

## **Riparian control of stream-water chemistry: implications for hydrochemical basin models**

**RICHARD P. HOOPER, BRENT T. AULENBACH**

*US Geological Survey, 3039 Amwiler Road, Suite 130, Atlanta, Georgia 30360, USA*

**DOUGLAS A. BURNS, JEFFREY McDONNELL,  
JAMES FREER**

*State University of New York, College of Environmental Science and Forestry, Syracuse, New York 13210, USA*

**CAROL KENDALL**

*US Geological Survey, 345 Middlefield Road, MS 434, Menlo Park, California 94025, USA*

**KEITH BEVEN**

*CRESS, University of Lancaster, Lancaster LA1 4YQ, UK*

**Abstract** End-member mixing analysis has been used to determine the hydrological structure for basin hydrochemical models at several catchments. Implicit in this use is the assumption that controlling end members have been identified, and that these end members represent distinct landscape locations. At the Panola Mountain Research Watershed, the choice of *controlling end members* was supported when a large change in the calcium and sulphate concentration of one of the end members was reflected in the stream water. More extensive sampling of groundwater and soil water indicated, however, that the geographic extent of the contributing end members was limited to the riparian zone. Hillslope solutions were chemically distinct from the riparian solutions and did not appear to make a large contribution to streamflow. The dominant control of the riparian zone on stream-water chemistry suggests that hydrological flow paths cannot be inferred from stream-water chemical dynamics.

## **INTRODUCTION**

Determining the structure of hydrochemical models for headwater basins has been generally subjective. The complexity of the structure reflects the features of the landscape believed by their authors to be important for determining stream-water chemistry and for predicting the response of the basin to different stressors. In the area of acid deposition, hydrochemical models have ranged from one-reservoir models (Cosby *et al.*, 1985), and two-reservoir models (Christophersen *et al.*, 1982) to multi-reservoir distributed models (Gherini *et al.*, 1985).

A more objective approach to determining the structure was promised by end-member mixing analysis (EMMA), in which variation in stream-water chemistry was explained by a mixture of soil-water and groundwater end members (Christophersen & Hooper, 1992). End members were assumed to be derived from soil environments that controlled stream-water chemistry. The chemical and physical characteristics of these environments, such as their depth, cation exchange capacity, and weathering rates were either measured directly or inferred from model calibration. Furthermore,

the number of end members identified by EMMA was used to determine the number of reservoirs used in a hydrochemical model, and the mixing proportions were used to determine the hydrological routing parameters (Hooper & Christophersen, 1992).

The objective of this paper is to test the structure determined from EMMA as used by Hooper & Christophersen (1992). The geographic extent of the end-member areas were tested by more extensive soil-water and groundwater sample collection. Temporal patterns in end-member concentrations were also observed, thereby enabling a further test of the end-member concept at PMRW.

## BACKGROUND

### Site description

The Panola Mountain Research Watershed, a 41-ha basin, is located in the Piedmont physiographic province, approximately 25 km southeast of Atlanta, Georgia, USA (Fig. 1). The basin is underlain primarily by granodiorite emplaced about 320 Ma in a host rock of biotite-plagioclase gneiss that contains amphibolite and K-feldspar (Higgins *et al.*, 1988). There is a 3-ha granodiorite outcrop in the headland

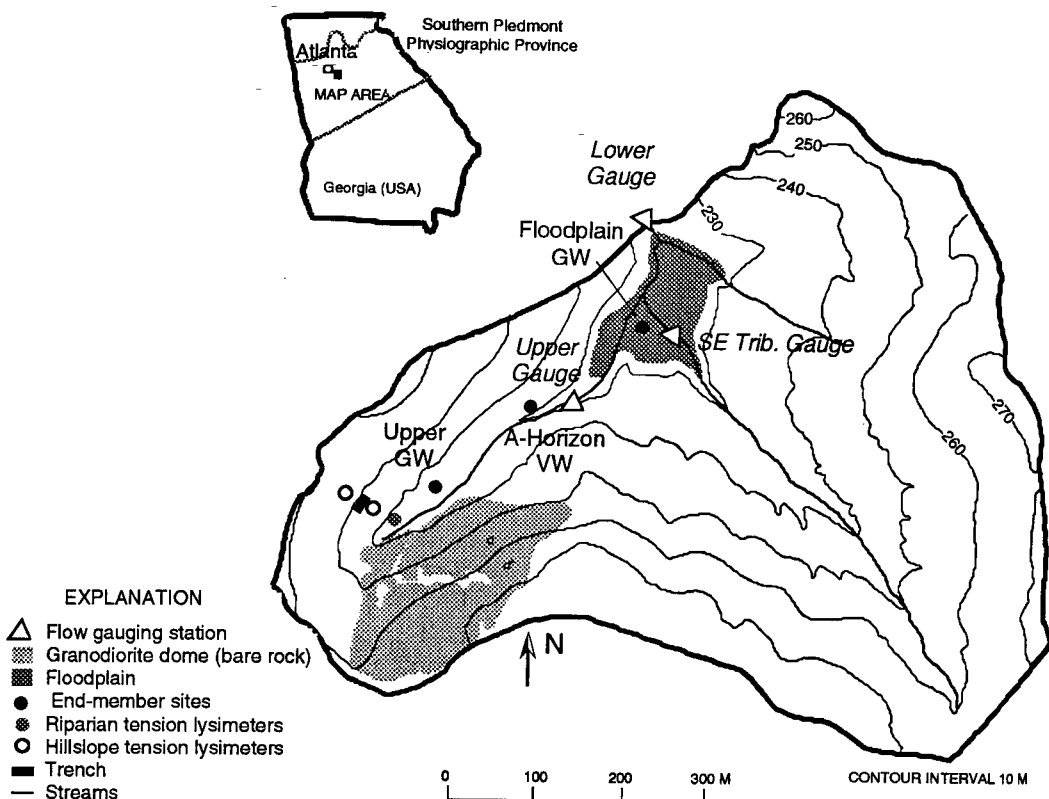


Fig. 1 Map of Panola Mountain Research Watershed indicating location of streamflow gauges, wells, lysimeters, and hillslope trench.

catchment. Soils at PMRW are classified as entisols near the base of the outcrop and as ultisols on hillslopes and ridgetops. Soils have developed to a thickness of 1–2 m, and saprolite underlies the soils to a depth of 0–5 m below land surface. The basin, with the exception of the outcrop, is completely forested with mixed southern hardwoods covering 70% of the forested area, and pine covering the remainder. The climate in the area is classified as warm temperate subtropical, with an annual average temperature of 16°C (Hodler & Schretter, 1986). The long-term annual average precipitation in the area is 1.24 m; annual average runoff is 30% of precipitation (Carter & Stiles, 1983), but this percentage varies widely from year to year as a function of both rainfall amount and timing. The stream at the catchment outlet (the lower gauge) and at the southeastern tributary streamflow gauge is perennial; flow at the upper gauge on the southwest tributary is ephemeral, with sustained flows between storms occurring only in the winter.

### End members identified at PMRW

Hooper *et al.* (1990) found that three end members could explain variations in stream-water chemistry: groundwater collected in the flood plain (“flood-plain groundwater”); groundwater collected at the base of the hillslope in the upper portion of the watershed (“upper groundwater”); and zero-tension soil water collected 10 cm below land surface (“A-horizon”). Site locations for the end members are shown in Fig. 1. Mixing of these solutions could explain between 82% and 97% of the variation in the stream-water chemistry for six solutes (Ca, Mg, Na, SO<sub>4</sub>, SiO<sub>2</sub>, and acid neutralizing capacity (ANC)).

The hydrograph separation using the end members indicated that the flood plain supplied most of the flow during the drier summer and autumn periods, and the upper groundwater was the dominant contributor to streamflow during the wetter winter and spring. The A-horizon contributed flow only during storms, generally a small volume except in intensive summer thunderstorms with dry antecedent conditions. In the terminology of Sklash *et al.* (1976), this is a “geographic-source” hydrograph separation, unlike the more common “temporal-source” separation which distinguishes new water (that is, water from this storm) from old water (water present in the catchment prior to the storm).

In applying this geographic-source separation to determine the hydrological structure used in a long-term acidification model, Hooper & Christophersen (1992) assumed that the A-horizon vadose water was found throughout the basin (excluding the outcrop), that the flood-plain groundwater was found only in the 2-ha flood plain, and that the upper groundwater was found in the 36-ha of the basin outside the flood plain. Routing through these reservoirs was determined by determining the proportion that each end member contributed to the annual average stream-water chemistry.

### STUDY DESIGN AND METHODS

The analysis performed by Hooper *et al.* (1990) only included data collected from

water year (WY) 1986 through WY88. (The USGS defines water years from 1 October to 30 September. WY88 began 1 October 1987 and ended 30 September 1988.) Continued monitoring of the A-horizon end member indicated that sulphate concentrations declined markedly between 1988 and 1990 (Fig. 2). By 1991, the sulphate concentration had reached about one-half the pre-1989 concentration, and the downward trend in concentration continued at a slower rate. Calcium concentration also declined to approximately one-half of the pre-1989 concentration. Other solutes diluted slightly, but sulphate and calcium were the two most strongly affected.

This change in concentration of one of the controlling end members provides the strongest test to date of the mixing model concept—would the stream water reflect this large change in concentration? Because the A-horizon end member contributes to streamflow significantly only during storms, the largest change in stream-water chemistry should be exhibited in the storm samples. Unfortunately, storm sampling at the lower gauge had been suspended in WY89; sampling was resumed in WY94.

Other data collected since WY88 also provide further testing of the geographic extent of the end members. Several nests of tension lysimeters were installed in 1991 and sampled monthly for approximately 2 years. Two nests were located on the hillslope opposite the outcrop and a third in the riparian zone (Fig. 1). Samples from these lysimeters provided the first extensive soil-water and groundwater data outside the riparian zone. For the geographic-source hydrograph separation to be supported, the shallow lysimeters should have a similar chemistry to the A-horizon end member, and the deep lysimeters should have a similar chemistry to the upper groundwater end member. To support the discrete three-component separation, the transition between the shallow and deep chemistry should be abrupt.

As part of a larger study of hillslope hydrology (McDonnell *et al.*, 1996), a 20-m long trench was excavated to bedrock in 1995 to isolate a hillslope segment just above the lower of the two hillslope lysimeter nests, approximately 50 m upslope of

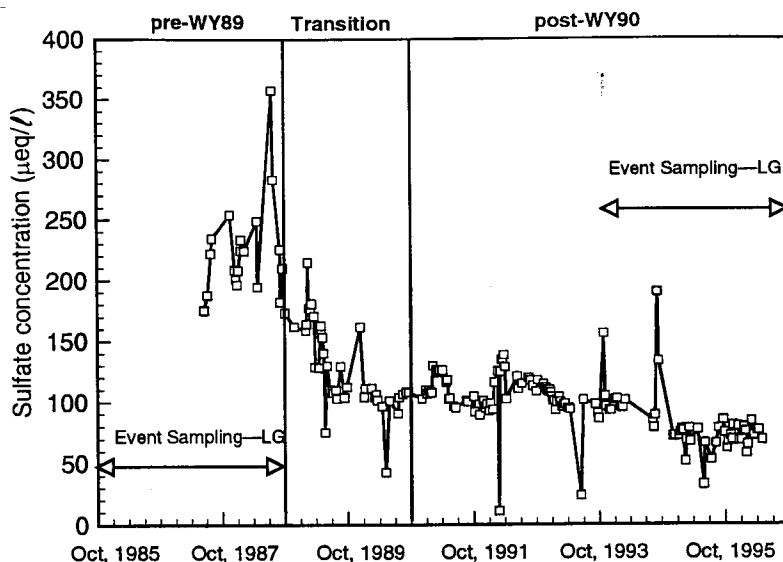


Fig. 2 Time series of sulphate concentration for the A-horizon end member.

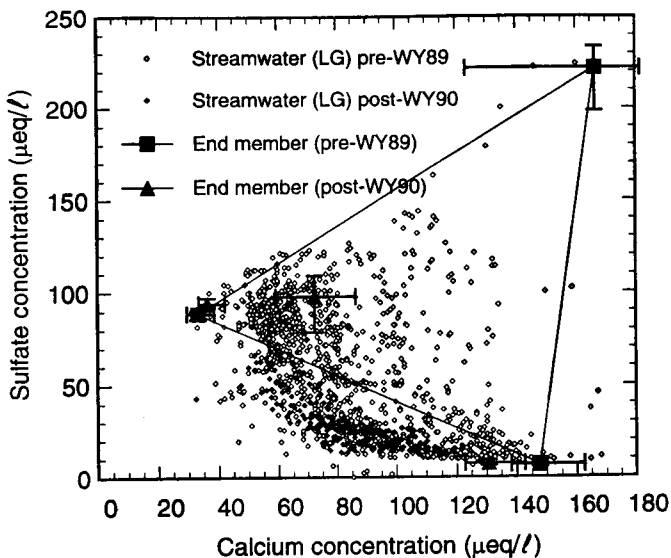
the stream (Fig. 1). The trench face was divided into 2-m segments, and water samples were collected during storms in the winter and spring of 1996. These samples are the first observation of water at PMRW from the saturated zone during storms. The chemistry of these samples was hypothesized to be similar to the upper groundwater end member.

To determine the influence of the granodiorite outcrop on stream-water chemistry at the catchment outlet, a streamflow-gauging station was established on the southeastern tributary, which drains a basin with no extensive bare-rock outcrops. Weekly and storm-based sampling was conducted at this site during WY93 and WY94; weekly sampling continued through WY96.

Chemical analyses were performed at the USGS laboratories in Atlanta, Georgia. Anions were measured using ion chromatography, and ANC determined using Gran titration for all samples. Prior to 1992, cations were measured using ion chromatography, and silica using automated colorimetric methods. Since May 1992, directly coupled plasma spectroscopy (DCP) has been used for both cations and silica. Chemical concentrations for all samples considered in this paper are well above detection limits for the methods employed; values have a precision between 5% and 10% of the reported concentration.

## RESULTS

The stream-water chemistry showed a marked change between the pre-WY89 and post-WY90 periods (Fig. 3), consistent with the change in the A-horizon end member. The upper groundwater end member does not describe the stream-water variation after WY90 very well (a lower sulphate concentration is needed); however, this lack-of-fit is now more obvious than it was in the pre-WY89 data because of the



**Fig. 3** Mixing diagram for calcium and sulphate, indicating relation between stream-water samples and hypothesized end members during two distinct periods.

lower variability of the stream-water concentration. The variation between the upper and flood-plain groundwater end members is similar between the two periods. This finding supports the hypothesis that mixing of end members controls the stream-water chemical variation.

When the same solutes are considered for the other soil-water and groundwater solutions, it is evident that the geographic-source interpretation of the end members is not supported. Samples from the shallow tension lysimeters have much higher concentrations than the post-WY90 A-horizon end member (Fig. 4). This difference may be dismissed because these tension waters are qualitatively different than the zero-tension water sampled for the end member. However, the three deepest hillslope lysimeters are still much higher in concentration than either the A-horizon or the upper-groundwater end members. There also is a large difference between the hillslope tension lysimeters and the riparian zone ones. The deeper riparian tension lysimeters have a chemistry more similar to the upper-groundwater end member. The 120-cm deep lysimeter, in fact, would be a better end member than the upper-groundwater solution.

The zero-tension trench face samples are similar in concentration to the deeper hillslope tension lysimeter samples (Fig. 4). This finding suggests that the samples from the tension lysimeters are representative of the hillslope saturated zone chemistry. Nonetheless, the trench face samples are chemically distinct from both the

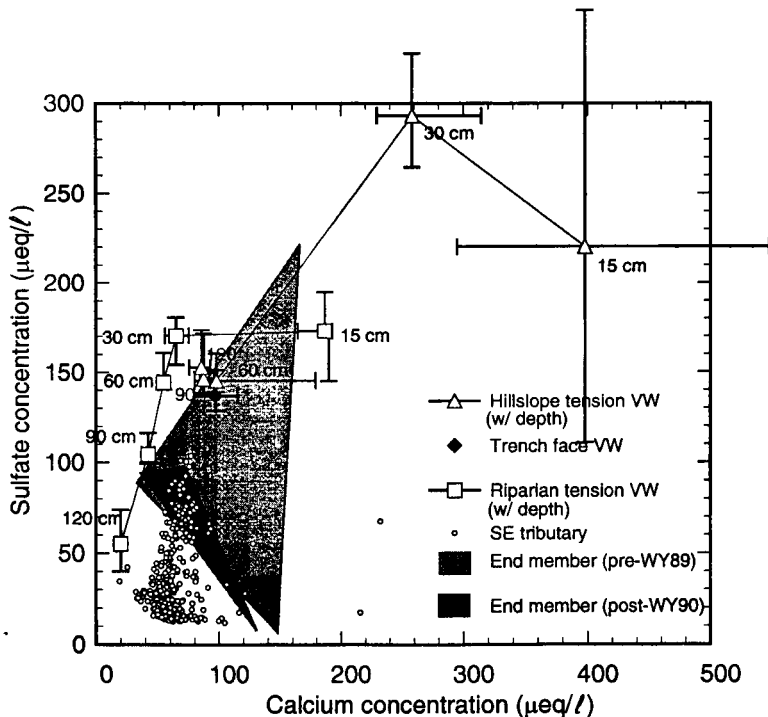


Fig. 4 Mixing diagram for calcium and sulphate contrasting lysimeter solutions, trench face samples, and stream-water samples from the southeastern tributary with hypothesized end members.

A-horizon end member and the upper-groundwater end member. The dominant cation and anion for the trench face samples were calcium and sulphate, respectively; the stream water is a sodium-bicarbonate water. This chemical difference exists despite the proximity of the trench to the stream.

Also shown in Fig. 4 are samples from the southeastern tributary. Overall, their chemistry is similar to those from the lower gauge. In particular, the same low concentrations of calcium and sulphate are evident. Thus, the dilution observed during events is not solely a function of the granite outcrop along the southwestern tributary.

## CONCLUSIONS

Although the change in stream-water concentration supported the mixing-model hypothesis, the large difference between hillslope and riparian zone solutions indicates that the geographic-source interpretation of the end members is incorrect. The hydrological structure of a hydrochemical model of PMRW must include hillslope reservoirs because the end members are representative of only the riparian zone and not the entire basin, as assumed by Hooper & Christophersen (1992). However, the linkage between the hillslope and riparian zone is not well understood. Either there are chemical reactions occurring at the hillslope/riparian zone interface or the hillslope groundwater is a volumetrically insignificant contributor to streamflow during storms. Other data collected at PMRW support the latter hypothesis because the hillslope contribution may lag the main stream response to storms (Peters *et al.*, 1998).

Whatever the explanation for the difference between hillslope and riparian zone chemistry, it is evident from these data that hydrological flow paths cannot be discerned from stream-water chemistry. The chemical signature of the hillslope, the largest landform of the basin, is not apparent in the stream. This finding calls into question the use of stream-water chemical dynamics to calibrate predictive hydrochemical models because those dynamics provide no indication of the chemical processes occurring outside the riparian zone. At PMRW, streamflow chemical dynamics largely reflect the relative contribution of different parts of the riparian area.

The applicability of these findings to other catchments is unknown at this time. We hypothesize that the volume of alluvial aquifer relative to streamflow is the most important factor because the alluvial aquifer provides physical storage for the storm runoff from the hillslope. During the interstorm period, chemical reactions may proceed which account for the chemical difference between the hillslope and riparian zones. Further instrumentation of the hillslope/riparian interface to quantify water fluxes and chemical differences is needed to determine the controlling physical and chemical processes.

## REFERENCES

- Carter, R. F. & Stiles, H. R. (1983) Average annual rainfall and runoff in Georgia, 1941–70. *Hydrol. Atlas 9*. Georgia Geol. Surv., Atlanta, Georgia, USA.
- Christophersen, N. & Hooper, R. P. (1992) Multivariate analysis of streamwater chemical data: the use of principal

- components analysis for the end-member mixing problem. *Wat. Resour. Res.* **28**, 99–107.
- Christophersen, N., Seip, H. M. & Wright, R. F. (1982) A model for streamwater chemistry at Birkenes, Norway. *Wat. Resour. Res.* **18**, 977–996.
- Cosby, B. J., Hornberger, G. M., Galloway, J. N. & Wright, R. F. (1985) Modeling the effect of acid deposition: assessment of a lumped parameter model of soil water and streamwater chemistry. *Wat. Resour. Res.* **21**, 51–63.
- Gherini, S., Mok, L., Hudson, R. J. M., Davis, G. F., Chen, C. & Goldstein, F. (1985) The ILWAS model: formulation and application. *Wat., Air and Soil Pollut.* **26**, 95–113.
- Higgins, M. W., Atkins, R. L., Crawford, T. J., Crawford, R. F., Brooks, R. & Cook, R. (1988) The structure, stratigraphy, tectonostatigraphy, and evolution of southernmost part of the Appalachian region. *USGS Prof. Pap.* **1475**, Reston, Virginia, USA.
- Hodler, T. W. & Schretter, H. A. (1986) *The Atlas of Georgia*. Univ. of Georgia Press, Athens, Georgia, USA.
- Hooper, R. P. & Christophersen, N. (1992) Predicting stream acidification in the southeastern United States: combining a long-term acidification model and the end-member mixing concept. *Wat. Resour. Res.* **28**, 1983–1990.
- McDonnell, J. J., Freer, J., Hooper, R. P., Kendall, C., Burns, D. A., Beven, K. J. & Peters, N. (1996) New method developed for studying flow on hillslopes. *EOS—Trans. AGU* **77**, 465.
- Peters, N. E., Ratcliffe, E. R., & Tranter, M. (1998) Tracing solute mobility at the Panola Mountain Research Watershed, Georgia, USA. In: *Hydrology, Water Resources and Ecology in Headwaters* (ed. by K. Kovar, U. Tappeiner, N. E. Peters & R. G. Craig) (Proc. HeadWater'98 Conf., Meran/Merano, April 1998). IAHS Publ. no. 248 (this volume).
- Sklash, M. G., Farvolden, R. N. & Fritz, P. (1976) A conceptual model of watershed response to rainfall, developed through the use of oxygen-18 as a natural tracer. *Can. J. Earth Sci.* **13**, 271–283.