

Regional Scale Transport in a Karst Aquifer

1. Component Separation of Spring Flow Hydrographs

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Large fluctuations in Ca and Mg concentrations occur in the discharge of karst springs in southeastern Missouri after major storm events. Rapid flow of relatively dilute, storm-derived water through solution conduits in the aquifer causes the fluctuations in chemistry. A cation balance for the discharge of one spring indicates that about 25% of the total spring flow is storm-derived water. These storm-derived contributions reach a maximum during the recession of storm responses in the spring flow hydrograph. At the peak of the responses, spring flow is composed primarily of prestorm water that has been displaced in the conduit system by the storm-derived water. The observed chemical fluctuations and hydrograph components differ from those observed in streamflow where the time of the maximum dilution usually coincides with the time of peak discharge.

INTRODUCTION

Water moves at highly variable rates through karst aquifers, rapidly through solution-enlarged fractures and conduits and more slowly through fine fractures and pores. The degree to which conduits exist and influence flow in a karst aquifer is the basis for a widely used conceptual method for classifying karst aquifers as either diffuse- or conduit-type aquifers [Shuster and White, 1971]. In conduit-type aquifers, solution features function as large-aperture, low-tortuosity pathways that greatly influence rates and directions of groundwater flow. The interaction and relative flow rates of water in conduits and secondary porosity lead to complex groundwater flow behavior. During times of rapid groundwater recharge, pressure heads increase in the conduits, and water flows rapidly through the conduits and enters adjacent pores and fractures. As pressure heads lower in the conduits, water migrates from the fine fractures and pores into the solution conduits. Under these circumstances, drainage from the pores and fractures controls flow rates in the conduits and at spring outlets.

In many regions with well-developed karst features, large springs act as outlets or drains for regional groundwater movement. Consequently, the rate and chemical composition of spring discharge reflect basin scale fluid and solute transport into and through the aquifer. Under natural conditions, the water discharging at a spring outlet is a combination of water draining from the secondary porosity and relatively dilute, storm-derived water associated with recent rainfall events. This paper describes chemical fluctuations in the discharge of three large karst springs in southeastern Missouri. The chemical history from one of the springs is then used to compute the storm-derived component of the spring discharge. This discharge component is a time series that represents the arrival of rapidly introduced and transported infiltration at the spring outlet. In a companion paper [Dreiss, this issue] a method is presented for describing regional scale transport in the karst conduit network by treating this component as the

output response of the aquifer to a series of naturally occurring, regional scale tracer events.

PREVIOUS RELATED WORK

Water chemistry and tracing methods are widely used for studying karst aquifers. Applications of these methods have, in general, focused on estimation of flow rates between two points in an aquifer or on regional descriptions of groundwater movement. Field work to locate points of recharge and discharge combined with extensive tracing studies has been used by numerous researchers to estimate the recharge areas of springs, rates of groundwater movement, and the water balance of aquifers [e.g., Atkinson *et al.*, 1973, Brown *et al.*, 1969]. Modern tracer methods using continuous or frequently collected samples give considerable information about the transport of dye between points and the areal extent of spring recharge areas [e.g., Mull and Smoot, 1986; Smoot *et al.*, 1987]. Although familiar physically based models for flow through porous media are generally infeasible for karst aquifers, conceptual models of flow in single or multiple conduit systems are useful for interpreting results from these tracer tests [e.g., Aston, 1966; Smart and Ford, 1986]

Shuster and White [1971, 1972] and Ternan [1972] demonstrated the existence of rapid and slow karst groundwater components with different chemical compositions on the basis of variations in hardness, Ca/Mg ratios, Ca and Mg saturation indices, and temperature. Hanshaw and Back [1974], Back *et al.* [1979], Wigley [1975], Scanton and Thrailkill [1987], and others have used temporal and spatial measurements of these parameters, as well as ^{14}C data, to describe sources and rates of groundwater movement and to compare spring flow characteristics in different regions. These studies have generally used data collected at biweekly or monthly intervals.

Although few detailed long-term data records are available of both spring discharge and chemistry, numerous studies have measured short-term fluctuations in spring flow composition. These studies have usually focused on isolated high-discharge events or on detection of tracer concentrations. Rapid transport of contaminants and tracers to conduit-type springs, from point and nonpoint sources on the ground sur-

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face, has been observed in many locations [e.g., *Quinlan and Alexander, 1987; Hallberg et al., 1985; Steele et al., 1985; Vandike, 1982*]. In addition, several investigations have reported fluctuations of ^{18}O and specific conductance in karst spring flow after large storm events [e.g., *Hess and White, 1974; Bakalowicz and Mangin, 1980*]. The timing and complexities of both tracer test results and naturally occurring chemical fluctuations vary greatly between springs in different regions.

Hull [1980] and *Hallberg et al. [1983]* computed hydrograph components in isolated spring flow storm responses using ^{18}O and NO_3 , respectively. *Hull* estimated prestorm and precipitation-derived components in stream and spring storm responses in the central Pennsylvanian karst. Even though the specific conductivity of the spring flow decreased during the recession of the hydrograph, a distinct change in ^{18}O contents was not observed. Using the ^{18}O data and a mass balance similar to the one performed here, *Hull* concluded that the peak response of the spring flow was almost entirely prestorm water and that the amount of storm-derived water throughout the storm response was small.

Hallberg et al. [1983] monitored discharge and NO_3 concentrations during several large storm responses at a karst spring in northeastern Iowa. They used two approaches for hydrograph separation: (1) analytical methods similar to those used to remove baseflow in stream flood hydrographs and (2) a component mixing model for NO_3 concentrations. *Hallberg et al.* observed a 12-to-14-hour lag time between peak spring discharge and the associated lowest NO_3 level. After shifting the NO_3 values to coincide with peak discharge for the component separation calculation, they noted that the adjusted NO_3 separation was in close agreement with the analytical separation.

Thus although chemical fluctuations have been measured in conduit-type springs in a number of karst aquifers, the fluctuations have rarely been described in detail for periods longer than the duration of isolated storm responses in the spring flow hydrograph. In addition, even though several studies have been made of spring flow hydrograph components, the magnitude and timing of the component contributions during storm responses remain poorly understood.

FIELD INVESTIGATION

In general, the lag time between a large storm and the initial response of a spring flow hydrograph is short, within 1–2 days of a storm event [e.g., *Dreiss, 1982*]. However, the memory of the response may be relatively long, with spring discharge and chemical concentrations requiring a month or more to return to prestorm levels. Most studies of spring flow chemistry either monitor the springs at biweekly or monthly intervals, or examine short-term responses to single storms or tracer events. These studies either do not accurately detect the initial response of spring flow chemistry or they sample over a time period that is too short to describe the long-term memory of the system.

The goal of the field investigation was to collect samples at intervals that were short enough to accurately measure the initial response of the spring flow chemistry to individual rainfall events. On the other hand, samples had to be collected over a sufficient length of time to record the long-term memory of the system. Thus the field study entailed exceptionally frequent, long-term measurements of spring discharge and composition. In addition, precipitation was measured and

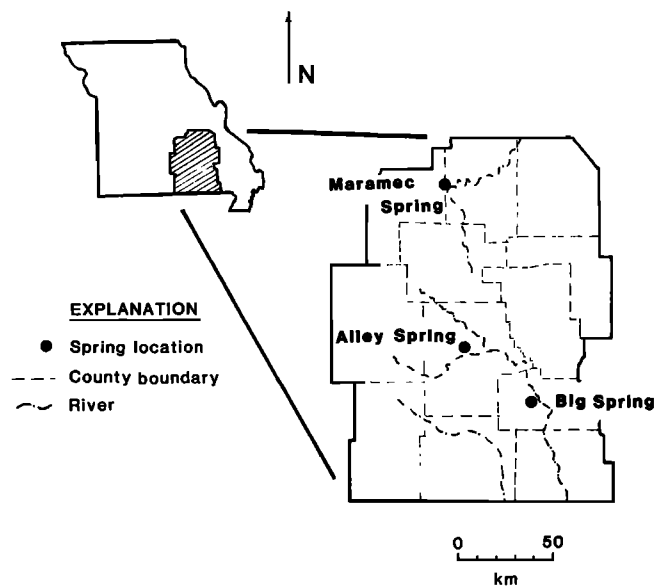


Fig. 1. Location map of monitored springs in southeastern Missouri.

used to estimate an excess moisture series that contributed recharge to the aquifer and springs.

Monitoring focused on major ion (Ca , Mg , HCO_3) concentrations. Most previous studies of hydrograph separation of either streamflow [e.g., *Sklash and Farvolden, 1979*] or spring flow [*Hull, 1980*] have used ^{18}O data. However, preliminary measurements of ^{18}O concentrations in precipitation and spring flow in the study area indicated that the ^{18}O concentrations in precipitation during individual storms were highly variable. This variability was greater than either seasonal trends in composition or the difference between precipitation and springflow concentrations. Thus isotope contents could not be used for hydrograph separation and emphasis was placed on major cation concentrations.

Spring Descriptions

Field measurements were made at three large springs located in central and southeastern Missouri (Figure 1). Big and Alley Springs are both in the Mark Twain National Forest in southeastern Missouri. Maramec Spring is in central Missouri approximately 115 km northwest of Big Spring. The regional climate is temperate and humid with an average annual rainfall of 1120 mm, distributed uniformly throughout the year. Snowfall occurs in only trace amounts. The region is underlain by 30–900 m of Ordovician and Cambrian strata, primarily dolomites, which have a regional dip to the south of less than 1%. The area exhibits classic karst features: (1) 1–10 m of red clay and chert residuum overlying the dolomitic bedrock, (2) numerous sinkholes in the uplands, and (3) swallow holes and losing reaches along stream channels.

Groundwater circulation to all three springs crosses beneath major surface drainage divides [*Aley, 1975; Dreiss, 1983*]. Both Big and Alley Springs occur in the Eminence Formation, a dolomitic aquifer with variable well yields between 6×10^{-4} and 1.3×10^{-2} m^3/s (10–200 gpm). Big Spring is the largest spring in the Ozark region, with an average flow rate of 12 m^3/s and an estimated maximum flow rate of 57 m^3/s . The recharge area to Big Spring is about 1500

km², and tracing studies indicate that water travels to the spring from distances as great as 65 km in less than 16 days [Aley, 1975]. Alley Spring is smaller than Big Spring with an average flow rate of 3.5 m³/s, a maximum measured discharge of about 30 m³/s, and an estimated recharge area of 1000 km². Divers have mapped a tubular channel at Alley Spring that extends about 45 m into the aquifer to a depth of about 30 m [Vineyard and Feder, 1982]. They have been unable to explore Big Spring because of strong current at the outlet.

Maramec Spring, with an average discharge of 4 m/s, is the third largest spring in Missouri. It exits from the Gasconade Dolomite, an aquifer with well yields similar to those in the Eminence Formation. The estimated recharge area of Maramec Spring is approximately 990 km². Divers have mapped a conduit extending 518 m from the spring outlet to a depth of 59 m. In a recent tracer study, Vandike [1982] observed that Rhodamine dye introduced in a nearby losing stream traveled 21 km to the spring in 11–12 days.

Sampling Methodology

Spring discharge was sampled at Big Spring between May 1984 and March 1985, at Alley Spring from July 1984 through October 1984, and at Maramec Spring from November 1985 to December 1986. The sampling was done automatically every 4 hours or manually at 24-hour intervals. In addition, replicate spring discharge samples and 20 baseline samples were collected in August 1984. Temperature and pH were measured at Maramec Spring every 4 days during site visits and at irregular intervals at Big and Alley Springs. Daily or continuous stage heights were recorded for each spring and converted to discharge using U.S. Geological Survey rating curves. Precipitation data from Climatological Data Service stations [U.S. Department of Commerce, 1986] were supplemented with two additional gages placed near Big Spring during the first year and in the Maramec Spring recharge basin in the second year.

Spring flow samples were retrieved from the automatic sampler every 4 days. To prevent evaporation and degassing during this time, the samples were collected in 500-mL bottles containing approximately 10 mL of Diala AX transformer oil. This oil was tested in the lab and shown to not interfere with the major cation composition of the water samples. After collection, the layer of oil was vacuumed from the top of the water sample, and the sample was divided into two subsamples. A 150-mL sample was immediately titrated for bicarbonate concentration. The remaining sample was filtered and preserved for cation analyses. The cation subsample was acidified with approximately 1 mL of 1 N HCl and refrigerated until the analyses were performed. Cation concentrations were determined with atomic absorption spectrophotometry [U.S. Environmental Protection Agency, 1979].

Data Reduction

Estimates of the total daily precipitation that occurred over the recharge area of each spring were computed from the precipitation measurements. This total daily precipitation series was calculated by weighting measurements from the rain gages with Thiessen polygons constructed over assumed spring recharge areas. I used recharge areas for Big and Alley Springs that were postulated in previous tracer and linear systems studies [Dreiss, 1983]. The recharge area for Maramec Spring was estimated (J. E. Vandike, personal communication,

1986) using tracer and water quality data from Vandike [1982].

For each spring, the amount of daily evapotranspiration loss from the total daily precipitation was computed using the Thornthwaite moisture balance method [Thornthwaite and Mather, 1957]. The remaining moisture, termed excess daily precipitation, refers to the daily total precipitation less the estimated daily evapotranspiration. Computed values of excess precipitation are sensitive to a soil moisture holding capacity parameter (MHC) used in the calculations. In a previous work [Dreiss, 1982] I investigated the effect of MHC values on linear systems models similar to those used in the companion paper [Dreiss, this issue]. For the Big and Alley Spring recharge areas, I found that MHC values between 8.0 and 10.0 cm minimized the error in kernel function identification. In accordance with those results, a MHC value of 10.0 cm was used here in computations for all three springs.

Observations

Figures 2 through 4 show measured spring discharge, excess daily precipitation, and Ca and Mg concentrations for the three springs. In addition, HCO₃ concentrations for Maramec Spring appear in Figure 2.

Although precipitation occurs uniformly throughout the year, no excess precipitation develops between mid-June and September at any of the springs. At all three springs, discharge decreases to a minimum in late August or mid-September. The Ca and Mg concentrations gradually increase in July and August, becoming constant at maximum values in September. Average values of pH, temperature, Ca and Mg concentrations, and Ca/Mg molar ratios are summarized in Table 1. The differences in average Ca and Mg concentrations for the three springs apparently reflects differences in the composition of the aquifers associated with the springs.

The data record for Maramec Spring exhibits large fluctuations in cation and bicarbonate concentrations after major recharge events (Figure 2). Following each storm with significant excess precipitation, spring discharge increases rapidly within 1 day of the storm event, then begins to recede 2–3 days after the storm. During this time, Ca and Mg concentrations initially remain at prestorm levels. About 2–3 days after the storm, cation concentrations begin to decline, reaching a minimum during the recession of the spring flow hydrograph, 5 or more days after the storm. Concentrations then increase gradually, requiring 30 days or more to return to prestorm levels. Throughout the period of measurement, pH, temperature, and Ca/Mg molar ratios remain constant at about 7.1, 12–13°C, and 1.1, respectively.

Measurements at Big and Alley Springs are less complete than those for Maramec Spring because of extremely high rainfall and spring discharge during the 1984/1985 field season. The gaps in cation concentrations for Big Spring in Figure 3 were caused by flooding of the automatic sampler and inaccessibility of the spring outlet during high flows. Moreover, measurements of discharge and cation concentrations are inaccurate during times of peak flow when the spring outlet was inundated by overflow from the nearby Current River. In spite of the data gaps, fluctuations in discharge and cation concentrations that are similar to those observed at Maramec Spring can be seen in the December 1984 through March 1985 portion of the Big Spring record. Spring discharge increases rapidly after major storms, reaching a maximum 1–2 days after large rainfall events. Ca and Mg con-

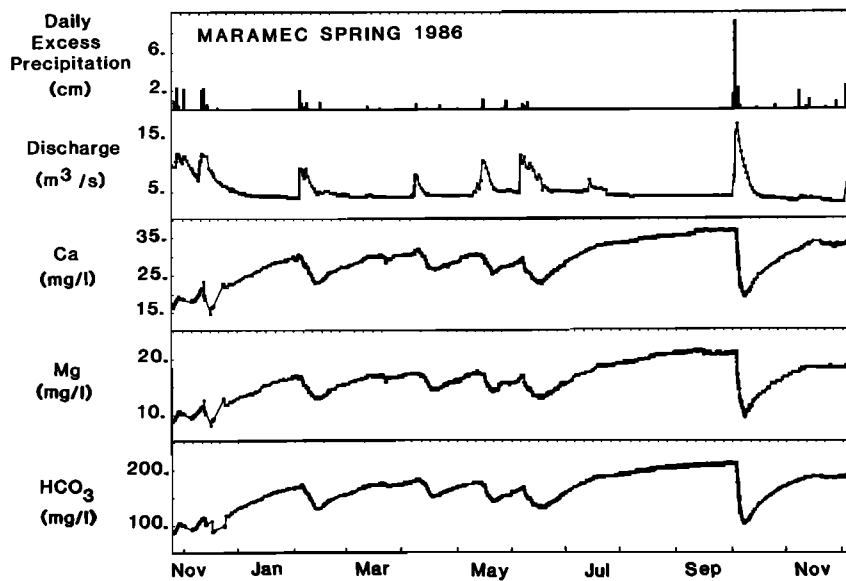


Fig. 2. Measured precipitation, discharge, and Ca, Mg, and HCO_3 concentrations at Maramec Spring between November 1985 and December 1986.

centrations begin to decrease 2–3 days after a storm, with minimum concentrations occurring during the recession of the spring flow hydrograph, about 7–12 days after the storm event.

A decline in cation concentrations can also be seen in the Alley Spring record after a series of storms in October 1984 (Figure 4). Concentrations begin to decrease on October 21 and reach a minimum between October 25 and 27. Unfortunately, the recovery portions of the concentration curves were not recorded.

Discussion

Discharge at all three Missouri springs responds very rapidly to rainfall with a time-to-peak similar to that of river discharge and a recession curve of similar or longer duration. During these flood events, concentrations of dissolved constituents fluctuate, with a rapid decrease and more gradual increase in concentrations after major storm events. These fluctuations represent the arrival of relatively dilute,

precipitation-derived water at the spring outlets. At the three springs, concentrations begin to decline within 1–3 days after a storm event. The delay time to the maximum perturbation in the concentration response varies and appears to be 3–5 days longer for the largest spring, Big Spring, than for Maramec and Alley Springs.

Oscillations in concentrations in Alley Spring discharge, which occur between October 15 and 21, are anomalous when compared to Big and Maramec Spring data. These oscillations may reflect sample collection and preservation errors. On the other hand, similar high-frequency fluctuations have been observed in studies of specific conductance and isotope concentrations during storm response at other springs [Bakalowicz and Mangin, 1980; Hess and White, 1974]. Conceptually, these oscillations can be explained by rapid entry of surface water into the conduit system at points close to the spring outlet. This water would bypass mixing in the regional conduit network. Such bypassing is most likely to occur in small springs with relatively shallow circulation systems, which may

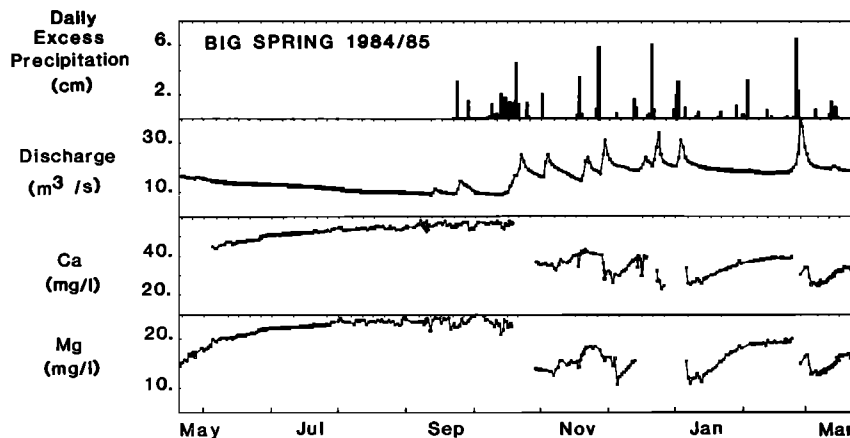


Fig. 3. Measured precipitation, discharge, and Ca and Mg concentrations at Big Spring between May 1984 and March 1985.

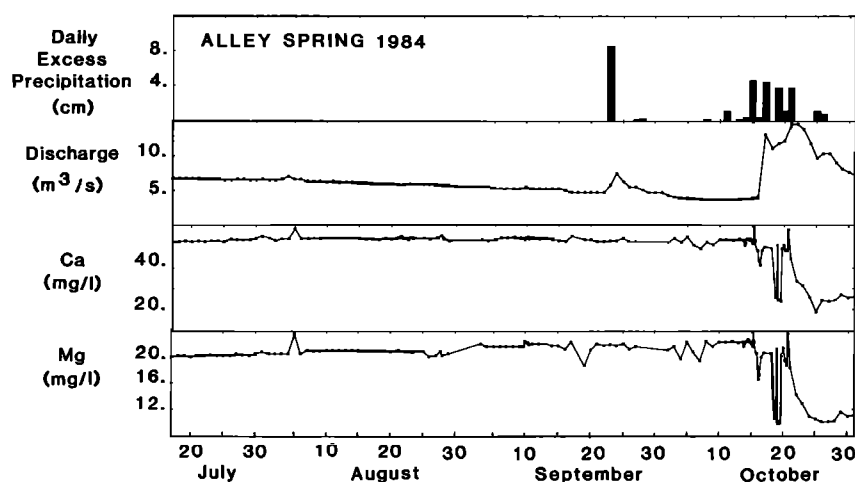


Fig. 4. Measured precipitation, discharge, and Ca and Mg concentrations at Alley Spring between July 1984 and November 1984.

explain the absence of oscillations in the Big and Maramec Spring data.

Although long-term detailed records of both spring discharge and cation concentrations are rare, similar fluctuations in spring flow chemistry have been described for isolated storm events. *Hess and White* [1974], *Hallberg et al.* [1984, 1985], and *Hull* [1980] reported changes in specific conductivity or contaminant concentrations in spring flow after large storms in karst terranes in Kentucky, Iowa, and Pennsylvania, respectively. These studies describe a decrease and subsequent increase in specific conductance or an increase in contaminant concentrations during the recession of the spring flow storm response. The springs generally have lower discharge rates and shorter lag times to the maximum chemical perturbation than the Missouri springs. Nevertheless, the similarity of the observations suggest that fluctuations in spring flow chemistry, which do not coincide with the peak of the spring flow discharge, are widespread in karst terrains with well-developed conduit networks. The magnitude and temporal structure of the fluctuations will vary with the bedrock chemical composition, the size, density, and interconnectedness of the conduits and fractures, the rate and spatial distribution of groundwater recharge, and the degree to which the conduit network occurs beneath a true regional water table.

SPRING FLOW COMPONENT SEPARATION

The amount of storm-derived water in the spring flow can be inferred from spring discharge and cation concentration measurements using a cation mass balance. This approach is similar to that used in stream base flow studies [e.g., *Pinder and Jones*, 1969; *Sklash and Farvolden*, 1979].

Cation Mass Balance

Assuming simple mixing of old, prestorm water, Q_{old} , and new water from recent precipitation, Q_{new} , the total spring discharge, Q_s , is the sum of the two components

$$Q_s = Q_{old} + Q_{new} \quad (1)$$

as shown schematically in Figure 5a. If chemical reactions do not significantly alter cation concentrations, the mass balance

of Ca or Mg in the spring discharge is

$$Q_s C_s = Q_{old} C_{old} + Q_{new} C_{new} \quad (2)$$

where C_s is the measured mass concentration of the cation in the spring discharge, C_{old} is the cation concentration in prestorm water, and C_{new} is the cation concentration in recent storm-derived water as it enters the conduit system. If C_{new} is very small relative to C_s and C_{old} , the mass flux of cations contributed by recent precipitation is small relative to the mass flux from prestorm water

$$Q_{new} C_{new} \ll Q_{old} C_{old} \quad (3)$$

$$Q_{old} \approx (Q_s C_s) / C_{old} \quad (4)$$

Combining (1) and (4),

$$Q_{new} \approx Q_s - (Q_s C_s) / C_{old} \quad (5)$$

Thus if C_{old} is known, the component of the spring discharge that enters the aquifer as rapid recharge to the conduit system after a storm can be estimated from field measurements of Q_s and C_s , the discharge and cation concentrations at the spring outlet.

A number of studies discuss the validity of assumptions that must be made when a cation balance approach is applied to base flow separation of stream flow [e.g., *Sklash and Farvolden*, 1979; *Pilgram et al.*, 1979]. Similar assumptions are made here in the application to karst aquifers. The major assumptions are that (1) the composition of water entering the aquifer C_{new} is distinct from the composition of water in the aquifer before the storm C_{old} ; (2) C_{new} is spatially and temporally uniform; (3) C_{old} is also spatially and temporally uniform; (4) effects from other processes in the hydrologic cycle are negligible, including contributions from surface storage and redistribution in the vadose zone; and (5) concentrations and trans-

TABLE 1. Arithmetic Means of Measurements

Spring	Discharge, m ³ /s	pH	T, °C	Ca, mg/L	Mg, mg/L	Ca/Mg, Molar Ratio
Maramec	5.2	7.1	12.8	28.7	16.0	1.1
Big	16.2	7.3	13.9	42.9	19.0	1.4
Alley	6.3	...	14.4	49.6	20.0	1.5

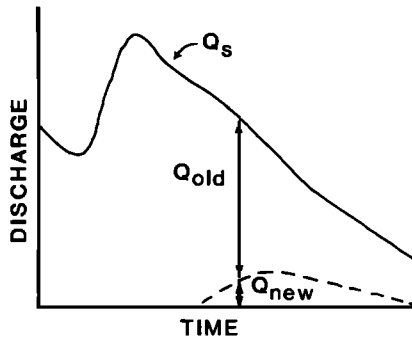
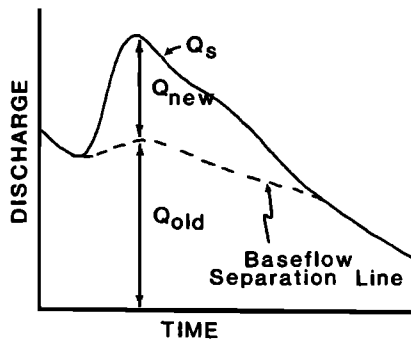
(a) Karst Springflow**(b) Stream Discharge**

Fig. 5. Schematic illustration of Q_s , Q_{new} , and Q_{old} components in (a) a spring flow storm response and (b) a stream discharge storm response.

port of cations are not altered by chemical reactions in the aquifer.

The first two assumptions are often limitations on the usefulness of environmental isotopes for stream base flow separation. However, they pose little difficulty for the use of major cation concentrations in karst spring flow, because the cation concentrations in precipitation are very low relative to those in carbonate groundwaters. The third and fourth assumptions are difficult to assess without further study. The fifth assumption may be of most concern. It requires that the chemical composition of the rapidly infiltrating water not be altered in

the soil zone and that little dissolution occurs in the aquifer as the relatively dilute water moves through the conduit system.

Results and Discussion

Figure 6 shows the total measured discharge at Maramec Spring, Q_s , and the Q_{new} component computed from Ca concentrations. Ca concentrations during the last 2 weeks of September, after 3 months of no excess precipitation, remained constant at approximately 36.9 mg/L. I assumed that this value was representative of pore water composition in the secondary porosity of the aquifer and used it for C_{old} in the hydrograph separation. Thus the computed dilute flow is zero in late September, increasing after winter and spring storms. Because Ca/Mg molar ratios were constant at 1.1 throughout the monitoring period, the Q_{new} series computed with Mg concentrations is similar to the series in Figure 6.

Figures 7 and 8 are more detailed illustrations of Q_{new} and Q_{old} during storm responses at Maramec spring. The October hydrograph is the spring flow response to two large and two smaller, consecutive, rainfall events (Figure 7a). The hydrograph peaks on October 2, after a large storm on the previous day. However, the maximum dilution takes place on October 6, 5 days after the storm event. Figure 7b shows the arrival of the relatively dilute water Q_{new} at the spring. The peak of dilute discharge occurred on October 5 and 6, 4–5 days after the storm event. The initial rise in the discharge hydrograph is composed of prestorm water Q_{old} . This component decreases rapidly as it is displaced by Q_{new} , then increases as the dilute water pulse passes and prestorm water again enters the conduit system from the secondary porosity in the aquifer.

A similar response can be seen, although less clearly, in the February/March record (Figure 8). In this case, a series of storm events occurred between February 3 and March 20. The spring flow hydrograph represents superimposed effects of this series, so the single event response is less apparent. Q_s exhibits two peaks, 2 days apart. The first peak occurs 1 day after a large event on February 3 and the second occurs after an event on February 6. Subsequent, smaller rises can be seen after storms on February 13 and March 11. The dilute discharge component also exhibits two peaks, one 5–6 days after the first large precipitation event, and a second 2 days later. Q_{old} peaks synchronously with Q_s , reaches a minimum 6 days after the second peak, then increases gradually as Q_{new} decreases.

The computed Q_{new} component is approximately 25% of

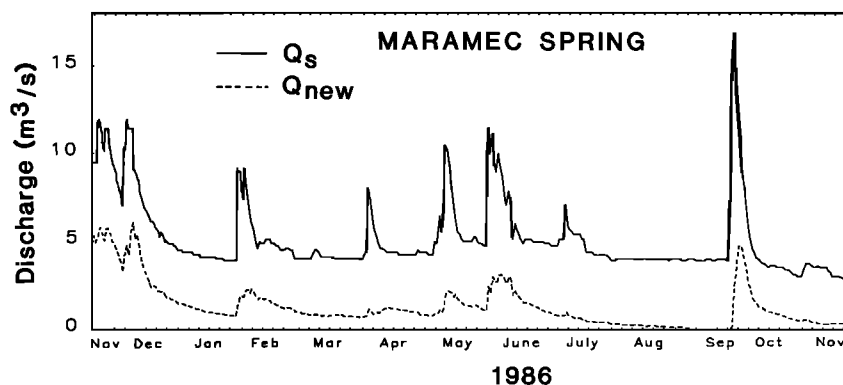


Fig. 6. Measured total discharge Q_s and computed storm-derived discharge Q_{new} in Maramec spring flow, November 1985 through December 1986.

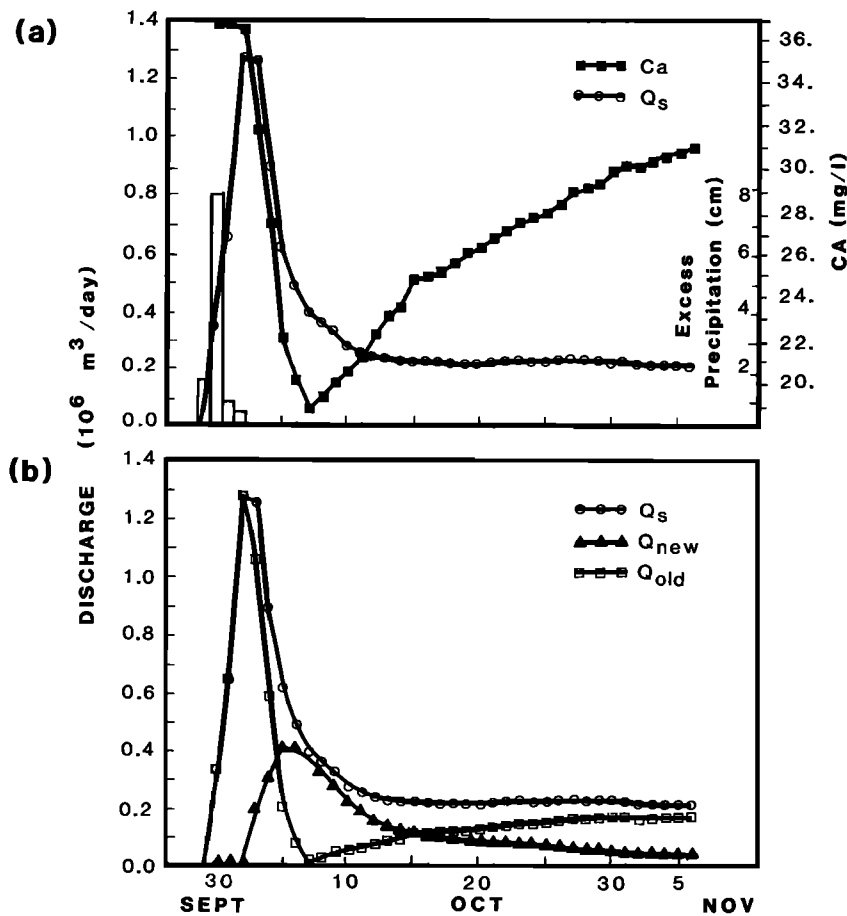


Fig. 7. Storm response of Maramec Spring in October 1986 showing (a) hydrograph response and Ca concentrations and (b) Q_{old} and Q_{new} components.

the total Maramec Spring discharge between November 1985 and November 1986. Q_{new} makes up about 37% of Q_s in the October response and approximately 25% of the response during February and March. The difference in the relative magnitude of Q_{new} and Q_s between the two response periods could reflect either errors in the excess precipitation estimate or seasonal differences in infiltration and transport times. It could also indicate that C_{old} does not remain constant throughout the year. If C_{old} decreases during winter and spring when high infiltration occurs, Q_{new} will be underestimated. This will not effect the lag time to the initial response or the time to the peak of the computed Q_{new} and Q_s portions of the storm responses. However, it will effect the magnitudes of the computed components and the accuracy of the transport analyses presented by Dreiss [this issue]. For this reason, time variance of C_{old} is considered in more detail in that paper.

As shown schematically in Figures 5a and 5b, the chemical fluctuations and hydrograph components for Maramec Spring differ from those observed in stream flow. Relative dilution also occurs in river storm responses, but minimum concentrations are usually simultaneous with peak discharge [e.g., Sklash and Farvolden, 1979; Pinder and Jones, 1969; Martinec, 1975; Kennedy, 1971; Hooper and Shoemaker, 1986; Hino and Hasebe, 1986]. The rapid decline in concentrations in stream flow is thought to be caused by precipitation directly on the stream overland flow, and rapid resurfacing of shallow groundwater or interflow through macropores and desiccation

fractures. On the other hand, the perturbation in spring flow chemistry results from the rapid entry of precipitation and surface runoff into enlarged fractures and conduits in the aquifer, and regional transport through the conduits and fractures to the spring outlet.

The primary objective of the field investigation was to examine chemical fluctuations in karst spring flow in detail in order to describe regional scale transport. However, the observations reported here have additional implications for studies of solution development in carbonate aquifers. First, the arrival of dilute water at the spring outlets indicates that dissolution of the dolomite bedrock is slow relative to the travel time of the groundwater. Dissolution rates of dolomite under field conditions presently are poorly understood. Nevertheless, our observations are consistent with recent laboratory results that suggest that several years may be required for laboratory solutions to reach equilibrium with respect to dolomite [Busenberg and Plummer, 1982; Herman, 1985; White, 1984]. Furthermore, the observations indicate that in karst aquifers with well-developed conduits and deep circulation systems such as those in Missouri, dissolution may occur episodically throughout the conduit network as pulses of relatively dilute water move through the aquifer.

CONCLUSION

This study presents the results of detailed monitoring of temporal changes in major dissolved constituents at three

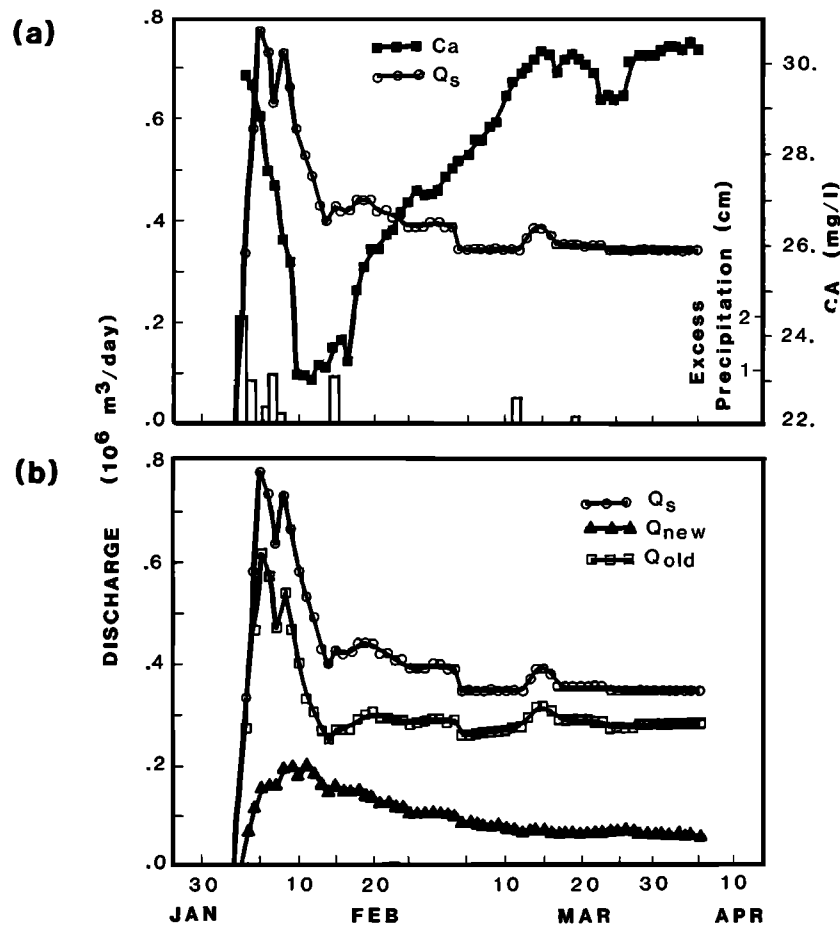


Fig. 8. Storm response of Maramec Spring, February through April 1986 showing (a) hydrograph response and Ca concentrations and (b) Q_{old} and Q_{new} components.

springs in Missouri. The most notable observation from the Missouri data is the presence of large fluctuations in Ca and Mg concentrations in spring flow waters after major rainfall events. The cation concentrations begin to decrease 1–2 days after a major storm, and the decline occurs within a relatively short time interval of 2–3 days. Recovery to prestorm concentrations takes place slowly, over a period of 30 days or more. Thus continuous monitoring or sampling at daily intervals, well after the peak of spring flow storm response, is necessary to adequately describe rapid changes in spring flow chemistry.

The maximum chemical perturbation occurs during the recession of the spring discharge hydrograph and represents the arrival of relatively dilute water at the spring outlets. On the basis of a cation balance of the spring flow, this dilute water appears to comprise at least 25% of the total discharge at one of the Missouri springs. The storm-derived water begins to arrive at the spring about 1 day after a storm event and reaches a maximum during the recession of the spring discharge hydrograph, about 4–5 days after the event. At the time of the peak discharge response, spring flow is composed primarily of prestorm water that has been displaced in the conduit system by the relatively dilute, storm-derived water. The presence of these pulses of relatively dilute water suggests that dissolution may occur episodically throughout this type of karst system after each major storm event.

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REFERENCES

- Aley, T., A predictive hydrologic model for evaluating the effects of land use and management on the quantity and quality of water from Ozark Springs, Ozark Underground Lab., Springfield, Mo., 1975.
- Aston, K., The analyses of flow data from karst drainage basins, *Trans. Cave Res. Group*, 7, 161–203, 1966.
- Atkinson, T. C., D. I. Smith, R. J. Whitaker, and J. J. Lavis, Experiments in tracing underground waters in limestone, *J. Hydrol.*, 19, 323–349, 1973.
- Back, W., B. B. Hanshaw, T. E. Pyle, L. N. Plummer, and A. E. Weidie, Geochemical significance of groundwater discharge and carbonate solution to the formation of Caleta Xel Ha, Quintana Roo, Mexico, *Water Resour. Res.*, 15, 1521–1535, 1979.

- Bakalowicz, M., and A. Mangin, L'aquifere karstique, Sa definition, ses caracteristiques et son identification, *Mem. H. Ser. Soc. Geol. France*, 11, 71-79, 1980.
- Brown, M. C., T. L. Wigley, and D. C. Ford, Water budget studies in karst aquifers, *J. Hydrol.*, 9, 113-116, 1969.
- Busenberg, E., and L. N. Plummer, The solubilities of calcite, aragonite, and vaterite in $\text{CO}_2\text{-H}_2\text{O}$ solutions between 0° and 90°C , and an evaluation of the aqueous model for the system $\text{CaCO}_3\text{-CO}_2\text{-H}_2\text{O}$, *Geochim. Cosmochim. Acta*, 46, 1011-1040, 1982.
- Dreiss, S. J., Linear kernels for karst aquifers, *Water Resour. Res.*, 18(4), 865-876, 1982.
- Dreiss, S. J., Linear unit-response functions as indicators of recharge areas for large karst springs, *J. Hydrol.*, 61, 31-44, 1983.
- Dreiss, S. J., Regional scale transport in a karst aquifer, 2, Linear systems and time moment analysis, *Water Resour. Res.*, this issue.
- Hallberg, G. R., R. D. Libra, E. A. Bettis, and B. E. Hoyer, Hydrogeologic and Water Quality Investigations in the Big Spring Basin, Clayton County, Iowa, *Open File Rep. 84-4*, Iowa Geol. Surv., Iowa City, 1983.
- Hallberg, G. R., R. D. Libra, and B. E. Hoyer, Nonpoint source contamination of ground water in karst-carbonate aquifers in Iowa, in *Perspectives on Nonpoint Source Pollution, Rep. EPA 44015-85-001*, pp. 109-114, Environ. Protect. Agency, Washington, D. C., 1985.
- Hanshaw, B. B., and W. Back, Determination of regional hydraulic conductivity through use of ^{14}C dating of groundwater, in *Extrait des Mémoires de l'Association Internationale des Hydrogeologues*, Congres de Montpellier, France, pp. 195-198, 1974.
- Herman, J. S., and W. B. White, Dissolution kinetics of dolomite: Effects of lithology and fluid flow velocity, *Geochim. Cosmochim. Acta*, 49, 2017-2026, 1985.
- Hess, J. W., and W. B. White, Hydrograph analysis of carbonate aquifers, *Res. Pub. 83*, 63 pp., Inst. Res. Land and Water Resour., Pa. State Univ., University Park, 1974.
- Hino, M., and M. Hasebe, Separation of a storm hydrograph into runoff components by both filter-separation Ar method and environmental isotope tracers, *J. Hydrol.*, 85, 251-264, 1986.
- Hooper, R. P., and C. A. Shoemaker, A comparison of chemical and isotopic hydrograph separation, *Water Resour. Res.*, 22(10), 1444-1454, 1986.
- Hull, L. C., Mechanisms controlling the inorganic and isotopic geochemistry of springs in a carbonate terrane, Ph.D. dissertation, Penn. State Univ., University Park, 1980.
- Kennedy, V. C., Silica variation in stream water with time and discharge, in *Nonequilibrium Systems in Natural Waters, Adv. Chem. Ser. 106*, pp. 94-130, American Chemical Society, Washington, D. C., 1971.
- Martinez, J., Subsurface flow from snowmelt traced by tritium, *Water Resour. Res.*, 11(3), 496-498, 1975.
- Mull, D. S., and J. L. Smoot, Ground water flow characteristics described by quantitative dye tracing in karst terrane in the Elizabethtown area, Kentucky, paper presented at Proceedings Environmental Problems in Karst Terranes and Their Solutions Conference, Nat. Water Well Assoc., Bowling Green, Ky., 1986.
- Pilgram, D. H., D. D. Huff, and T. D. Steele, Use of specific conductance and contact time relations for separating flow components in storm runoff, *Water Resour. Res.*, 15(2), 329-346, 1979.
- Pinder, G. F., and J. F. Jones, Determination of the groundwater component of peak discharge from the chemistry of total runoff water, *Water Resour. Res.*, 5(5), 438-445, 1969.
- Quinlan, J. F., and E. C. Alexander, How often should samples be taken at relevant locations for reliable monitoring of pollutants from an agricultural, waste disposal, or spill site in a karst terrane? A first approximation, paper presented at Proceedings 2nd Multidisciplinary Conference on Sinkholes and Environmental Impacts of Karst, Fla. Sinkhole Res. Inst., Orlando, Fla., 1987.
- Scanlon, B. R., and J. Thrailkill, Chemical similarities among physically distinct spring types in a karst terrain, *J. Hydrol.*, 89, 259-279, 1987.
- Shuster, E. T., and W. B. White, Seasonal fluctuations in the chemistry of limestone springs: A possible means for characterizing carbonate aquifers, *J. Hydrol.*, 14, 93-128, 1971.
- Shuster, E. T., and W. B. White, Source areas and climatic effects in carbonate groundwaters determined by saturation indices and carbon dioxide pressures, *Water Resour. Res.*, 8(4), 1067-1073, 1972.
- Sklash, M. G., and R. N. Farvolden, The role of groundwater in storm runoff, *J. Hydrol.*, 43, 45-65, 1979.
- Smart, C. C., and D. C. Ford, Structure and function of a conduit aquifer, *Can. J. Earth. Sci.*, 23, 919-929, 1986.
- Smoot, J. L., D. S. Mull, and T. D. Liebermann, Quantitative dye tracing techniques for describing solute transport characteristics of ground-water flow in karst terrane, paper presented at 2nd Multidisciplinary Conference on Sinkholes and the Environmental Impacts of Karst, Fla. Sinkhole Res. Inst., Orlando, Fla., 1987.
- Steele, K. F., R. K. Widman, D. S. Wickliff, and D. L. Parr, The effect of rainstorm events on spring water chemistry in limestone terrane, paper presented at Proceedings, Association of Ground Water Scientists and Engineers, Southern Regional Ground Water Conference, Nat. Water Well Assoc., San Antonio, Tex., Sept. 18-19, 1985.
- Ternan, J. L., Comments on the use of a calcium hardness variability index in the study of carbonate aquifers with reference to the Central Pennines, England, *J. Hydrol.*, 16, 317-321, 1972.
- Thornthwaite, C. W., and J. R. Mather, Instructions and tables for computing potential evapotranspiration and the water balance, *Publ. Climatol. Drexel Inst. Technol.*, 10(3), 1957.
- Vandike, J. E., The effects of the November 1981 liquid-fertilizer pipeline break on groundwater in Phelps County, Missouri, Open File Report, Mo. Dep. Natl. Resour., Rolla, 1982.
- Vineyard, J. D., and G. L. Feder, Springs of Missouri, *Rep. WR29*, Mo. Dep. Natl. Resour., Rolla, 1982.
- White, W. B., Rate processes: Chemical kinetics and karst landform development, 10, in *Groundwater as a Geomorphic Agent*, Allen and Unwin, Winchester, Mass., 1984.
- Wigley, T. M. L., Carbon-14 dating of groundwater from closed and open systems, *Water Resour. Res.*, 11(2), 324-328, 1975.
- U.S. Department of Commerce, Climatological data for Missouri, Natl. Oceanic Atmos. Adm., U.S. Environ. Data Serv., Washington, D. C., 1986.
- U.S. Environmental Protection Agency, Methods for chemical analysis of water and wastes, *Rep. EPA-600/4-79-020*, U.S. Environ. Protect. Agency, Washington, D. C., 1979.

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