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Inferring source waters from measurements of carbonate spring response to storms

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Abstract

We infer information about the nature of groundwater flow within a karst aquifer from the physical and chemical response of a spring to storm events. The spring discharges from the Maynardville Limestone in Bear Creek Valley, Tennessee. Initially, spring discharge peaks approximately 1–2 h from the midpoint of summer storms. The initial peak is likely due to surface loading, which pressurizes the aquifer and results in water moving out of storage. All of the storms monitored exhibited recessions that follow a master recession curve very closely, indicating that storm response is fairly consistent and repeatable, independent of the time between storms and the configuration of the rain event itself. Electrical conductivity initially increases for 0.5–2.9 days (longer for smaller storms), the result of moving older water out of storage. This is followed by a 2.1–2.5 day decrease in conductivity, resulting from an increasing portion of low conductivity recharge water entering the spring. Stable carbon isotope data and the calcite saturation index of the spring water also support this conceptual model. Spring flow is likely controlled by displaced water from the aquifer rather than by direct recharge through the soil zone.

Keywords: Groundwater; Aquifer; Karst; Springs; Hydrochemistry; Isotopes

1. Introduction

Springs emanating from karst aquifers are one of the few overtly visible signs of the influence of groundwater hydrology on the Earth's surface. Historically, karst spring research has been motivated by both a desire to understand spring origins, and the potential of springs to yield qualitative and quantitative inferences about the physical and chemical nature of the aquifer that is their source. Here we focus on using spring measurements to understand aquifer flow.

Water chemistry and tracer tests in springs have been used extensively to study aquifers. Shuster and White (1971), based on chemical data collected from 14 carbonate springs, classified springs into two general physical types, conduit feeder systems and diffuse-flow feeder systems, with the former having the greatest temporal chemical variability. Ternan (1972) studied approximately 70 springs in the Central Pennines of England, and used temporal variations in calcium hardness and flow-through time to classify the springs in a manner similar to that of Shuster and White (1971).

Scanlon and Thrailkill (1987), using dye tracing and water chemistry in the Bluegrass Karst region of central Kentucky, found that the length of flow path exerted a strong influence on temporal chemical variations. Diffuse springs had short flow paths and conduit springs had long flow paths.

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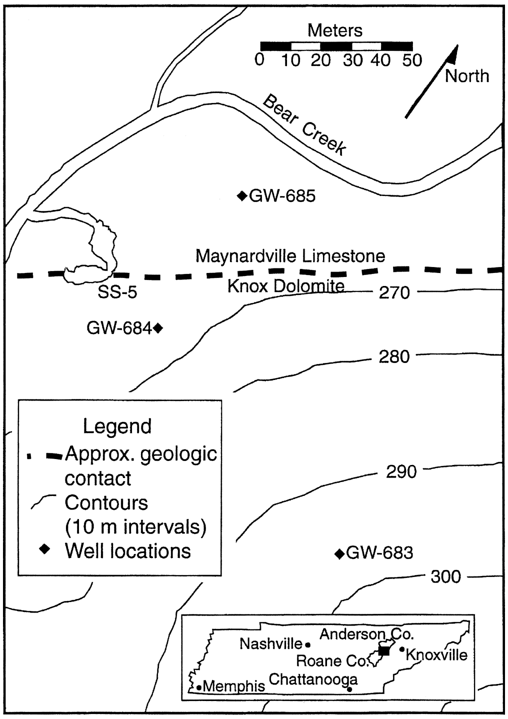

Fig. 1. Study site showing South Spring 5 (SS-5), surrounding wells, topography, and surface hydrology. Study site location is shown as a solid rectangle in the State of Tennessee map inset.

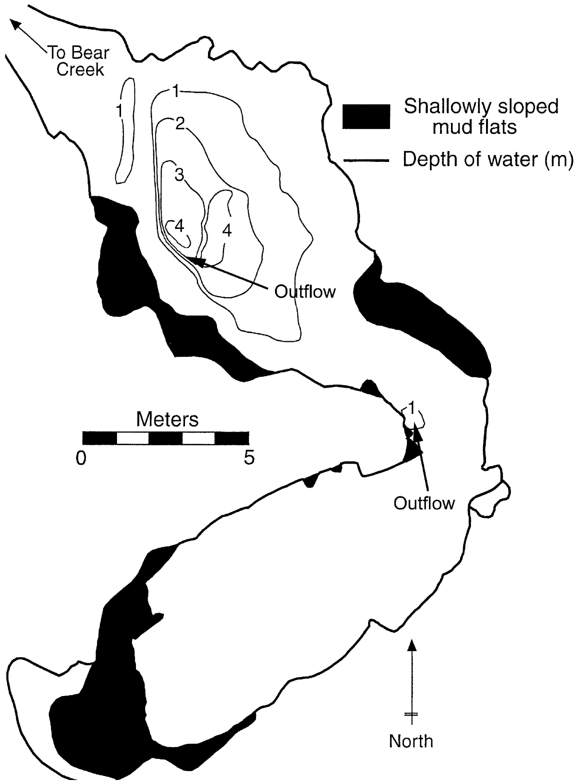

Fig. 2. Map of spring SS-5 (constructed from field measurements) showing water depth and estimated locations of discharge points (Desmarais, 1995).

Typically, studies have focused on either: long-term data collected at biweekly or monthly intervals or higher resolution analysis of single storm events. An exception to this rule can be found in Dreiss (1989) who examined daily stream discharge and chemistry records for a large spring in Missouri. From this data set, Dreiss (1989) was able to infer the magnitude and timing of storm-derived contributions in spring flow. More recently, analysis of deuterium and δ^{18}O in spring waters has yielded information about groundwater residence times (Frederickson and Criss, 1999).

Here we examine high-resolution (typically hourly or less) variations in spring flow, temperature, and chemistry over several months in conjunction with quarterly measurements taken over several years to infer detailed information about the nature of groundwater flow in an aquifer associated with a karst spring. Unlike other studies, sampling from nearby wells allows us to gain additional insight into the groundwater flow system. The measured chemical variations within the spring sampled are not, as noted later, amenable to the analysis of Dreiss (1989). However, detailed information on temperature and carbon isotopes, in addition to standard major ion data allow us to make quantitative estimates of the sources of spring flow.

2. Data collection and methods

2.1. Site location

The field site, South Spring 5 (SS-5) and the surrounding area, is located on the Oak Ridge Reservation near Oak Ridge, Tennessee, in Bear Creek Valley (Fig. 1). This spring is in the vicinity of three wells: GW-683, GW-684 and GW-685. SS-5 was chosen as the study site because it is one of the largest carbonate springs in Bear Creek Valley discharging from the Maynardville Limestone. Several years of quarterly measurements at this site provide a historical database and there is a known connection between the spring and two of the surrounding wells (GW-683 and GW-684) that allows for additional insight into aquifer response (Powers and Shevenell, 2000).

SS-5 is a perennial carbonate spring consisting of two main pools (Fig. 2). The larger, northern pool is 6 m wide, 10 m long, and 4 m at its deepest point. Inflow to this pool appears to be from an opening originating under the base of the west wall near the deepest portion of the spring. The south pool is 5.5 m wide, 12 m long and has an average depth of 0.5 m. The entrance to this shallow pool is underneath the peninsula of land separating the two pools.

2.2. Continuous monitoring

SS-5 and GW-684 were monitored for stage, conductivity and temperature changes for three months during the summer of 1994, from mid-June to mid-September. GW-685 was monitored for 40 days, beginning in August. Science Applications International Corporation (SAIC) provided additional spring discharge data at 5 min resolution from a 0.46 m H flume at the outlet of SS-5 from March through December of 1994.

GW-684 (total depth of 39.5 m) is collared in the Copper Ridge Dolomite, but is screened in the Maynardville Limestone. The monitoring interval consists of a 2.3 m gravel pack followed by a 4.4 m pre-packed screen from 34.7 to 39.1 m below land surface (mbls). GW-685 is steel cased with a 16.5 cm well bore and an open interval from 27.0 to 42.2 m bls located entirely within the Maynardville Limestone.

SS-5 was instrumented in both the north and south pools as close as possible to their respective discharge points. The two wells were instrumented in their screened (or open) interval. Data loggers recorded all parameters measured at 15 min intervals.

Field instrumentation consisted of a Hydrolab H_2O Multiparameter Water Quality Transmitter to measure conductivity and temperature, and a Druck Pressure Transducer (either 3.4×10^4 or 6.9×10^4 Pa) vented to the atmosphere to record water level fluctuations. These two instruments were connected to an Omnidata EasyLogger 900 powered by a 12 V gel cell rechargeable battery. The battery and data logger were protected and kept dry in a grounded metal shelter. It was noted that when these shelters were exposed to direct sunlight during at least part of the day there was a slight (0.6–0.9 cm) daily cyclic variation in water level recorded due to temperature changes affecting lead-wire resistance. The effect was minor relative to storm water level fluctuations.

2.3. Chemistry data

Using a peristaltic pump, samples were collected from the spring at approximately the same two locations as the monitoring equipment. The wells were sampled with a bailer at the screened interval in GW-684 and in the middle of the open interval in GW-685. The bailer was left in the well for 24 h prior to sampling to minimize disturbance in the well. The wells were not purged prior to sampling. All samples were pumped through a 0.45 μm filter, placed in an ice-filled cooler immediately following collection, and were then either transported to the laboratory for analysis or left in a 5 °C refrigerator overnight.

Cations and anions (except bicarbonate) were analyzed (with an ICP and ion chromatography) at Oak Ridge National Laboratory (ORNL). Bicarbonate was determined by titration in the field within one half hour of collection.

Additional measurements of pH, conductivity and temperature were taken with every water sample collected and were used to verify the continuous monitoring data from the Hydrolab H_2O probe. Temperature and pH were measured with a Horiba meter. Conductivity and temperature were measured with a Yellow Spring Instrument (YSI) meter, Model #3560 with a digital readout. Quarterly Ground Water Quality Assessment Report (GWQAR) data that have been collected from the area since August 1990 were used to put the chemistry data obtained during the summer of 1994 into historical perspective.

2.4. $\delta^{13}C$ Analyses

Thirty-five $\delta^{13}C$ analyses with a precision of 0.1‰ (reported relative to the Pee Dee Belemnite, PDB, standard) were obtained from the spring and from surrounding locations: 26 from the north pool of SS-5, three from the south pool, three from GW-684, two from GW-685, and one from Bear Creek at kilometer (BCK) 9.4. The analyses were performed on a fully

Table 1
Summary of response to 14 storms (from largest to smallest) occurring between 15 June 1994 and 8 December 1994

Storm #	Start of storm	Storm type[a]	Previous storm (days)[b]	Total precipitation (cm)	Precipitation duration (hours)[c]	Time until return to base level (days)[d]
1	26 June	d, s	16 (4)	8.89	4, 3, 6	10
2	11 July	m, s	14	6.93[e]	8, 1, 1	9
13	27 Nov	d, s	17	6.22	10, 9	i
8	17 Sep	d, s	17	5.26	2, 1	i
3	26 July	d, s	9	4.39	10, 2	i
5	14 Aug	s	10	3.96	4	i
10	9 Oct		15	3.76	7	i
6	19 Aug	d, s	5 (4)	3.25	1, 3, 7	9
12	9 Nov	s	21	2.03	8	12
14	2 Nov		6	1.88	23	End of record
11	19 Oct		10	1.83	9	11
4	5 Aug	s	7 (3)	1.60	1, 2	8
9	23 Sep		5	1.52	12	6
7	31 Aug	s	10	1.42	2	6

[a] d: double storm, 2 (or more) storms causing overlapping responses; m: many small storms less than one day apart; s: sharp spike at beginning of storm flow response.
[b] Numbers in brackets indicate days since last minor storm.
[c] Numbers reflect duration of each precipitation pulse during the event.
[d] i: the recession interrupted by next storm.
[e] Primary precipitation gauge not functioning. Estimated from secondary gauge response.

automated VG 903 Triple Collector Mass Spectrometer at the Department of Geological Sciences at the University of Tennessee.

2.5. Well testing

Hydraulic conductivity was measured at GW-684 and GW-685 with slug tests. A volume of water was displaced by quickly inserting (or removing) a 'slugger'—a solid plastic pipe—into the water in the well bore.

Three slug tests were performed in GW-684 and two in GW-685. Water levels were logged every second for the GW-684 well tests. With the insertion (or removal) of the slugger, water levels in GW-6814 were displaced between 0.30 and 0.35 m and the response dissipated in ≤12 s.

Water levels were logged every 15 min for the slug tests in GW-685 because the response was significantly slower. Total water displacement in GW-685 with the insertion of the slugger was between 0.11 and 0.17 m and the response dissipated after approximately 8 h.

2.6. Precipitation data

We used hourly precipitation data from a recording station 700 m NNE of SS-5. The station is maintained continuously by ORNL staff and uses a Belfort Weighing Bucket rain gage that records data on a strip chart. For one storm, this station was not functioning and we used data from an auxiliary station less than 400 m distant.

3. Precipitation, discharge, and nearby well response

Table 1 summarizes some of the relevant information about the 14 storms that occurred during the period of monitoring (15 June 1994–8 December 1994); Fig. 3 shows a subset of the data. Analysis of six precipitation-gauging stations in the area (Desmarais, 1995) indicates that at the scale of this study, spatial variation in precipitation is minor. Generally, summer and fall precipitation events are 1–10 h in duration. The initial spring discharge response is very sensitive to the configuration and timing of the

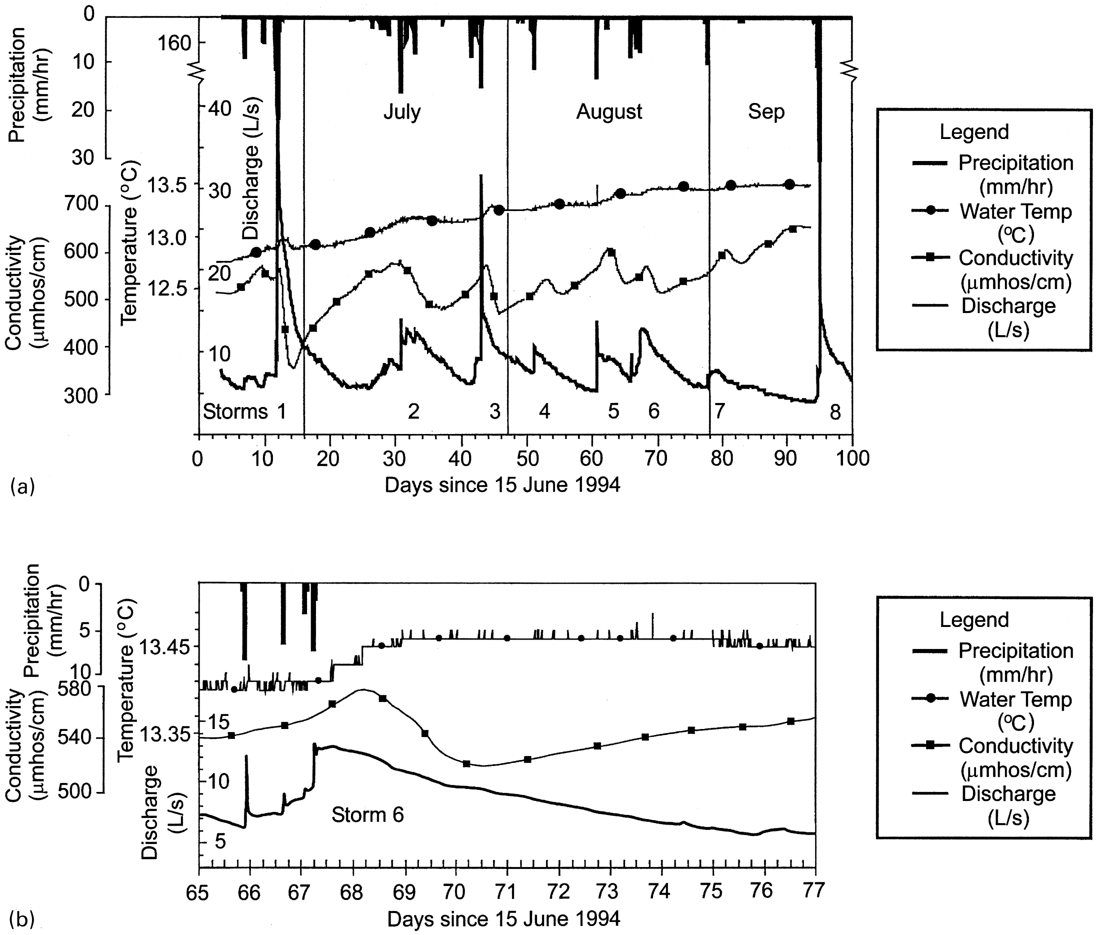

Fig. 3. Discharge, conductivity and temperature at SS-5 for storms 1–8 (a). Detailed discharge, conductivity and temperature at SS-5 for storm 6 (b).

storm. Typically, there is a very abrupt increase in discharge from the spring within 1–2 h following the major portion of the storm event, commonly forming a 1–2 h duration 'spike' in the discharge record. This is followed by a recession period that lasts approximately 6.5 days for smaller storms and 9–10 days for mid-size to larger storms (Fig. 3).

The largest storms encountered during the study period were actually 2 or 3 smaller individual storm pulses that occurred within 8–24 h of each other, resulting in 'double' storms (indicated in Table 1 with a 'd'). These double storms show up clearly in the flood records: 1–2 h after the start of the storm there is an initial rapid increase in discharge corresponding with the first part of the storm. At the second storm event, there is another sharp increase in discharge. The recessions for these storms follow the same pattern as the other storms. The initial rapid increases are likely due to rain loading on the system and concomitant compression to the aquifer. The rain loading causes a transient pressure pulse to travel through the system resulting in the discharge spike from the spring. This inferred response is consistent with the absence of a barometric signal in the sampled wells, which indicates that the aquifer has a high surface loading efficiency (Rojstaczer and Agnew, 1989).

The drilling record for GW-684 indicates that this well is screened in a 0.6 m thick, very productive, water bearing cavity or large fracture in the Maynard-

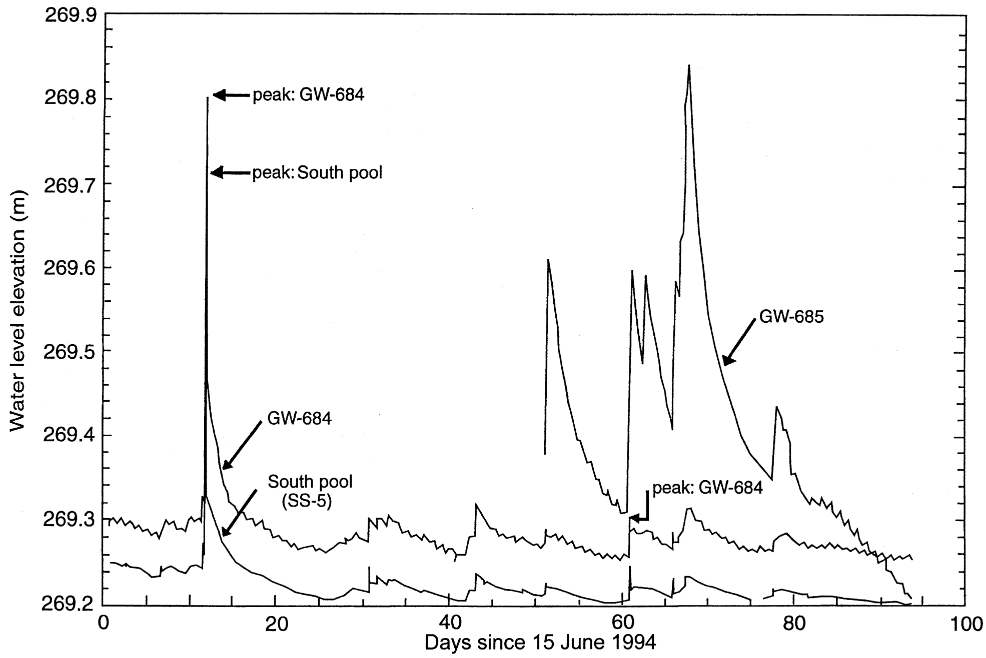

Fig. 4. Comparison of stage between GW-684, GW-685 and SS-5 (from Desmarais, 1995).

ville limestone. During drilling, changes in turbidity and discharge in SS-5 suggested significant hydrologic communication between the south pool of the spring and the well (Powers and Shevenell, 2000).

Fluctuations in groundwater level in GW-684 also correspond with stage level changes in SS-5 following precipitation events (Fig. 4). On average, the water level in the well is 5.8 cm higher than that of the spring. The hydraulic head difference increases 1–2 cm (medium storms) 1.7–2.8 days following precipitation events. This is then followed by a slow decrease in the difference between GW-684 and SS-5 water levels. As noted earlier, because of thermal effects on the well instrumentation, there is also a daily oscillation in the well record. The instrumentation for the spring was not affected by this thermal problem because it was not located in direct sunlight.

The drilling record for GW-685 indicates that although several water bearing fractures (or solution intervals) were encountered in the borehole, the well was lowly permeable and slow to recover from purging. As a result of the lower permeability of the monitoring interval, GW-685 responds quite differently to rain events (Fig. 4). The amplitude of the water level response in GW-685 following a storm is 24.4–45.7 cm and the spring variation and 3.1–6.1 cm. Additionally, it takes longer to reach the water level peak in GW-685 and there are no sharp initial spikes as are found in the responses of the spring and GW-684. Slug tests performed in these two wells indicate large differences in permeability. GW-684 had a mean hydraulic conductivity (K) of 4.6×10^{-2} cm/s and GW-685 had a much lower mean K of 1.6×10^{-5} cm/s. These values are similar to that reported in Powers and Shevenell (2000).

Unlike many karstic springs (e.g. Felton and Currens, 1994), spring flow recession is surprisingly repeatable from storm to storm. To examine consistency of recession response, a master recession curve (Nathan and McMahon, 1990) for SS-5 was constructed for 15 storms (1 June through 8 December 1994) by the strip method (discharge records were supplied by SAIC). Storms 1 and 13 formed the basis for the upper portion of the curve and storms 7 and 12 formed framework for the lower portion of the curve. With the exception of two storms (storms 5 and 8) the curves matched very well: the large storms join the master recession curve at higher discharges,

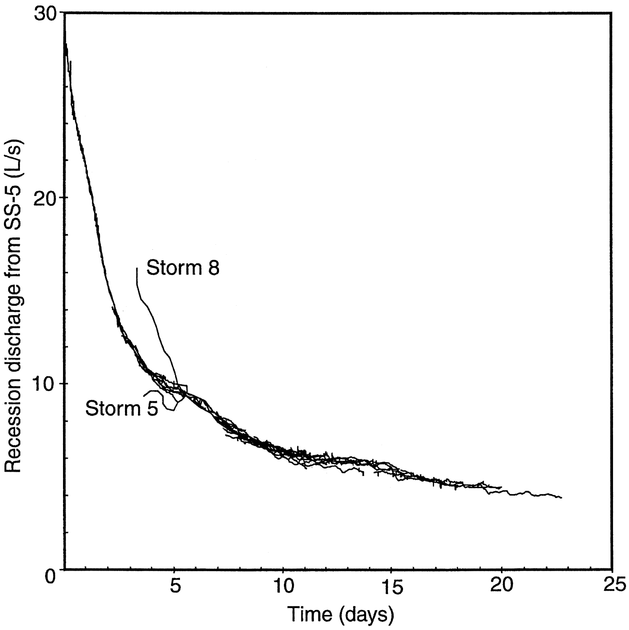

Fig. 5. Master Recession Curve (MRC) composed of 15 storms recorded by the SAIC flume on SS-5 (May–December, 1994). Note that time equals zero represents the start of the largest storm over the period of monitoring (storm 1).

whereas the smaller storms join the curve at the lower discharge levels (Fig. 5). The recessions for both storm 5 and 8 were only 5 days long before they were interrupted by subsequent storms. Storm 5 has the additional complication of having a small but steady rain event in the middle of its 5-day recession.

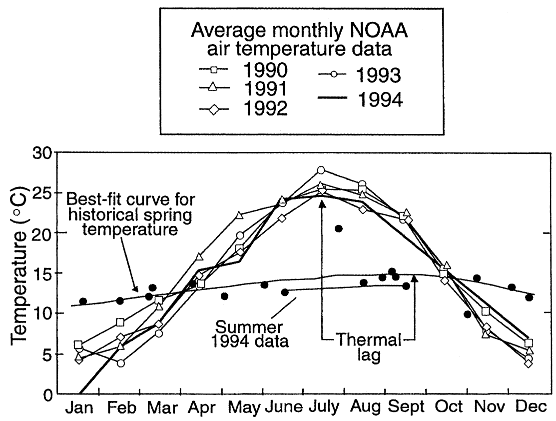

Fig. 6. Comparison of quarterly spring temperature data (solid circles, 1990–1994) and monthly average air temperature data from the Oak Ridge NOAA station. Summer 1994 data is included for reference.

The recession for storm 8 was generally steeper than the other recessions during this time period, which could be due to the relatively high rainfall intensity associated with this storm.

4. Temperature

4.1. Regional long-term data

Davies (1991) evaluated temperature variations in nearby carbonate springs by examining the response of 11 springs emerging from the Knox Group dolomites for most of 1991. Temperature in these springs was measured on 2–3 day intervals to a resolution of 0.1 °C. The 11 springs were divided into 2 main groups based on their coefficient of variation (CV), or coefficient of dispersion, which is defined as the standard deviation divided by the mean, during the year of 1991. None of the springs became turbid during high flow levels, indicating that although were two distinct groups, both groups were fed mainly by diffuse flow. Six of the 11 springs fell into the first group characterized by temperature CV's between 0.9 and 1.2% with an outlier at 2%. The mean temperature in each of these

Table 2
Temperature response in the north and south pools of spring SS-5 following precipitation events

Storm #	Total precipitation (cm)	Initial temperature spike (s) North Pool (°C)	Initial temperature spike (s) South Pool (°C)	Total temperature change North Pool (°C)	Total temperature change South Pool (°C)
1	8.89	0.05, 0.06	0.08, 0.13	0.11	0.24
2	6.93	0.03	0.07	0.21	0.20
3	4.39	None	None	0.14	0.12
5	3.96	0.20	0.51	0.12	0.09
6	3.25	0.03	0.15	0.06	0.08
4	1.60	0.02	0.15	0.07	0.04
7	1.42	None	0.09	0.05	0.05

6 springs remained at 13.9–14.6 °C ± 0.1–0.3 °C throughout the year. The second group was much more variable, with temperature CV's ranging from 2 to 10%, and mean temperatures of 14.1–16.2 °C ± 0.3–1.5 °C. For these five springs, temperature remained fairly constant and relatively low from January through May, increased from June through September, and then decreased from September through December to values similar to the previous January.

This pattern of the second group is seen in SS-5 (Fig. 6). The coefficient of variation calculated for SS-5 (based on only 3 months of data) is 1.8%, with a standard deviation of 0.2 and a mean temperature of 13.2 °C. However, when the quarterly data are used to calculate the same values (excluding two outlying points), the resulting CV = 8.4%, with a standard deviation of 1.1 and the same mean as before, 13.2 °C. Our summer data set comes from a relatively less variable time of year. Other source waters might be observed at other times. Spring SS-5 does become turbid for several days following precipitation events and therefore falls at the upper end of the second group defined by Davies (1991), a spring fed by both diffuse and conduit flow. Quinlan and Ewers (1985) suggest CV's between 5 and 10% represent springs with a mixture of conduit and diffuse flow, whereas, springs with CV's of less than 5% are mostly diffuse flow.

Quarterly temperature data collected over the last several years from SS-5 (Fig. 6) indicate that there is a systematic lag time of about 45–60 days between the peak monthly air temperature and the temperature peak in the spring. On a yearly basis, temperature varies approximately 4 °C in the spring whereas air temperature varies approximately 25 °C.

4.2. Summer 1994 data

Temperature was measured in the north and south pools of SS-5, as well as in two local wells (GW-684, GW-685). The details of temperature changes that occurred following each of the seven distinct storm events are summarized in Table 2. Additionally, the north pool temperature record is graphed in Fig. 3. The thermal responses to storm events of SS-5's two pools were slightly different, probably reflecting slightly different water sources contributing to each pool.

Generally, in the north pool, the temperature increased almost immediately after a storm. This increase continued for 2–5 days, then decreased slightly (commonly for not more than half a day), and ultimately stayed level until the next storm. Additionally, some responses have a relatively small temperature spike coincident with the discharge spike. The south pool generally had an initial temperature spike corresponding with the spike in discharge, which lasted for 1.0–1.5 h. This was followed by an increase in temperature for 2–5 days. There was no further change until the next storm.

Temperature was also measured in two nearby wells: GW-684 and GW-685. Unlike the thermal response in the spring to storm events, well temperatures were constant for the duration of the study period.

5. Electrical conductivity

5.1. Spring response

Table 3 and Fig. 3 summarize the overall conductivity

Table 3
Electrical conductivity summary for the precipitation events, North Pool

Storm #	Total precipitation (cm)	Time from slope change to peak (days)	Electrical conductivity maximum (μmhos)	Electrical conductivity minimum (μmhos)	Time from maximum to minimum (days)
1	8.89	0.5	569	360	2.1
2	6.93	3.6	582	482	7.1
3	4.39	1.4	577	475	2.1
4	3.96	2.0	614	538	2.4
5	3.25	1.2	575	517	2.3
6	1.60	2.0	547	515	2.5
7	1.42	2.9	611	581	2.5

changes in the spring following a precipitation event. All single and 'double' storms followed the same general pattern. Corresponding with the abrupt increase in discharge from the spring, the slope of the electrical conductivity increased and the new slope persisted for 0.5–2.9 days. The conductivity then reached a maximum, followed by a steady decrease for 2.1–2.5 days when a minimum electrical conductivity was reached. The spring water conductivity then steadily increased until the next storm.

The only difference between the conductivity data from the north and south pools is that the south curve is slightly jagged around the maxima and minima storm responses. This is especially true for storms 1, 3 and 6 (the 'double storms'). However, the overall shape and values are very similar. There is a possibility that this jaggedness is due to instrument error.

5.2. Well response

The conductivity response of both wells was very different than the response of SS-5 (Fig. 7). GW-685

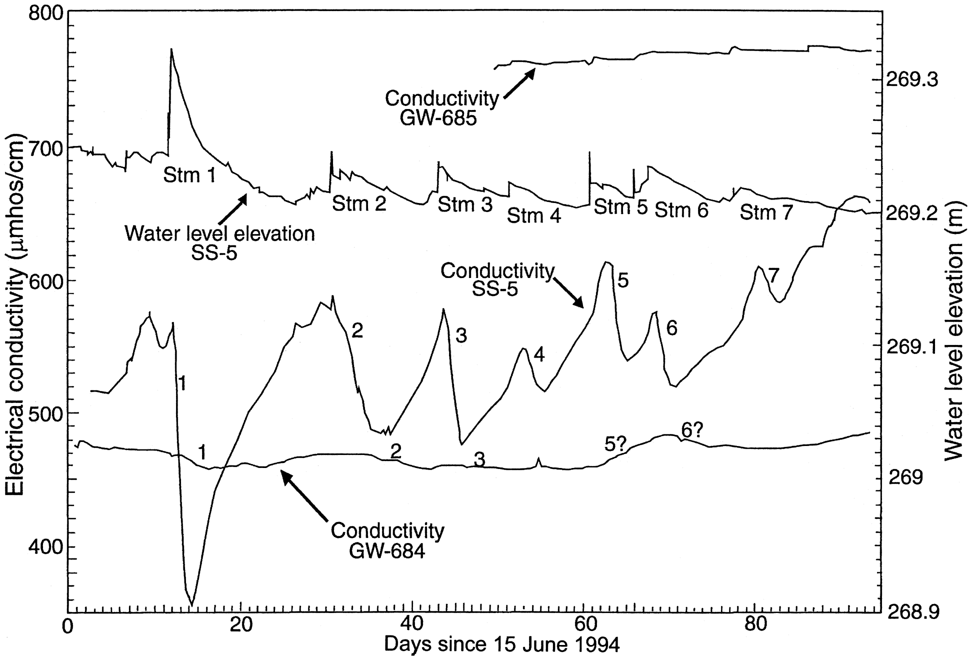

Fig. 7. Electrical conductivity in GW-684 and GW-685 relative to SS-5. Spring stage also graphed for reference.

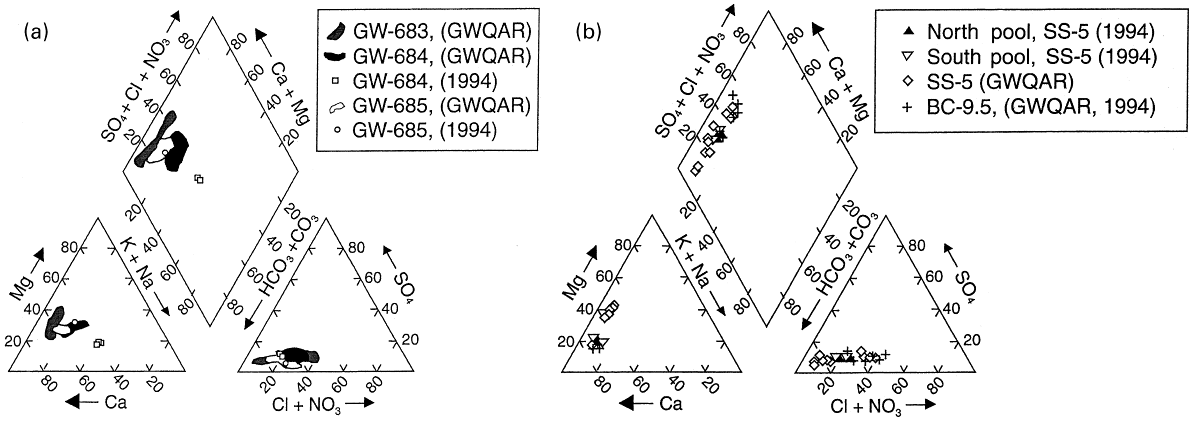

Fig. 8. Piper diagrams comparing Maynardville groundwater type from three wells (a) to the chemistry of the spring water (b). Fields (a) defined by 10 quarterly samples.

had a higher overall conductivity than SS-5 or GW-684 and exhibited only small perturbations, generally with very minor overall electrical conductivity increases. As noted earlier, this well is drilled into a relatively low permeability zone.

The conductivity in GW-684 was at the lower end of that observed in the spring. Although GW-684 did respond to precipitation events, the response was small, slow, and inconsistent relative to the spring's response. Changes in the turbidity and discharge rate of the south pool of SS-5 were observed during drilling (Powers and Shevenell, 2000). The range of the electrical conductivity response to various storms over the summer in GW-684 was between 3 and 15 μmhos/cm on average. The response also appears to lag behind the spring's response by several days. The inconsistency and the lag in response indicate that it is difficult to link a specific response to a specific rain event. Additionally, for the smaller storms (storms 4 and 7), there was no electrical conductivity response in GW-684. A puzzling aspect of this well was a relatively large (23 μmhos/cm) increase in electrical conductivity between 16 August and 23 August. This increase appears to be caused by the moderately sized storm 5 and could be unique because of the unusual intensity of this particular storm.

6. Chemistry

Discharge from the spring following three storms (3,4 and 5) was sampled during the summer of 1994, with most of the samples concentrated in the north pool. We were interested in detecting changes in ionic concentration following a storm event that could provide information about the source(s) of water feeding the spring. Possible sources include the Maynardville Limestone, the Knox Dolomite (which overlies the Maynardville Limestone) and the overlying soils (epikarst). Samples were taken simultaneously in both the north spring and the south spring to evaluate similarities between the chemistry of these two inputs. Prior chemistry data for the spring consisted of quarterly sampling for the preceding two years whereas we collected samples at approximately one-day intervals.

The chemistry data from the spring and surrounding wells indicate that the water is a Ca–Mg–HCO_3-type, as is expected for the shallow flow regime in the Maynardville Limestone and Knox Group dolomites (Saunders and Toran, 1994; Haase, 1991). The data collected during the summer of 1994 in the spring are within the range of the several previous years of quarterly GWQAR data and indicate that water chemistry variations during the year are significantly greater than the variation in chemistry caused by an individual summer storm (Fig. 8). The 1994 data and the previous year's GWQAR data match very closely with the water chemistry in GW-683. In contrast, GW-684 has a higher concentration of potassium and chloride and GW-685 has higher concentrations of sodium, bicarbonate and chloride and a lower

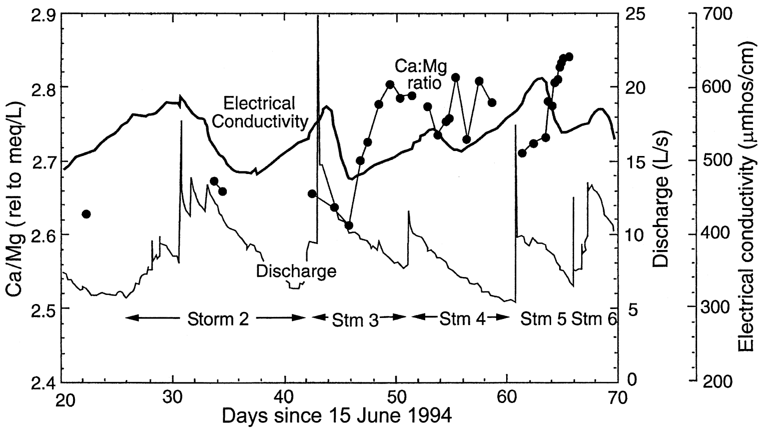

Fig. 9. Variation in Ca:Mg ratios over time for spring water. Electrical conductivity and discharge data shown for reference.

concentration of nitrates. Changes in chemistry data over time, with the partial exception of sulfate, follow the conductivity response to storms.

Because recharge to the system is through the Knox Dolomite to the underlying Maynardville Limestone, calcium to magnesium ratios were examined. Shuster and White (1971) report Ca:Mg molar ratios near unity for waters discharging from dolomite and significantly higher ratios for spring water discharging from limestone (1.5–7.5). For the 20-day period sampled, Ca:Mg molar ratios in this study area vary over a relatively small range from 2.6 at the beginning of the study to 2.8 after storm 5 (Fig. 9). This is a reasonable range if the water first recharges through dolomite and then resides for an unspecified period in the Maynardville Limestone (mainly limestone, some dolomite).

Variations in Ca:Mg ratios (Fig. 9) are not consistent from storm to storm. This suggests that there are unique mixtures of source waters for each storm that depend on storm size, storm duration and antecedent moisture conditions. The decreasing Ca:Mg ratio during the conductivity decrease of storm 3 seems to indicate that recharge water is moving through dolomite. The ratio increases when flow through limestone begins to dominate again.

A mass balance calculation after Dreiss (1989) was attempted using the changes in calcium over time in spring discharge. Based on mass balance, assuming a simple mixture of old and new water, Eq. (1) should hold.

$$Q_s C_s = Q_{old} C_{old} + Q_{new} C_{new} \tag{1}$$

where: Q the discharge; C is the concentration of Ca; s is spring.

Assuming that the mass flux of cations is minor from the new storm water relative to pre-storm water:

$$Q_{new} C_{new} \ll Q_{old} C_{old} \tag{2}$$

If Eq. (1) is solved for Q_{old}, accounting for the assumption in Eq. (2), and is substituted into:

$$Q_s = Q_{old} + Q_{new} \tag{3}$$

Eq. (4) results:

$$Q_{new} \approx Q_s - (Q_s C_s)/C_{old} \tag{4}$$

Use of Eq. (4) makes assumptions that likely do not apply to this system. It assumes that the 'new' water is traveling through the system fast enough that it is not dissolving any carbonate and that the aquifer's 'old' water Ca is constant over time. However, Eq. (4) should still give a minimum estimate of the percentage of new water entering the spring following a storm event. The percentage of recharge water discharging from the spring was calculated based on Eq. (4), assuming $C_{old} = 74$ mg/l for storms 3 and 4 and $C_{old} = 82$ mg/l for storm 5. These values are the peak values following the storms, and should be the most representative value of old water for the system. The results for storms 3–5 indicate that 4–5% of discharge during the recession period is 'new' water. As stated earlier, this is probably a minimum value

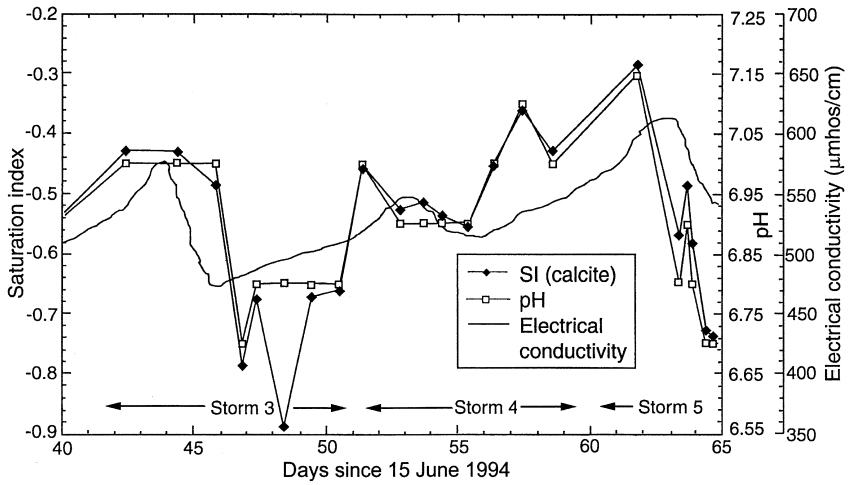

Fig. 10. Variation in saturation index of calcite over time relative to changes in pH and conductivity.

because the recharge water likely rapidly dissolves carbonate on its way to the spring.

6.1. Saturation index

The saturation index (SI) of both calcite and dolomite was determined for each sample by the computer program WATEQF (Truesdell et al., 1974). Calcite is undersaturated in all of the samples collected from the spring and ranges from −0.9 to −0.3 (Fig. 10). Because the SI is directly dependent on pH, and the uncertainty in pH measurements might be as large as ±0.1, a little care is needed in interpreting the results. Assuming that 'old' or pre-storm water is at or near equilibrium, and new water is undersaturated with respect to calcium, the SI of the spring water likely moves toward equilibrium during the initial upswing of conductivity following a storm. Spring water moves away from saturation during the conductivity decrease. This indicates that the water causing the initial increase in the slope of electrical conductivity is older water, whereas some

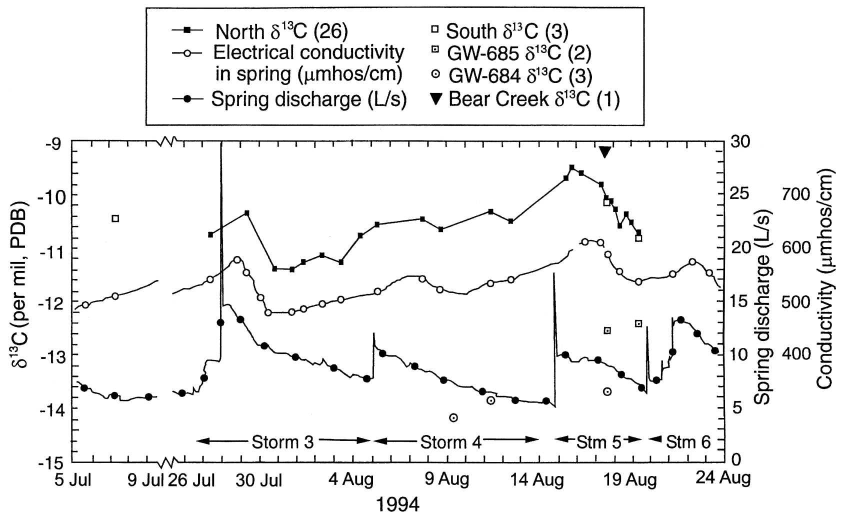

Fig. 11. Stable carbon isotope data collected during the summer of 1994 with electrical conductivity and discharge shown for reference.

component of the water causing the decrease in conductivity is newer water.

7. Stable carbon isotopes

Stable carbon isotopes were analyzed to aid in determining the flow paths of water entering the spring and to distinguish between source waters. Additionally, $\delta^{13}C$ values over time should give some information on old versus new water entering the spring following a rain event.

$\delta^{13}C$ values are graphed in Fig. 11 along with both the discharge and electrical conductivity of the spring for reference. These data cover a period of about 25 days, during which there were three storms. Storm 3 had the most complete coverage of all the storms.

Overall, $\delta^{13}C$ values increased, possibly indicating a larger component of baseflow (i.e. older groundwater in contact with the carbonate rock for a longer period of time and therefore closer to the stable carbon isotope equilibrium value for the system). Following a precipitation event, $\delta^{13}C$ in the spring continued to increase for approximately two days. It then decreased for approximately two days before increasing again.

This pattern of $\delta^{13}C$ response is very similar to the overall electrical conductivity response. It is likely that no 'new' water from the storm is seen in the spring until both conductivity and $\delta^{13}C$ decrease. New water should have a more negative $\delta^{13}C$ signature relative to the 'old' water in the system, since new water is heavily influenced by contact with soil zone CO_2 (not measured in this system, but several reports document values from -25 to $-16‰$ PDB for an area composed mainly of C_3 vegetation; Bishop and Lloyd, 1990; Deines et al., 1974; Back et al., 1983; Rightmire, 1978).

Based on the earlier model it is a bit problematic to account for the $\delta^{13}C$ values in wells GW-684 and GW-685. It would be logical for $\delta^{13}C$ in the well waters to be as heavy as, or heavier than, $\delta^{13}C$ measured in the spring. These two wells, in theory, should represent 'old' water from the Maynardville Limestone. However, $\delta^{13}C$ in the wells is instead consistently lighter relative to the spring. Based on the lack of temperature and conductivity changes in GW-684 and GW-685 relative to the spring, it is evident that these wells either do not tap the main source of water feeding the spring or, represent a very minor portion of the water entering the spring. While the wells may be connected to the spring by a permeable pathway, the natural flow paths to the spring apparently bypass the wells. Additionally, the chemistry in GW-683 is very similar to that of the spring, so this is a possible 'other source' of water for the spring. No stable carbon isotope data are available for this well.

It is possible that the large discrepancy in values between the wells measured and the spring indicates that water flow in the Maynardville Limestone is compartmentalized. The water in wells GW-684 and GW-685 could represent a first water type, the spring water under baseflow conditions and possibly GW-683 could represent a second water type. Recharge water could represent a transient third water type. Compartmentalization undoubtedly would be more complex than can be explained with multiple source waters (e.g. Loop and White, 2001).

8. Conceptual model

The spring response to the seven precipitation events recorded during the three months of the summer of 1994 has many characteristics in common, and an overall conceptual model of the events taking place in the surrounding aquifer and the spring can be constructed. We have divided the spring response into three stages based on the electrical conductivity response, which is a surrogate for the chemistry data, temperature, discharge and $\delta^{13}C$ data from SS-5. The storm responses for each of the earlier mentioned characteristics have been described in detail in Sections 8.1–8.3. The three stages of the model are: (1) flushing, (2) dilution, and (3) recovery.

8.1. Flushing

This stage marks the initial response in the spring (SS-5) to storms. It begins within one hour following the most intense portion of the rainstorm and lasts 0.65–3.8 days. The beginning of this stage is signaled by the increase of the slope of the conductivity curve in the spring. There are 2 hypotheses for the source of the water that causes this flushing of the spring:

1. The flushed water is water that has interacted or

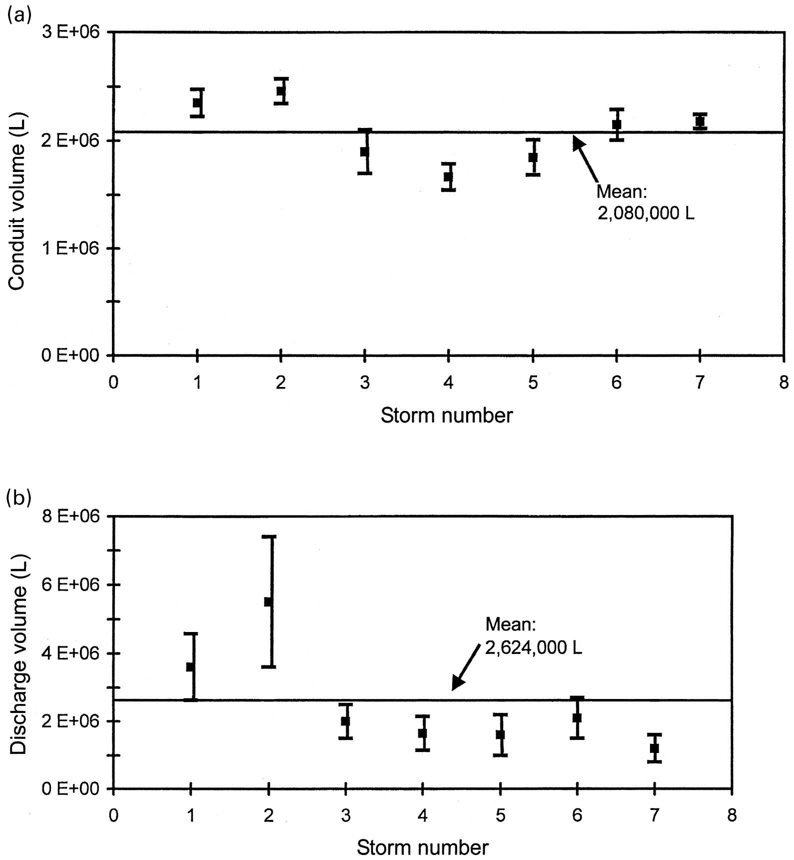

Fig. 12. Conduit volume estimated for each storm from discharge data (a) and discharge volume for dilution phase determined from peak to trough of conductivity curve (b).

equilibrated within the soil zone, and possibly resides in small pores or fractures near the land surface. This water would be relatively warm and likely would contain dissolved salts (or would dissolve salts from the soil during transit), which would give the water a relatively high conductivity. This warmer, high conductivity water would be mobilized by the rainwater infiltrating into the soil and pushed toward the spring.

2. The new rain water is able to rapidly recharge the aquifer, possibly through fractures or surface swallets, and is mobilizing older, deeper water out of the aquifer that has been residing in smaller fractures and pores. This 'older water' is at or near equilibrium with the limestone, but the new water is not. The old water, because it has resided in the aquifer for a relatively long time, would have a higher conductivity than the baseflow spring water. Because of its different pathway it might also be slightly warmer.

The second hypothesis appears to be more probable. The carbon isotope values available from the flushing stage have heavier values of $\delta^{13}C$ relative to samples collected prior to the onset of flushing. If this water moved through the soil zone, it should be lighter, not heavier, than the spring water.

An additional argument against a soil zone source for the flushing phase is that it is unlikely that water moving through a near surface flow zone would actually have a higher conductivity than the spring baseflow value. Nonetheless, it is still possible that a small portion of the water incoming to the spring has a soil or near-surface origin. There are two storms with oscillating temperature signatures that seem to indicate that some portion of the water comes from a near surface source, at least for the larger storms.

Another characteristic of this stage is that many of the storm responses have a sharp initial spike in the discharge and temperature. These spikes are likely caused by precipitation loading on the system. This would aid in the mobilization of the 'old' water trapped in small fractures and pores. The residence times of these waters might be able to be inferred from long-term analysis of deuterium and $\delta^{18}O$ of the spring, well water, and precipitation (Frederickson and Criss, 1999).

The flushing phase lasts between 0.65 and 3.8 days. An explanation for this range is that there is a certain volume of water that must be displaced out of the system before enough new, relatively dilute water can reach the spring. This volume should be relatively constant and should be represented by the total discharge that occurs from the time of initial increase in discharge until the peak in the conductivity curve (Hess and White, 1988). The volume of water calculated for each of the seven storms available (Fig. 12) averages $2{,}080{,}000 \pm 140{,}000$ l. The uncertainty in this estimate results from the error introduced in identifying the conductivity peak. While flushing is observed in this spring, it is not typical of all carbonate springs (e.g. Ryan and Meiman, 1996).

8.2. Dilution

The dilution phase begins with the peak in the conductivity curve and ends when the conductivity minimum is reached. The start of the conductivity decrease represents the first arrival of storm water at the spring. During this phase, the temperature commonly levels off and then remains constant until the next storm whereas discharge continues to decrease. The length of this phase is much less variable than that of the first phase and, with the exception of storm 2, lasts between 2.1 and 2.5 days.

There are two alternative explanations for factors controlling the length of this phase. It could be controlled by the area of the recharge basin. For example, by the end of this 2.1 to 2.5 day period, the water from the farthest extent of the basin has reached the spring. After that time period, the spring begins to 'recover' because there is very little recharge water remaining.

However, the system response can also be explained by a competition between the velocity at which recharge water is moving through the system, how fast this 'new' water dissolves carbonate to gain the same chemistry signature as the 'old' aquifer water, and the amount of mixing that takes place between these two water sources.

Similar to our analysis of the volume of water associated with the flushing phase, we can estimate the quantity of water associated with dilution (Fig. 12). The volume of water discharged from the spring during this phase, from the peak in conductivity to the trough in conductivity, is slightly greater than the average volume of water calculated for the initial flushing phase. However, median value is nearly the same. Perhaps the similarity indicates that these volumes are a measure of a characteristic length scale in the subsurface aquifer.

8.3. Recovery

This phase begins when the minimum is attained in conductivity. During this phase conductivity increases steadily until the next storm begins. The slopes of the recovery curves are different for each of the storms. The concentrations of all the major cations and anions increase during this period. The stable carbon isotope values also become heavier during recovery. All of these changes indicate that the system is returning to equilibrium conditions. The conductivity minimum likely indicates that the last of the recharge water has been in contact with the aquifer rock long enough to begin to dissolve limestone and/or dolomite in sufficient quantity to allow the overall system to begin to recover from dilution.

9. Conclusions

A detailed study of discharge, temperature, conductivity major ion chemistry, and $\delta^{13}C$ variations in a karst spring has revealed a relatively simple conceptual model of the hydrology controlling the spring's response to precipitation event. The spring's discharge response to precipitation events is very well behaved and repeatable over time. The recession of the spring qualitatively appears to be very diffusional in nature. The chemistry of the spring indicates a patchy connection to the groundwater system.

The spring responds rapidly, within 1–2 h following a storm event with regular and rapid changes in the parameters measured. The initial changes in the spring appear to be the result of mobilization of older, and possibly deeper, water from small fractures and pores into the main system feeding the spring. These initial changes include increases in temperature and discharge, heavier carbon isotope values and an increase in the slope of the electrical conductivity curve. The volume of the conduits feeding the spring is apparently constant from storm to storm. This is indicated by the variable length of this initial 'flushing' period, lasting longer for smaller storms. After the conduits are 'flushed', the recharge water reaches the spring, causing dilution until the 'new' water has time to dissolve the amount of carbonate needed to match the 'old' water. This stage takes approximately 2.5 days and is then followed by a stage during which the spring recovers to its previous state.

Recharge water is initially very dilute and does not appear to have any major ionic constituents that can be used to distinguish it from older water. This is different from the situation encountered in nearby Walker Branch where sulfate provided a natural tracer of soil water moving through the system (Mulholland, 1993).

There is minor evidence that a small amount of the recharge water reaching the spring spends some time in the soil zone. Most of the recharge water, however, does not, as is evidenced by the heavy $\delta^{13}C$ values and variable length of the flushing phase. The absence of a significant soil signature was not expected. In contrast to what is likely more typical carbonate spring behavior (e.g. Lakey and Krothe, 1996), older water significantly influences the ionic composition and isotopic signature of this spring.

A consistent conduit volume of discharge has to be removed from the system before the dilution phase begins. Perhaps, the relatively well-behaved and repeatable nature of spring flow and chemistry in the spring analyzed is due to deep circulation of recharge water. This study indicates that relatively simple detailed measurements of flow and chemistry associated with rainfall induced spring flow can yield useful information about the nature of karst subsurface hydrology.

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