1). Sampling was activated by changes in stream stage to obtain sample representation over the entire hydrograph. Stage was recorded by a data-logger connected to a potentiometer driven by a float-counterweight in a stilling well just upstream of a 90° V-notch weir. Stage was recorded every minute during stormflow and every 5 min between storms. Discharge was calculated from a stage-discharge rating relation. Rainfall amount was measured by a tipping-bucket rain gauge near the base of the outcrop; tips were recorded every minute (Figure 1). Runoff from the outcrop was sampled near its base about 150 m upstream of the gauge (Figure 1), which was different than the location of the outcrop runoff gauge described by Peters (1989, 1994). Subsurface stormflow from the hillslope was collected from a 20 m long trench that had been excavated to bedrock on the hillslope opposite the outcrop in 1995 (Figure 1). Subsurface stormflow samples were collected from each of ten 2 m segments of the trench during each storm. Discharge from each 2 m trench section and from five areas of pipeflow was measured by routing the outflow to tipping-bucket gauges. Additional details of the trench and flow-collection system are described elsewhere (McDonnell *et al.*, 1996; Freer *et al.*, 1997; Burns *et al.*, 1998).

Groundwater representative of the riparian area was collected as stream baseflow samples prior to each storm. A comparison of the chemistry of baseflow collected prior to the March storm with the mean chemistry of samples from six riparian piezometers (Figure 1) suggests that baseflow reflects the chemistry of riparian groundwater (Table I). Water levels were recorded every 5 min at each of six wells (not the six piezometers mentioned above) in the riparian area by a data logger connected to a float-driven potentiometer (Figure 1). The water level in each well is reported relative to an arbitrary datum.

The areal extent of, and mean depth to, bedrock on the hillslope and in the riparian area were determined by interpolation of 164 measurements made with a knocking pole penetrometer (Yoshinaga and Onuki, 1995) as described by Zumbuhl (1999), and from 31 measurements of the depth of unconsolidated deposits from previous installations of wells in the catchment. The riparian area was defined as the area that occupied the stream valley and extended up the hillslopes until the depth to bedrock was less than 3 m. The resulting estimates of the outcrop, hillslope, and riparian area were 3.6, 5.9, and 0.8 ha respectively. The volume of water stored in the riparian area before and after each storm was estimated from three equations:

$$\Delta \text{Vol}_{\text{sat}} = (\text{GW}_{\text{post}} - \text{GW}_{\text{pre}}) \times \text{Area} \times \text{Porosity} \times \Delta \text{Pore Vol} \quad (1)$$

$$\Delta \text{Vol}_{\text{peak}} = (\text{GW}_{\text{peak}} - \text{GW}_{\text{post}}) \times \text{Area} \times \text{Porosity} \times \Delta \text{Pore Vol} \quad (2)$$

$$\Delta \text{Vol}_{\text{unsat}} = (\text{Surface} - \text{GW}_{\text{peak}}) \times \text{Area} \times \text{Porosity} \times \Delta \text{Pore Vol} \quad (3)$$

where $\Delta \text{Vol}_{\text{sat}}$ is the change in storage in the depth interval that was saturated after, but not before the rainstorm, $\Delta \text{Vol}_{\text{peak}}$ is the change in storage in the depth interval that was saturated at the peak but not after the rainstorm, $\Delta \text{Vol}_{\text{unsat}}$ is the change in storage in the depth interval that remained unsaturated throughout the rainstorm, and GW_{post} , GW_{pre} , and GW_{peak} are water table levels after the rainstorm, before the rainstorm, and at the maximum level respectively. Surface is the level of the land surface relative to the level of the water table, Area is the surface area of the riparian zone, $\Delta \text{Pore Vol}$ is the change in water-filled pore space, and Porosity is the estimated pore volume/total volume.

A mean water level was calculated from six continuously recording riparian wells (Figure 1), and porosity was assumed to be 0.50 (typical of soils at PMRW, as reported by McIntosh *et al.*, 1999). The saturated thickness above the pre-storm water table was 45 mm after the 2 February storm (4 February) and 660 mm after the 6–7 March storm (9 March). This zone encompasses the capillary fringe, which can remain saturated despite negative potential; however, the soils at PMRW probably do not have a significant capillary fringe (McDonnell and Buttle, 1998). Therefore, the area above the pre-storm water table that remained saturated on 4 February was assumed to have had 90% of its pore space filled with water before the rainstorm—a

Table I. Solute concentrations of stream baseflow on 13 February, 1996,^a and the mean and standard deviation of solute concentrations in riparian groundwater samples collected on 6 March, 1996 at PMRW, Georgia

Solute	Baseflow	Riparian groundwater	
		Mean concentration	Standard deviation
Ca ²⁺ (µeq l ⁻¹)	40.8	54.7	10.8
Mg ²⁺ (µeq l ⁻¹)	23.2	27.7	4.7
Na ⁺ (µeq l ⁻¹)	66.0	61.8	18.9
K ⁺ (µeq l ⁻¹)	9.1	11.1	1.0
H ₄ SiO ₄ (µmol l ⁻¹)	117.8	123.9	34.6
SO ₄ ²⁻ (µeq l ⁻¹)	78.3	80.5	24.8
Cl ⁻ (µeq l ⁻¹)	31.9	32.1	6.7

^a 13 February is the last date on which a baseflow sample was collected prior to the rainstorm of 6–7 March; streamflow ceased on 14 February.

value between saturation and the field capacity. Because this saturated region was much thicker (660 mm) and conditions were drier prior to the 6–7 March rainstorm, only 70% of the pore space was assumed to be filled with water—a value close to the field capacity. The water-filled pore space in the part of the riparian zone that remained unsaturated during both storms was assumed to have increased by 3 to 5%. This estimate was based on typical changes in volumetric soil-moisture content during storms at a site on the hillslope adjacent to the stream gage (N.E. Peters, unpublished data). For example, the net gain in soil moisture at 0.7 m depth on the hillslope during the 6–7 March storm was equivalent to 4% of the pore space. The net change in the volume of water stored in the soil on the outcrop was estimated from the assumption that about one-quarter of the outcrop is covered by soil with a mean thickness of 1 m (based on measurements by Zumbuhl (1999)) and a porosity of 0.65. The net gain in water-filled pore space was assumed to range from 5 to 10% during the 2 February storm, and 10 to 20% during the 6–7 March storm. These net gains were assumed to be greater than those for riparian soils because the outcrop soil continued to discharge water after each storm, an indication of near-saturated conditions.

Laboratory analyses

Samples for chemical analysis were collected in 250 ml polyethylene bottles and then passed through a 0.45 μm cellulose nitrate filter. About 50 ml of each filtered aliquot was then acidified to pH 1 to 1.5 with HCl, and stored at room temperature prior to analysis for Ca^{2+} , Mg^{2+} , Na^+ , K^+ , and H_4SiO_4 concentrations by direct-coupled plasma emission spectroscopy. A second, untreated 50 ml filtered aliquot was analysed for SO_4^{2-} and Cl^- concentrations by ion chromatography. Analytical methods are described in Fishman and Friedman (1989). An unfiltered aliquot from samples collected during the 2 February storm was analysed for $\delta^{18}\text{O}$ by mass spectrometry with an analytical precision of 0.1‰. Analytical precision for chemical constituents was 0.2 $\mu\text{eq l}^{-1}$ for SO_4^{2-} , 0.3 $\mu\text{eq l}^{-1}$ for Cl^- and K^+ , 0.4 $\mu\text{eq l}^{-1}$ for Na^+ , 0.8 $\mu\text{eq l}^{-1}$ for H_4SiO_4 , 1.0 $\mu\text{eq l}^{-1}$ for Ca^{2+} , and 2.0 $\mu\text{eq l}^{-1}$ for Mg^{2+} ; these values were based on long-term measurements of duplicate samples (Huntington *et al.*, 1993).

Model analysis and procedures

An EMMA model was used to calculate the proportion of stream water derived from each of three principal geographic sources of runoff in the 10 ha catchment for each rainstorm (the outcrop, the hillslope, and the riparian area). The EMMA model was developed according to the procedure outlined by Christopherson and Hooper (1992):

- (1) a dataset was obtained that consisted of the concentrations of seven solutes (Ca^{2+} , Mg^{2+} , K^+ , Na^+ , H_4SiO_4 , Cl^- , and SO_4^{2-}) in 130 samples of stream water at the 10 ha catchment during 1992–96;
- (2) the data were standardized into a correlation matrix such that solutes with greater variation would not exert more influence on the model than those with lesser variation;
- (3) a principal-components analysis (PCA) was performed on the correlation matrix using all seven solutes, and all combinations of six and five solutes. A model was selected that accounted for the greatest amount of variability with two principal components, implying a three end-member model;
- (4) the concentrations of the end members were standardized and projected into the U space defined by the stream PCA by multiplying the standardized values by the matrix of eigenvectors;
- (5) The extent to which the end members bounded the stream-water observations for the February and March rainstorms was examined in U space;
- (6) The goodness-of-fit of solute concentrations predicted by the EMMA were compared with the concentrations measured during the two storms through least-squares linear regression.

The seven solutes selected for possible inclusion in the model included five of the solutes used in a previous EMMA model of the PMRW (Hooper *et al.*, 1990). Alkalinity was not used in this study because

measurements were not available for stream water collected during the rainstorms in 1996. The analysis did not use stream-chemistry data from the 1980s because the solute concentrations appear to have shifted by the 1990s, possibly as a result of climatic change at the site (Hooper *et al.*, 1998).

The EMMA model was then used to calculate the proportion of stream water derived from each of the three end members for each sample collected during both storms by solving the following mass-balance expressions:

$$Q_{st} = Q_o + Q_h + Q_r \quad (4)$$

$$U1_{st}Q_{st} = U1_oQ_o + U1_hQ_h + U1_rQ_r \quad (5)$$

$$U2_{st}Q_{st} = U2_oQ_o + U2_hQ_h + U2_rQ_r \quad (6)$$

where Q is the discharge, and $U1$ and $U2$ are the first and second principal components of the PCA; the subscripts st, o, h, and r signify stream, outcrop, hillslope, and riparian areas respectively.

The concentrations of solutes for the riparian end member were based on a sample of stream baseflow collected prior to each rainstorm. The baseflow sample for the 2 February storm was collected on 1 February 1996 at 11:25 a.m., the baseflow sample for the 6–7 March storm was collected on 13 February 1996 at 12:52 p.m. This sample date preceded the date of the storm by 3 weeks because the stream ceased flowing at the stream gauge on 14 February.

The temporal variations in solute concentrations of subsurface flow samples collected in the hillslope trench were small—particularly during the period of greatest flow (Burns *et al.*, 1998). Consequently, the hillslope end member was represented by median values for all samples collected in the trench during each storm. The temporal variations in solute concentrations at the base of the outcrop were large (standard deviations exceeded 100% for many of the constituents); therefore, the chemical composition of the outcrop end member was allowed to vary with time during each storm. This approach is similar to that of others who have varied the tracer concentration of new water during storms (McDonnell *et al.*, 1990; Pionke *et al.*, 1993).

Solute concentrations during the 2 February storm decreased exponentially with time; therefore, exponential functions were derived for each solute. The temporal pattern for the 6–7 March storm was more erratic, so linear interpolations based on eight outcrop-runoff samples were used to derive time-dependent changes in the concentrations of the outcrop end member.

The uncertainty in EMMA model results for the percentage of streamflow contributed by each end member during each storm was calculated through an adaptation of a method described by Genereux (1998). An uncertainty value was calculated for each of the two principal components used in the model through incorporation of analytical uncertainty in each of the chemical constituents (Huntington *et al.*, 1993) as follows:

$$W_{ui} = ((V_{ia}W_a)^2 + (V_{ib}W_b)^2 + \dots)^{0.5} \quad (7)$$

where W_{ui} is the uncertainty value for principal component i , $V_{ia}V_{ib}$ are the eigenvectors for constituents a and b on principal component i , and W_a and W_b are the analytical uncertainties in the values of constituents a and b .

The uncertainty value for each principal component was then successively added and subtracted from the values of $U1$ and $U2$ for each end member and for each stream sample collected during the storms to create two new sets of values for $U1$ and $U2$. These new values of $U1$ and $U2$ were then used in Equations (4)–(6) to calculate an uncertainty range for each stream sample collected during the two storms. This uncertainty range is displayed in Figures 2, 3, and 6.

RESULTS

A total of 62 mm of rain fell during the rainstorm of 2 February 1996 (Table II). The maximum 15 min rainfall rate was 16.4 mm h⁻¹, and the rainfall rate for the entire storm was 3.4 mm h⁻¹. This storm

Table II. Characteristics of the two rainstorms that were sampled during the winter of 1996 at PMRW, Georgia

Characteristic	2 February	6–7 March
Rainfall amount (mm)	62	96
7 day antecedent rainfall (mm)	115	10
Max. 15 min rainfall rate (mm h ⁻¹)	16.4	35.6
Rainfall rate (mm h ⁻¹)	3.4	4.5
Peak stream runoff rate (mm h ⁻¹)	3.0	4.4
Stream yield (% of rainfall)	68.3	38.6

followed wet winter antecedent conditions—115 mm of rain had fallen during the previous 7 days. Prior to the rainstorm, volumetric soil-moisture content at a depth of 40 cm on a hillslope near the stream gauge was 0.31—greater than the mean value on 86% of the days during the 1995–96 dormant season. The stream was flowing at the gauge prior to the storm, and a small rate of flow was measured in the trench before the storm. The stormflow hydrograph was broad, and the runoff rate peaked at about 3 mm h⁻¹ during the afternoon of 2 February (Figure 2). The maximum soil-moisture content was 0.31, 0.34, and 0.29 at depths of 15 cm, 40 cm, and 70 cm below land surface respectively—an increase of about 0.03 from pre-storm conditions at each depth. Stream yield was more than two-thirds of total rainfall by 24:00 on 4 February.

A total of 96 mm of rain fell during the 6–7 March 1996 rainstorm (Table II). The storm consisted of two closely spaced smaller storms—49 mm of rain on 6 March, and 47 mm on 7 March—separated by about ten rain-free hours. The maximum 15 min precipitation rate during this storm was 35.6 mm h⁻¹ on 6 March, and the precipitation rate for the entire storm was 4.5 mm h⁻¹. The storm hydrograph shows two distinct peaks; stream runoff returned to almost zero late on 6 March before the second storm arrived. Peak stream runoff rate was about 3.7 mm h⁻¹ on 6 March, and almost 4.5 mm h⁻¹ on 7 March (Figure 3). Streamflow rose and receded more sharply during the 6–7 March storm than during the 2 February storm. The March storm, unlike the February storm, occurred after dry winter antecedent conditions—only 10 mm of precipitation had fallen during the previous 7 days, and the stream had not flowed at the gauge in the preceding 3 weeks. Volumetric soil-moisture content at a depth of 40 cm on the hillslope was 0.28 prior to the rainstorm, less than the mean value on 84% of the days during the 1995–96 dormant season. Stream yield was just greater than one-third of total rainfall for the March storm.

Solute chemistry

A mixing diagram is shown for Na⁺ and SO₄²⁻ concentrations in stream water and each of the end members during the two storms to illustrate the general pattern of solute evolution (Figure 4). Solute concentrations in the stream were similar to those in riparian groundwater (by definition) at the beginning of both storms, then evolved towards those of the outcrop runoff before returning to values for riparian groundwater near the end of the storm. These solute concentrations did not evolve linearly towards the outcrop end-member, indicating an influence from mixing with hillslope runoff. Stream water Na⁺ and SO₄²⁻ concentrations approached those of outcrop runoff more closely during the 6–7 March storm than during the 2 February storm. Stream chemistry during the 6–7 March storm showed a bivariate pattern of evolution toward outcrop runoff chemistry, followed by a reversal toward riparian runoff chemistry on 6–7 March, and then a repeat of this pattern on 7–8 March. Mean solute concentrations in stream water and the three end members and their standard deviations are given in Table III. Of the five solutes, H₄SiO₄ concentrations generally varied the most, and Mg²⁺ concentrations varied the least.

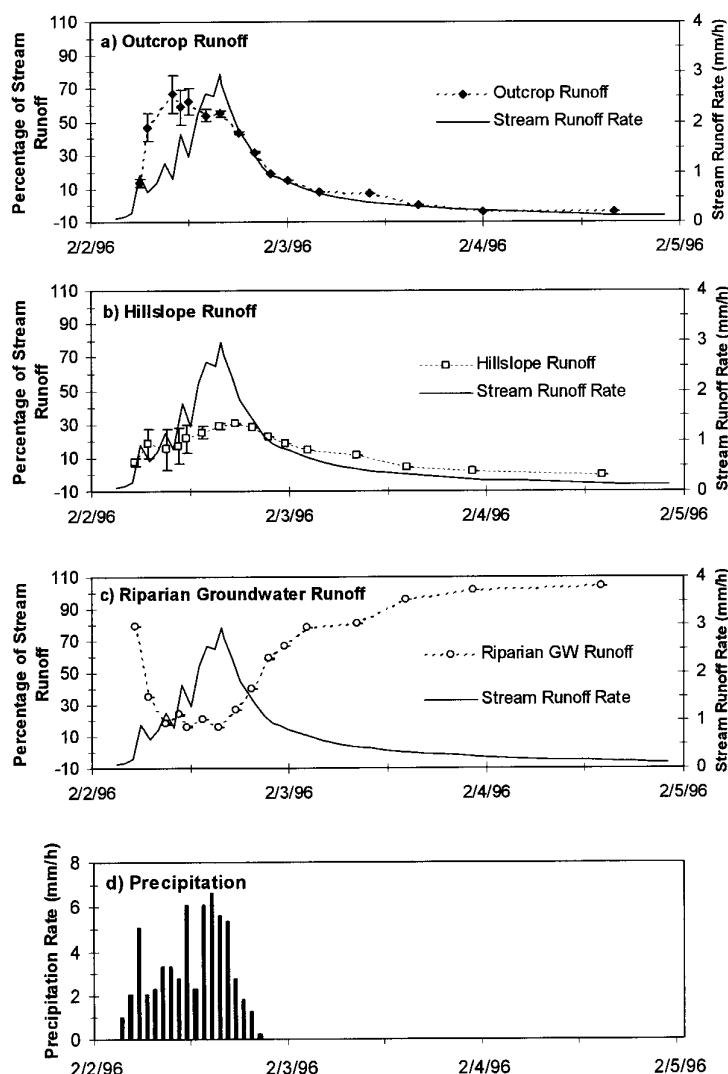


Figure 2. Measured stream runoff and precipitation, and percent contribution of each runoff component (with error estimates) to stream runoff predicted from the EMMA model during the 2 February rainstorm: (a) outcrop runoff, (b) hillslope runoff, (c) riparian groundwater runoff, and (d) precipitation

EMMA model

The PCA that was chosen for use in the EMMA incorporated five solutes (Mg^{2+} , Na^+ , H_4SiO_4 , Cl^- , and SO_4^{2-}) because the first two principal components explained 93% of the variability in these data, the greatest amount of any model that was examined. The three end members selected for the model encompassed the variability in stream water measured during both storms (Figure 5). A general evolution of stream water from the riparian end member towards the outcrop end member and then a return to the riparian end member is evident in the diagram. Linear-regression relations between predicted and measured concentrations for each solute gave r^2 values that ranged from 0.95 to 0.99, and slopes that ranged from 0.86 to 1.03, an indication that the EMMA model is a strong, unbiased predictor of stream solute concentrations.

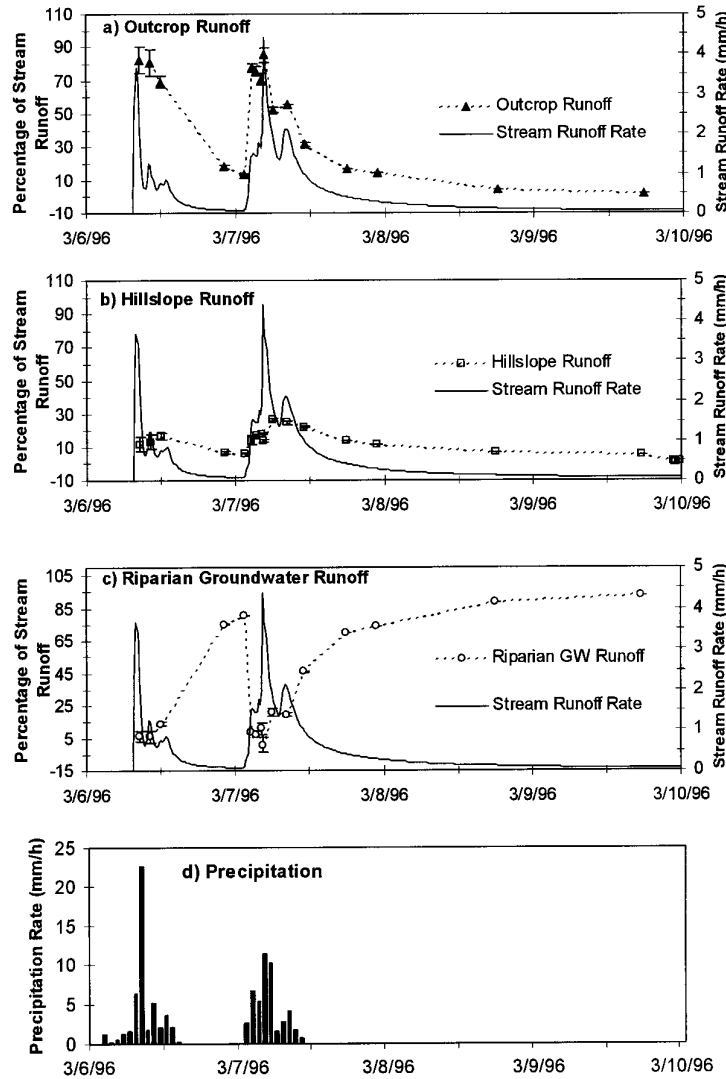


Figure 3. Measured stream runoff and precipitation, and percent contribution of each runoff component (with error estimates) to stream runoff predicted from the EMMA model during the 6–7 March rainstorm: (a) outcrop runoff, (b) hillslope runoff, (c) riparian groundwater runoff, and (d) precipitation

2 February rainstorm

Outcrop runoff dominated stream runoff during the period of increasing flow on 2 February, when it provided a maximum of about $66 \pm 11.7\%$ of stream runoff (Figure 2a). At peak flow, outcrop runoff provided about 50% of stream runoff. The outcrop runoff contribution to stream runoff then declined late on 2 February in parallel with stream runoff, and by the beginning of 3 February it provided only about 15% of stream runoff. The outcrop runoff contribution to stream runoff from the EMMA model agrees closely with the event component contribution to stream runoff determined through ^{18}O data, providing additional support for conservative behaviour of the solutes during this storm (Figure 6). Hillslope runoff provided about 30% of

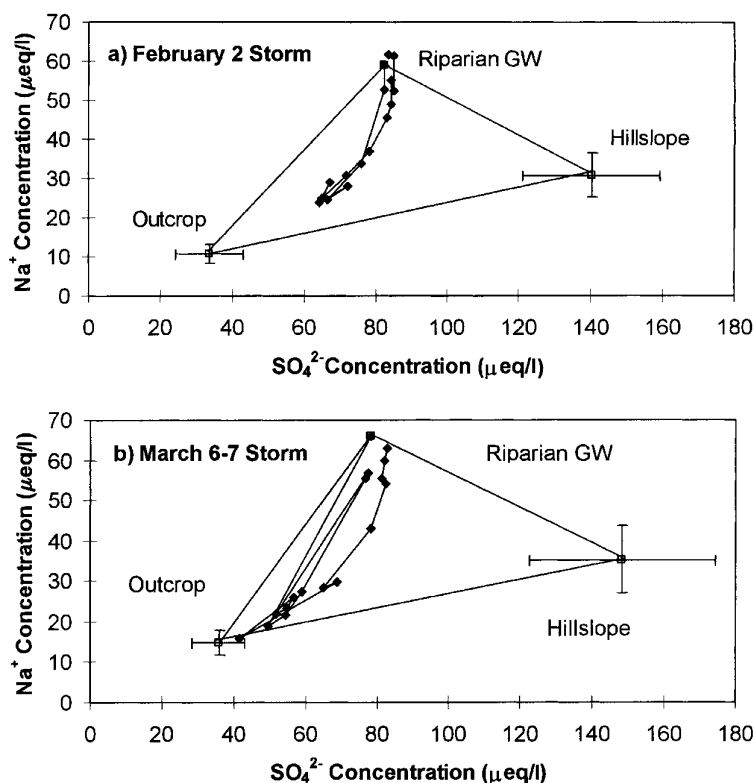


Figure 4. Mixing diagram showing stream water evolution and end-member Na^+ and SO_4^{2-} concentrations during: (a) 2 February rainstorm, (b) 6–7 March rainstorm

Table III. Mean concentration and standard deviation of solutes (only those used in EMMA model) in streamwater and in the three end-members sampled during the two winter rainstorms at PMRW, Georgia, 1996

Solute	Stream water		Riparian groundwater	Outcrop runoff		Hillslope runoff	
	Mean	Std. Dev.	Mean	Mean	Std. Dev.	Mean	Std. Dev.
2 February							
Na^+ ($\mu\text{eq l}^{-1}$)	43.0	14.6	58.8	11.0	3.4	30.8	5.7
Mg^{2+} ($\mu\text{eq l}^{-1}$)	21.1	3.3	22.8	0.6	1.5	46.8	7.1
H_4SiO_4 ($\mu\text{mol l}^{-1}$)	72.6	30.7	111.2	3.9	0.8	87.8	17.3
Cl^- ($\mu\text{eq l}^{-1}$)	24.3	7.3	33.8	4.9	1.7	25.0	4.8
SO_4^{2-} ($\mu\text{eq l}^{-1}$)	77.3	7.7	82.5	31.3	7.0	140.1	19.2
6–7 March							
Na^+ ($\mu\text{eq l}^{-1}$)	39.1	17.7	66.0	14.6	2.5	35.3	8.4
Mg^{2+} ($\mu\text{eq l}^{-1}$)	18.3	4.4	23.2	2.5	2.6	50.0	10.8
H_4SiO_4 ($\mu\text{mol l}^{-1}$)	64.5	36.8	117.8	13.4	9.8	100.2	29.3
Cl^- ($\mu\text{eq l}^{-1}$)	21.3	8.3	31.9	8.2	1.7	25.4	8.0
SO_4^{2-} ($\mu\text{eq l}^{-1}$)	67.1	13.8	78.3	31.3	8.5	148.4	26.0

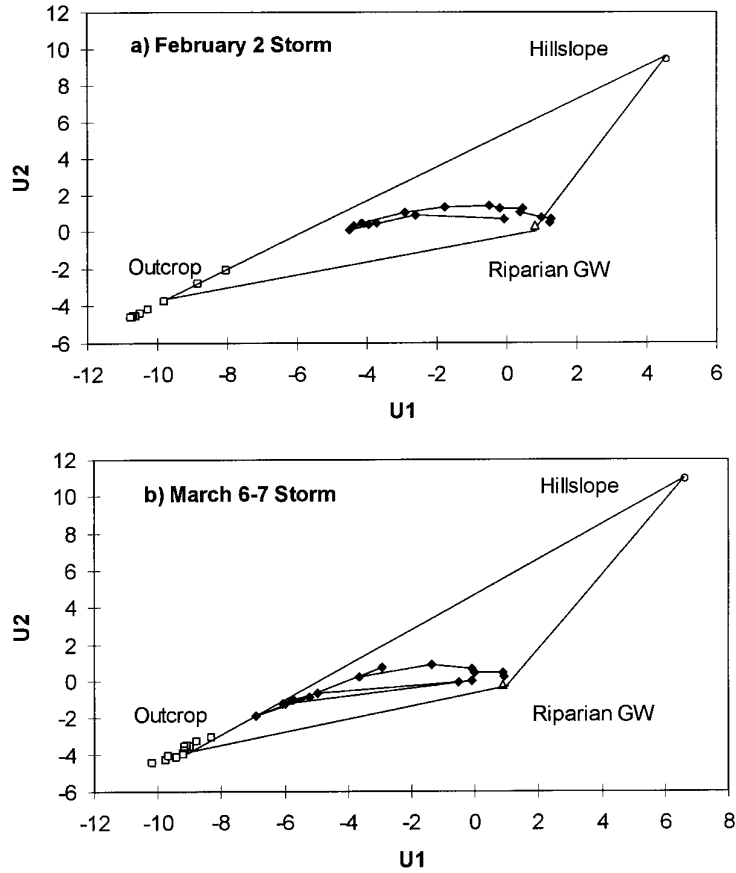


Figure 5. Mixing diagram showing stream water evolution and end-member composition in U space during: (a) 2 February rainstorm, (b) 6–7 March rainstorm

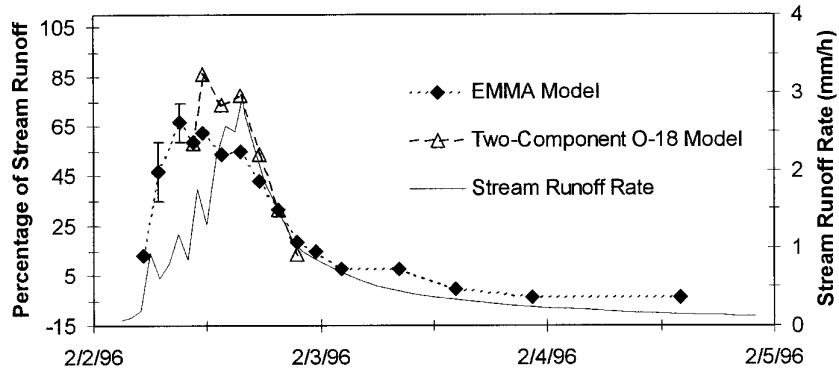


Figure 6. Measured stream runoff, contribution of outcrop runoff to stream runoff predicted from the EMMA model and contribution of the event-water component to stream runoff from a two-component model using $\delta^{18}\text{O}$ values for the 2 February rainstorm

Table IV. Contribution of each end member to total stream runoff and total amount of runoff from each end member and the stream (expressed on a whole catchment basis) during two winter rainstorms sampled at PMRW, Georgia, 1996

Runoff component	2 February		6–7 March	
	Percent of stream runoff	Total amount (mm)	Percent of stream runoff	Total amount (mm)
Outcrop	31	13	49	18
Hillslope	19	8	16	6
Riparian groundwater	50	21	35	13
Stream	–	42	–	37

stream runoff through the period of peak flow (uncertainty $\pm 10\%$) and decreased gradually to about 15% of stream runoff early on 3 February (Figure 2b). The contribution of riparian groundwater to stream runoff varied widely, from about 80% early during the period of increasing flow, to about 15% at peak flow, to more than 95% as stormflow receded on 4 February (Figure 2c). Uncertainty in the riparian groundwater runoff contribution was low, and never exceeded $\pm 1\%$ for any of the samples collected.

Mass balances for the entire storm (2–4 February) indicate that the riparian groundwater end member provided about 50% of stream runoff for the storm, despite its minimal contribution at peak runoff, whereas the outcrop runoff, which dominated peak runoff, provided only about 31% of total stream runoff for the storm (Table IV). Hillslope runoff contributed only about 19% to total stream runoff for the storm.

6–7 March rainstorm

Outcrop runoff provided an even greater contribution to stream runoff during the 6–7 March storm than during the 2 February storm—about 82% at the first peak flow on 6 March, and nearly 85% at the second peak flow on 7 March (Figure 3a). Uncertainty in the outcrop runoff contribution was about $\pm 8\%$ for the peak flow on 6 March and about $\pm 4\%$ for the peak flow on 7 March. The contribution of outcrop runoff to streamflow decreased steadily to about 15% late on 7 March. Hillslope runoff provided a maximum of about $25 \pm 1.2\%$ to stream runoff, and peaked after the hydrograph on 7 March (Figure 3b). The contribution of riparian groundwater to stream runoff varied even more sharply than during the February storm—from less than 5% near the peak flows of 6 and 7 March, to 80% between the two storms, and to about 90% of stream runoff by the end of 8 March (Figure 3c). Uncertainty of the outcrop runoff contribution to stream runoff was higher than for the 2 February storm, but never exceeded $\pm 5\%$.

A mass balance for the 6–7 March storm (6 through 9 March) indicates that outcrop runoff provided 49% of total stream runoff, a greater fraction than the 31% contributed during the 2 February storm, whereas riparian groundwater contributed 35%, less than the 50% contributed during the 2 February storm. Hillslope runoff contributed about the same percentage of stream runoff in both storms.

Relation of predicted end-member runoff to hydrometric measurements

Several recently published studies have provided evidence of the importance of linking hydrochemical and isotope tracer modelling with hydrometric measurements to test the physical plausibility of model results (Bazemore *et al.*, 1994; Harris *et al.*, 1995; Elsenbeer and Lack, 1996; Anderson *et al.*, 1997). In the present study, we compared: (1) predicted outcrop runoff with measured rainfall intensity, (2) predicted hillslope runoff with measured trench outflow, and (3) predicted riparian groundwater runoff with measured changes in riparian water table levels.

(1) *Predicted outcrop runoff and measured rainfall intensity.* A detailed record of outcrop runoff was developed by interpolating between samples to provide a modelled runoff value for every hour on 2 February,

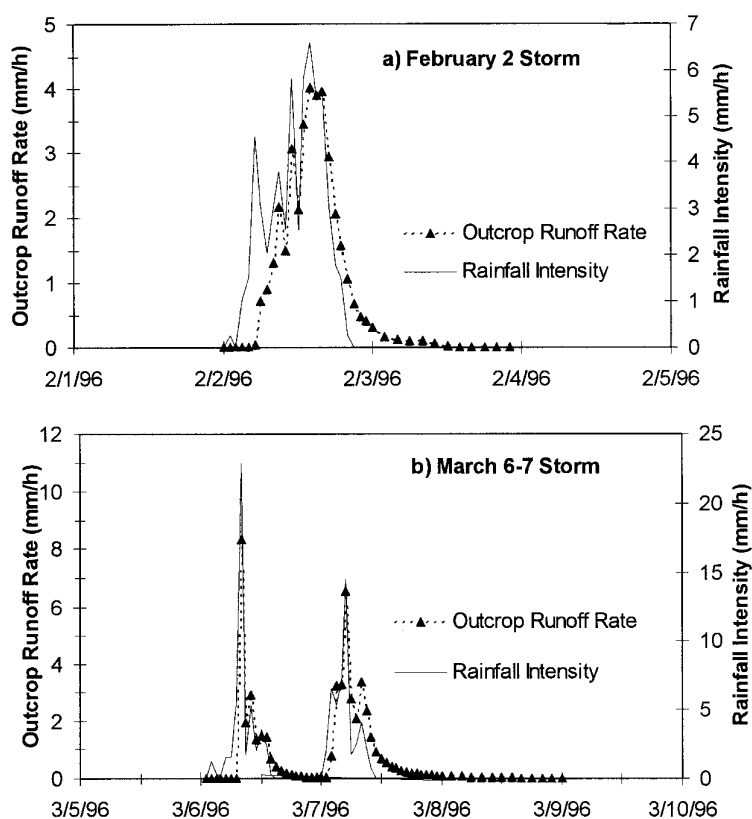


Figure 7. Predicted outcrop runoff and measured rainfall intensity: (a) 2 February rainstorm, (b) 6–7 March rainstorm. (Specific runoff calculated based on areal extent of end member)

every 2 h on 3 February, and every 2 h during 6–8 March. These outcrop runoff values were compared with measured rainfall-intensity values over the same time intervals (Figure 7). Both storms show a lag between the onset of rain and the initiation of outcrop runoff; this lag results from the time necessary for rainfall to (1) travel from where it landed on the outcrop to the stream channel, and (2) saturate the numerous pockets of organic soil underlying vegetation islands on the outcrop (Huntington *et al.*, 1993). A previous study at this site showed that 1.6 mm of rainfall was necessary to produce runoff from a small 0.054 ha catchment on the outcrop, although this value varied seasonally (Peters, 1989). Once outcrop runoff was initiated, its rate was generally coincident with rainfall intensity until the latter began to decline. During both storms, the peaks in the two rates coincided. Outcrop runoff continued for several hours after rainfall ceased because the pockets of soil continued to drain. The predicted outcrop-runoff rate was always less than the rainfall-intensity rate during both storms except for the recession period, when rainfall had ceased and the soil continued to drain. The rainfall and outcrop-runoff rates were strongly correlated during each storm; r^2 values obtained by linear regression were 0.75 ($p < 0.01$) for the 2 February storm and 0.81 ($p < 0.01$) for the 6–7 March storm. Total predicted stream runoff from the outcrop was 38 mm, about 61% of the 62 mm of rain that fell during the 2 February storm, and 51 mm, about 53% of the 96 mm of precipitation that fell during the 6–7 March storm.

(2) *Predicted hillslope runoff and measured trench outflow.* The predicted hillslope runoff hydrograph was similar to the measured trench outflow hydrograph during the 2 February storm, except that the trench-flow

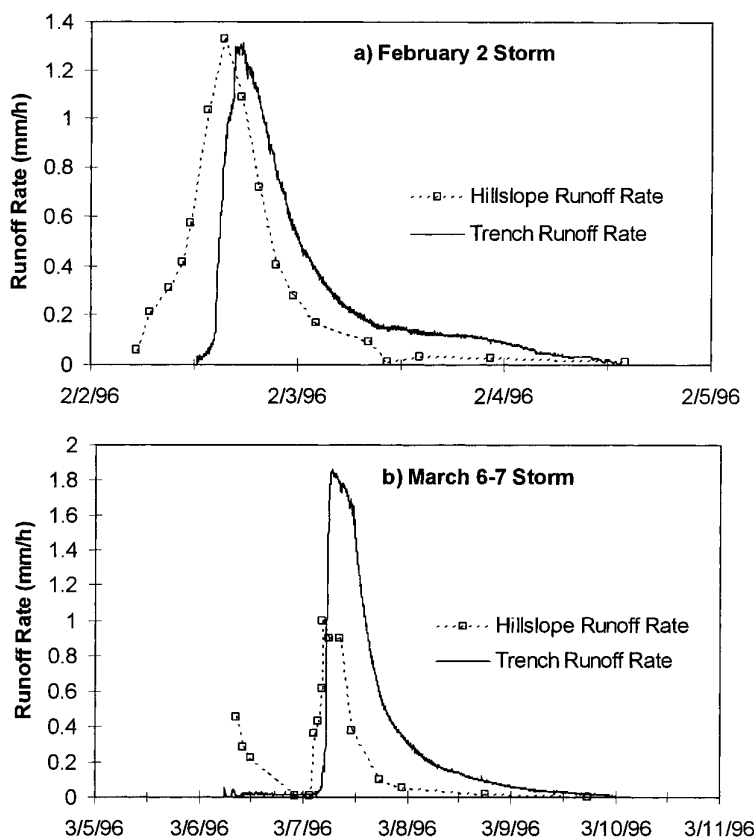


Figure 8. Predicted hillslope runoff and measured trench flow: (a) 2 February rainstorm, (b) 6–7 March rainstorm. (Specific runoff calculated based on areal extent of end member)

response lagged slightly behind the predicted hillslope-runoff response (Figure 8a). This lag ranges from several hours at the initiation of flow and on the recession limb of the hydrograph, to about 2 h at peak flow. The maximum runoff rates for the measured trench flow and predicted hillslope runoff were similar—about 1.3 mm h^{-1} , and total runoff for this storm, as indicated by the measured trench outflow and predicted hillslope runoff values, was about 14 mm.

Large differences between measured trench outflow and predicted hillslope runoff during the 6–7 March storm are evident (Figure 8b). The model indicated that hillslope runoff contributed to stream runoff on 6 March, but little trench flow was measured during the first storm. The predicted values for 7 March were similar to the measured values on the rising limb of the hydrograph, except that the predicted values had a lower peak than the measured values and receded more rapidly. The measured trench runoff for the storm was 23 mm, whereas predicted hillslope runoff was only about 10 mm.

(3) *Predicted riparian groundwater runoff and observed riparian water table levels.* On 2 February, the predicted riparian groundwater runoff rate decreased from an initial value of about 4.5 mm h^{-1} over the next four sampling intervals, then increased to a peak value of about 8 mm h^{-1} late in the day (Figure 9a). The water levels in riparian wells 611 and 642 gradually rose as runoff declined, and reached their peak

about 2 h before the predicted riparian groundwater runoff reached its peak. The peak water table levels persisted through the predicted runoff peak, then the water levels and predicted groundwater runoff began a simultaneous decline.

The variations measured in riparian water table levels on 6 March were similar to those of the predicted riparian runoff, but peaked before the predicted riparian runoff (Figure 9b). The measured water table levels rose on 7 March and peaked several hours before the predicted riparian runoff, then decreased slightly, followed by a sharper decline coincident with predicted riparian runoff. A departure from this pattern is seen on the rising limb of the predicted riparian runoff hydrograph for 7 March, which shows a sudden decrease to a value of less than 1 mm h^{-1} at the time of peak stream runoff when water table levels were rising rapidly.

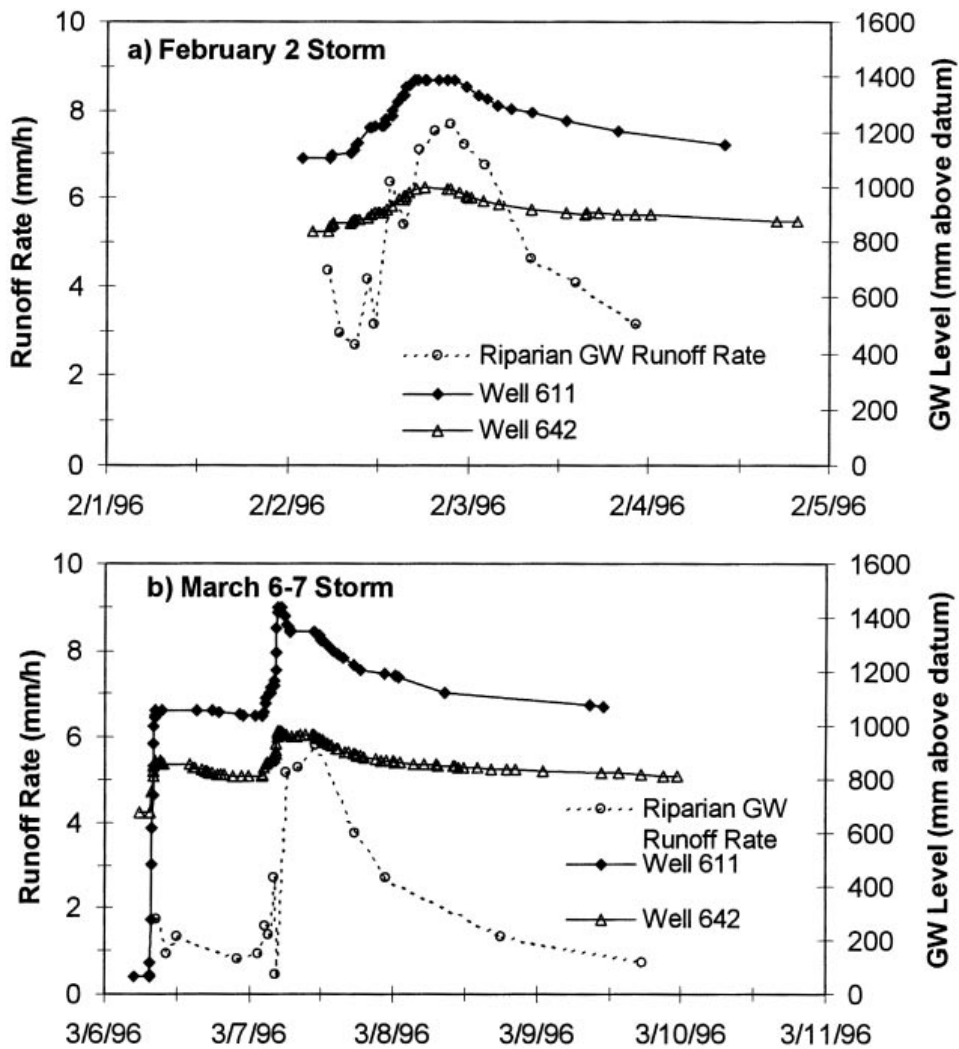


Figure 9. Predicted riparian groundwater runoff and measured water table levels at two wells: (a) 2 February rainstorm, (b) 6–7 March rainstorm. (Specific runoff calculated based on areal extent of end member)

Change in storage volume of riparian reservoir relative to excess outcrop runoff

The measured rainfall amount was combined with EMMA model results to estimate the residual volume of runoff from the outcrop that did not contribute to stream runoff, and thus provided recharge to the riparian area. These estimates of recharge ranged from 160 to 450 m³ for the 2 February storm, and from 380 to 960 m³ for the 6–7 March storm. The second method of calculating riparian recharge was based on the mean water table level measured in the six riparian wells. This level was 1500 mm below land surface prior to the 2 February storm, and 2060 mm below land surface prior to the 6–7 March rainstorm. The increase in the mean water table level from the beginning to the end of the 2 February storm (end of day on 4 February) was 45 mm, and it was 660 mm for the 6–7 March storm (end of day on 9 March). The net changes in storage implied by these changes in water table levels, combined with estimated net changes in storage in the unsaturated zone, yielded an estimated increase in riparian storage of 190 to 310 m³ for the 2 February storm, and 960 to 1100 m³ for the 6–7 March storm. These calculations should be viewed only as estimates, however, because no direct measurements of changes in storage were obtained from the unsaturated part of the riparian area, nor from the soils on the outcrop; yet the similarity of these two independent estimates of recharge are essentially indistinguishable for both rainstorms. The riparian area probably received recharge from hillslope soils as well, but this was not included in these calculations.

DISCUSSION

Outcrop runoff

Runoff from the outcrop clearly dominated stream runoff at peak flow during both storms, but it was transient, and its contribution to stream runoff decreased rapidly as rainfall intensity declined. This pattern is consistent, though of a greater magnitude, with the transient contribution of new water from rainfall or throughfall to stream runoff as reported in many other mixing-model studies of forested catchments (Sklash *et al.*, 1976; DeWalle *et al.*, 1988; Ogunkoya and Jenkins, 1993; Bazemore *et al.*, 1994). On a whole-storm basis, outcrop runoff was the dominant component of stream runoff during the 6–7 March storm but was second to riparian groundwater runoff during the 2 February storm. This result is different from most others reported in temperate-zone forested catchments, in which the old water or groundwater component dominates stream runoff at peak flow as well as on a whole-storm basis (Buttle, 1994; Genereux and Hooper, 1998). The presence of the large outcrop that occupies a third of the 10 ha catchment area clearly has an important effect on stormflow response; the model results are consistent with the observed flow of runoff from the outcrop over the land surface of the riparian area (most likely as Hortonian overland flow) and into the stream during both storms.

Comparison of the results of this study with those of past studies of stream chemistry during rainstorms at this site reveals disagreement as to the importance of various runoff sources. This disparity results, in part, from differences in the drainage basin scale that was studied and from differences in the seasons in which storm runoff was collected. For example, Shanley and Peters (1993) found that despite SO₄²⁻ concentrations of outcrop runoff that varied from 120 µeq l⁻¹ at the onset of runoff, to about 20 µeq l⁻¹ later in the storm, stream SO₄²⁻ concentrations at the 10 ha gauge varied only between 80 and 100 µeq l⁻¹. They suggested that mean SO₄²⁻ concentrations were buffered by rapid sorption reactions as the outcrop runoff was transported through shallow soils. In contrast, we found stream SO₄²⁻ concentrations that were lower (40–80 µeq l⁻¹), but that varied by a similar amount (about 40 µeq l⁻¹) at the 10 ha catchment stream gauge. Our results are consistent with conservative mixing of SO₄²⁻ (and the other solutes in the EMMA model) from outcrop runoff before entering the stream. The reason for these differences is unclear. The March 1996 rainstorm reported in this study resembled the February 1988 rainstorm reported by Shanley and Peters (1993), in that both contained two small storms and both occurred under dry winter antecedent conditions. About twice the amount of precipitation fell during the March 1996 storm, however, which may have resulted in more

unaltered SO_4^{2-} from outcrop runoff arriving at the stream gauge. Another possible reason for the discrepancy in these results is that the February 1988 storm occurred during an extended period of drought at PMRW when soil SO_4^{2-} concentrations were higher due to a lower flushing rate (Huntington *et al.*, 1994).

A more recent study by Peters and Ratcliffe (1998) used new–old water hydrograph separation models, and concluded that a large amount of new water must contribute to stream runoff at the 41 ha gauge. For the peak-of-record rainstorm in July 1995, they estimated that 95% of stream runoff consisted of new water at peak flow.

Comparison with previous EMMA results at Panola

In a previous study that used EMMA at this site, Hooper *et al.* (1990) modelled stream water as a mixture of organic-horizon soil water, hillslope groundwater, and riparian groundwater. Runoff from the outcrop was not considered to contribute significantly to stream runoff. They applied their model to a larger 41 ha catchment at PMRW, in contrast to the 10 ha catchment used in this study. The 3.6 ha outcrop occupies less than 10% of the 41 ha catchment, so its role in stormflow should be significantly less than in the 10 ha catchment. Additionally, hillslope groundwater was represented by data from a well that is now believed to be in the stream riparian area, and has a chemical composition significantly different than subsurface stormflow from the hillslope trench (Hooper *et al.*, 1998; Zumbuhl, 1999). Therefore, groundwater from this well is now assumed to be a mixture of riparian groundwater with runoff that has recharged from the outcrop. These new interpretations of data from past studies demonstrate the importance of obtaining detailed hydrogeologic data—of types that have been lacking in many previous small catchment studies.

Role of outcrop runoff in groundwater recharge

The model results from this study indicate that not all of the rain that fell on the outcrop during the two storms became stream runoff. The volume of outcrop runoff that recharged the riparian aquifer (including water stored in outcrop soils) was estimated to range from 7 to 20% of rainfall for the 2 February storm, and 11 to 28% of rainfall for the 6–7 March storm. These values were consistent with independent estimates of recharge to the riparian aquifer, and confirmed that the model estimates of the volume of runoff from the outcrop that contributed to stream runoff during both storms were reasonable. Substantial groundwater recharge from the outcrop is further confirmed by the lower concentrations of chemical constituents at the riparian sampling piezometers on the outcrop side of the stream than at piezometers on the opposite side of the stream (D.A. Burns, unpublished data).

Hillslope runoff

Predicted hillslope runoff never provided more than 25 to 30% of stream runoff. It provided a greater contribution during the 2 February storm than during the 6–7 March storm, probably because wet winter soil conditions prior to the 2 February storm promoted a greater contribution of hillslope runoff to the stream. The March storm began with a large soil-moisture deficit that had to be satisfied before hillslope runoff could begin, as evidenced by the low value for this runoff component on 6 March, and a higher value on 7 March. The hillslope-runoff component can be viewed as similar to the soil-water component that is measured in hillslope zero-tension lysimeters in many catchment studies (Bazemore *et al.*, 1994; Rice and Hornberger, 1998), because stored soil water dominates this component once saturated conditions are reached. A trench is preferable to lysimeters, however, because the spatially integrated (across 20 m) shallow hillslope stormflow that was collected from the trench is the mobile water moving down the hillslope toward the stream, whereas soil water has been typically collected from small, isolated pans at a mid-point depth in the soil profile. Despite this difference, the chemical composition of subsurface flow from the trench was generally similar to that of soil water collected in lysimeters at PMRW (Hooper *et al.*, 1998).

The smaller proportion of hillslope runoff in stream water during the 6–7 March storm than the 2 February storm provides a basis for comparison with previously reported results from a nearby hillslope at the site.

Peters and Ratcliffe (1998) found greater penetration of rainfall to depth by preferential flow in hillslope soils during dry summer antecedent than wet winter antecedent conditions. Additionally, laboratory experiments with soil cores indicated that preferential flow should not have been present in hillslope soils at rainfall intensities typical of the highest 15 min values reached during the two winter 1996 storms (McIntosh *et al.*, 1999). Despite evidence of significant preferential flow to depth in a hillslope soil, Peters and Ratcliffe (1998) suggested that flow through the hillslope was too slow to contribute significantly to stream water during individual rainstorms except in areas immediately adjacent to stream channels. The present study observed a small but significant contribution from the hillslope soil to the stream during both winter storms; this contribution was greater during wet winter antecedent than dry winter antecedent conditions. The presence of saturated flow at the hillslope trench prior to the 2 February storm apparently enhanced the delivery of hillslope water to the stream by providing a continuously connected saturated zone that was not present during the dry winter conditions prior to the 6–7 March storm.

Two additional factors may have affected the delivery of hillslope waters to the stream during the winter rainstorms of 1996: (1) rainfall intensity and (2) the presence of surface saturation. Preferential flow in soils generally increases with rainfall intensity (Bouma, 1981; Trudgill *et al.*, 1983); thus, if preferential flow played a significant role in the hydrologic response of the hillslope soils, the high-intensity 6–7 March storm would be expected to produce a greater contribution to stream runoff than the low-intensity 2 February storm. Just the opposite response was measured, however; and the hillslope runoff was found to contain almost no 'event' water during the 2 February storm (Burns *et al.*, 1998). Surface saturation and delivery of water to the stream from the hillslope as overland flow from hollows was observed, but not quantified during either storm. Chemical analysis of samples of this overland flow, indicated a chemical composition similar to that of subsurface stormflow from the trench (D.A. Burns, unpublished data). Rainfall intensity probably did not affect the delivery of hillslope runoff to the stream; instead, the antecedent conditions assumed greater importance.

Relations of hydrologic measurements to runoff components

The measurements of rainfall intensity, subsurface stormflow in the trench, and riparian water table levels were sometimes consistent with the contribution of modelled runoff components to stream runoff, and in other instances disagreement existed. For example, predicted outcrop runoff followed a pattern similar to that of measured rainfall intensity with expected lags on the ascending and descending hydrograph limbs, and was strongly correlated with rainfall intensity. In contrast, only a weak relation was apparent between stormflow measured at the trench and predicted hillslope runoff during the 6–7 March storm, despite a strong relation during the 2 February storm. The hillslope trench was about halfway up the hillslope; thus, the runoff pattern there may be expected to differ from that at the base of the hillslope near the stream, especially under dry winter antecedent conditions. Additionally, some of the subsurface stormflow that moved downslope probably provided recharge to the riparian aquifer and did not contribute directly to stream runoff during the storms. The difference between flow measured at the trench (and projected over the entire hillslope area), and the predicted hillslope contribution to stream runoff was equivalent to 13 mm, or a volume of about 760 m³. A net increase of only 3% in the amount of water-filled pore space in hillslope soils alone could account for this discrepancy. Therefore, storage in hillslope soils and recharge to the riparian aquifer from the hillslope are plausible explanations for the discrepancy between the observed flow response at the hillslope trench and the predicted hillslope-runoff contribution to stream runoff during the 6–7 March storm.

The weakest relation between hydrologic measurements and predicted end-member response was in the riparian component. Some similarity between the patterns of predicted riparian groundwater runoff and measured riparian water table levels was apparent, but decreases in predicted riparian runoff near the time of peak stream runoff on 2 February and 7 March are inconsistent with changes in water table levels. These declines coincided with peak outcrop runoff and, therefore, were probably concurrent with the transit of a large volume of water from the outcrop through the riparian aquifer, which should not be accompanied by declines

in the riparian water table. In general, the riparian aquifer serves as a dynamic reservoir in which outcrop runoff and hillslope subsurface stormflow can mix during transport to the stream. Therefore, the measured hydrologic response of the riparian area is likely to differ from the predicted contribution of riparian runoff to stream water to a greater extent than would be expected for the other two runoff components.

SUMMARY AND CONCLUSIONS

The EMMA modelling approach used in this study is an improvement over many past modelling efforts because of its basis on the collection of spatially integrated and temporally detailed samples of mobile waters believed to represent source areas of the catchment that contribute waters with unique chemical signatures to the stream. The success of this modelling approach is reflected in the goodness-of-fit ($r^2 = 0.95\text{--}0.99$) between actual and predicted concentrations of the five stream solutes that are represented in the model.

Runoff from an outcrop, which occupies about a third of the 10 ha catchment, dominated stream runoff during peak flow conditions during two rainstorms in the winter of 1996. This result differs from those reported in most other mixing model studies in small forested catchments, in which 'old' water or groundwater dominates peak flow. Even on a whole-storm basis, in which the stream recession was included, outcrop runoff was the dominant source of stream runoff during the 6–7 March storm (preceded by dry winter antecedent conditions), and was the second largest source of stream runoff after riparian groundwater runoff during the 2 February storm (preceded by wet winter antecedent conditions). In contrast, hillslope runoff was a minor but significant component of stream runoff at peak flow and on a whole-storm basis.

Riparian groundwater runoff dominated stream runoff on the ascending and receding limbs of the stream hydrograph during both storms, and was the largest runoff component on a whole-storm basis during the 2 February storm. The results of this study indicate that part of the outcrop runoff and hillslope runoff transit through the riparian subsurface prior to entering the stream during storms. The EMMA modelling results support conservative mixing of runoff components within the riparian area during the two storms that were sampled. This result suggests that the apparent resetting of chemical signatures observed in other hillslope–riparian studies (Robson *et al.*, 1992; Hill, 1993) may result simply from the mixing of a small volume of water from upslope with a larger volume of riparian storage during transit. Additionally, and especially during the 6–7 March rainstorm, two independent methods indicated that riparian groundwater received significant recharge from the outcrop. The mixing and geochemical interaction of these waters from the outcrop and the hillslope with riparian groundwater merits additional study at this site. Our results indicate that the effect of the riparian zone in stream hydrochemistry will vary, depending on antecedent water table levels and, therefore, the antecedent moisture conditions throughout the catchment. The relative storage volumes of the hillslope and riparian area also affect the mixing dynamics—we are currently investigating this hypothesis at PMRW and other catchments.

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