The Case of the Underground Passage: Putting the Clues Together to Understand Karst Processes

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ABSTRACT

Contaminants in surface water entering karst aquifers in focused recharge can be transported rapidly through the system to discharge at springs. Such contaminants act as anthropogenic tracers of ground-water transport; analysis of their breakthrough curves as they discharge from springs allows identification and apportionment of contaminant sources, and can provide insight into aquifer structure and function. At Barton Springs, the principal outlet for the Barton Springs segment of the Edwards aquifer, near Austin, Texas, breakthrough curves for several anthropogenic and natural tracers have been analyzed. The proportion of discharge composed of recent recharge is determined with a mixing model for oxygen-18: following rainfall, an initial increase in discharge related to pressure transfer is clearly seen, followed by a further increase consisting of an increasing proportion of recently recharged water, which reaches a maximum about 48 hours after rainfall. First appearance of contaminants varies from less than 20 to more than 40 hours after rainfall, depending on the contaminant, aquifer conditions, and location of contaminant source. Decomposition of breakthrough curves of sediment, nutrients, pesticides, and volatile organic compounds at the different spring orifices indicates the existence and approximate location of multiple conduit flow routes, contaminant times of travel, and probable contaminant sources. Differences in breakthrough curve shape and magnitude indicate urban runoff, contaminant spills, and infiltration through the soil zone as sources of different contaminants. Comparison of contaminant loads in recharging surface water to those estimated for the decomposed breakthrough curves allows apportionment of contaminants to the five watersheds contributing recharge to the aquifer.

Spatial and Temporal Variations in Epikarst Storage and Flow in South Central Kentucky's Pennyroyal Plateau Sinkhole Plain

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ABSTRACT

The well-developed karst aquifers of south central Kentucky's Pennyroyal Plateau are impacted by contamination from animal waste and other agricultural inputs. Understanding fate and transport of these and other contaminants first requires knowledge of flow and storage behaviors within the impacted aquifers, complicated by significant heterogeneity, anisotropy, and rapid temporal variations. Here we report on spatial and temporal variations in vadose zone flow and water chemistry (or quality) within Cave Spring Caverns, Kentucky beneath agricultural lands on a well-developed sinkhole plain. Weekly sampling of three underground waterfalls show statistically significant differences in water quality, though the sites are laterally within 160 m and are all located about 25 m underground, in a groundwater basin of about 315 km^2. These reflect a combination of differences in epikarst flow and land use above the cave. High-resolution (minutes) monitoring of precipitation recharge along with flow and specific conductance in one of the waterfalls reveals a significant storage and mixing reservoir within the soil/epikarst zone. Varying precipitation rates and antecedent moisture conditions result in a range of storm responses observed at the waterfall, depending in part on whether this reservoir is filled or depleted. Slow and rapid flow paths through this storage zone were observed, the latter triggered by high recharge rates. These observations are generally consistent with the interpretations of Perrin and others (2003) from a Swiss limestone aquifer in a somewhat different hydrogeologic setting, strengthening the idea that epikarst and, more generally, vadose zone storage play a key role influencing flow and transport within karst aquifer systems.

INTRODUCTION

Well-developed karst aquifers are extremely vulnerable to contamination due to the ease and rapidity with which fluids can enter and move through these systems. For example, within south central Kentucky's Pennyroyal Plateau, contamination of groundwater by agricultural contaminants associated with animal waste such as fecal bacteria and nitrate is widespread (Currens, 2002; Conrad and others, 1999). Understanding agricultural impacts on karst aquifers is particularly challenging due to significant heterogeneity and anisotropy typically found in these systems, which can lead to large spatial and temporal variations in flow and water chemistry conditions.

The *epikarstic,* or *subcutaneous* zone (Williams, 1983; Perrin and others, 2003; Jones and others, 2003) forms an important component of many karst flow systems. The typically perched epikarst aquifer forms in the vicinity of the soil/bedrock interface where fractures have been widened from dissolution by acidic soil water. As the infiltrating water quickly approaches equilibrium with respect to the limestone bedrock, dissolution rates drop, as does solutionally-enhanced permeability. As a result the epikarst constitutes a relatively high permeability zone in comparison with less permeable rocks below. Evaluating the impacts of epikarst flow and storage is critical for understanding the fate and transport of agricultural contaminants within karst aquifers.

Recently progress has been made in understanding the details of karst flow and geochemical processes by high-resolution monitoring with electronic probes and digital data loggers (e.g. Baker and Brunsdon, 2003; Charleton, 2003; Groves and Meiman, 2005; Liu and others, 2004). The importance for understanding karst dynamics comes not as much for the ability to automatically collect data in relatively remote locations, as for the ability to collect high temporal resolution data. Flow and chemical data with a resolution of minutes capture all significant structures of hydrologic variation, even for karst systems. This can be useful for interpreting information about aquifer structure by comparing the detailed timing and magnitudes of related phenomena. In a recent example, Liu and others (2004) interpreted controls on aquifer behavior in southwest China's tower karst by comparing rates, directions, and magnitudes of changes in water levels, specific conductance (spC), saturation indices, and PCO_2 in storm responses from a large karst spring and nearby well.

While the long-term goal of the research we describe here is to quantitatively understand fundamental controls on relationships between agricultural land use and karst groundwater quality, here we evaluate epikarst flow and storage within south central Kentucky's Pennyroyal Plateau sinkhole plain based on vadose water sampling from three waterfalls located beneath active farming land. Evaluating the hydrologic behavior of the epikarst at the site is a critical step to quantitatively evaluating the fate and transport of agricultural contaminants.

FIELD SITE

Three subsurface waterfalls are being monitored, as well as rainfall and other atmospheric parameters, within and above Cave Spring Caverns (Figures 1-4) near Smiths Grove, Kentucky. The cave is located beneath a small portion of the extensive sinkhole plain of the Pennyroyal Plateau within the Mississippian Plateaus Section of the Interior Low Plateaus Physiographic Province. Just over 2 km of large horizontal cave passages pass beneath several farm fields, with the cave floor typically

about 25 m below the ground surface. Water enters at numerous locations as perennial or intermittent streams or waterfalls. The recharge area lies within the Graham Springs Groundwater Basin (Ray and Currens, 1998) which discharges at Wilkins Bluehole on the Barren River, 18 km to the southwest. Wilkins Bluehole is the second largest spring in Kentucky, with a minimum discharge of 0.56 m^3/s (Ray and Blair, in press).

The cave is formed within the upper part of the Mississippian St. Louis Limestone (Richards, 1964). The Lost River Chert, a discontinuous unit of silica-replaced limestone typically 2-3 m thick near the site, lies between the ground surface and the cave. Locally, beds dip gently to the west at about 1-2º.

South central Kentucky has a humid-subtropical climate. Using climatic data from the Mammoth Cave and Bowling Green areas, Hess (1974) estimated that the area has a mean precipitation of 1,264 mm/yr, and the mean-annual temperature is 13ºC. Late summer and early fall are drier than other months. Hess (1974) estimated that mean-annual potential evaporation is 800 mm, varying from near zero to over 100 mm/mo.

The three percolation waterfalls--1, 2, and 3 in order moving into the cave--fall between about 5 and 8 m from the ceiling along the east side of the main passage starting about 40 m north of the cave's entrance, within a 160 m section of the passage (Figure 1).

METHODS

There are three related sampling programs: surface weather conditions, weekly sampling and laboratory analysis of water at the three waterfalls, and 2-minute monitoring of flow, specific conductance (spC), pH, and temperature at waterfall 1. Details of these sampling programs are provided as follows:

Surface Rainfall

On the surface 110 m south of the cave entrance is an automated HOBO[TM] weather station that collects rainfall, temperature, wind speed and direction,

relative humidity, and solar radiation (Figure 2). Rainfall is resolved to the nearest 0.25 mm, and summed every five minutes. Due to interference by birds over part of the reported period, we utilized five-minute rainfall after 25 March 2005 (including storms 2, 3, and 4 discussed below) from the National Park Service Atmospheric Monitoring Station near the town of Pig, 9.5 km to the northeast.

Field Collection and Laboratory Analysis

Water was collected from each waterfall weekly in sterile, acid-washed HDPE bottles and stored on ice. In most cases water was analyzed within three hours of collection. Water samples were analyzed for a suite of parameters indicative of limestone weathering (e.g. Ca, Mg, alkalinity, and specific conductance (spC)) and agricultural impact (e.g., NO_3, PO_4, and NH_4). Alkalinity was measured using the inflection point titration method (Rounds and Wilde, 2001) and reported as mg/L $CaCO_3$ mg/L. Ca and Mg were analyzed in triplicate using inductively coupled plasma optical emission spectroscopy (ICP-OES). NO_3, PO_4, and NH_4 were measured in triplicate using a Lachat "QuickChem" method. Preliminary analysis indicated that particulate-associated Ca, Mg, and nutrients were minimal; subsequently water samples were not filtered prior to analysis. Dissolved oxygen (DO), pH and spC were measured in the field with a YSI 556 multi probe system (YSI Environmental). Data were collected from February 23, 2005 to May 25, 2005 for Ca, Mg, spC, and DO (n=13), March 3, 2005 to May 25, 2005 for alkalinity (n=12), and March 23, 2005 to May 25, 2005 for NO_3, PO_4, and NH_4 (n=10).

Data Logging at Waterfall One

The site is equipped with an array of electronic sensors and loggers and tied to a common tipping bucket rain gauge (Campbell Scientific (CSI) TE525) resolving tips of 0.1 mm. Discharge from the rain gauge is directed into 10-mm Tygon tubing which feeds a PVC flow-through chamber (20 mm ID) mounted with a series of three Cole-Parmer double-junction industrial in-line ATC pH sensors.

Each pH sensor is connected to a three-meter shielded coaxial cable and terminates in the instrument box (Pelican 1400) at a Cole-Parmer preamplifier to increase signal stability. This pH system can resolve pH to +/- 0.01 SU. The pH flow-through chamber discharges into a section of 10-mm Tygon tubing where it is split into three paths, each passing through a CSI CS547A-L specific conductance/temperature sensor. This sensor can resolve temperature to +/- 0.1°C and specific conductivity to +/- 0.001 mS. The three paths are then rejoined into a single section of tubing and positioned at an elevation approximately 40 cm higher than the sensors to assure pipe-full conditions. The signal from the rain gauge is split into three cables, each connected to a CSI CR10X digital micrologger (Figure 3). Each micrologger is connected to its corresponding set of pH, conductivity (spC) and temperature sensors. This redundancy in spC, temperature, pH, and data loggers not only ensures backup in the case of malfunction, but when fully operational we calculate means, standard deviations, and coefficients of variation (CV) for each observation. The 14,359 spC observations (each made in triplicate) reported in this paper had an average CV of 2.7%. This value is similar to the CV of Waterworks Spring (2%) which has been considered the only perennial "diffuse flow" spring in the region. Waterworks Spring is located near conduit dominated Wilkins Bluehole, which has a greater CV at 14% (Quinlan and others, 1983; p. 57).

Every 30 seconds the micrologger program is executed. The program is set to output tip totals from the rain gauge every five minutes, and to average the 30-second pH, spC, and temperature values every two minutes. To reduce redundant data the program compares the current two-minute average values of each sensor to that of the previous two-minute average. If the absolute value of change exceeds a preset value--the current two-minute average values for all sensors is committed to final storage. In any event, the current two-minute values are always stored once per hour. In this way we achieve two-minute resolution even during hourly recording, because we know under those static conditions the observations have not varied beyond the threshold value.

The waterfall flow data are given in tips per minute for the tipping bucket gage, but these do not yield discharge directly because some of the water, especially at higher flows, falls outside of the bucket orifice. These data thus only give a relative flow indication, but the signals (Figure 5) give a clear indication of dry and wet conditions and their correlation with rainfall events. We are in the process of developing a rating curve relating tips per minute to actual discharge, which we measure periodically by catching the flow in a large tarp and measuring the volumetric flow rate with a 10 liter bucket.

Statistical Analysis of Water Quality Data

Single-factor analysis of variance (ANOVA) was used to determine if statistically significant differences exist in important water quality parameters between the three waterfalls. Differences between waterfall locations may reflect different residence times and land use activities at the surface. Prior to analysis, Ca, NO_3, PO_4, and spC were log-transformed whereas Mg was inverse-transformed to obtain approximately normal distributions. Alkalinity, on the other hand, was normally distributed so no transformation was needed. Fisher's t-test was used to compare means between different waterfalls (Helsel and Hirsch, 1993). All statistical analyses were performed using SAS version 9.1 (SAS Institute Inc., 2003).

RESULTS

Temporal Variations at Waterfall One

Between 21 March and 10 April 2005, precipitation, waterfall flow, and spC data reflect four succeeding rain events that occurred over progressively wetter antecedent moisture conditions. Although we currently lack data for a rating curve, discharge directly measured under very dry conditions at the waterfall (31 May 2005) was 0.04 L s^{-1}. Using an empirical value of 1.98 L s^{-1} km^{-2} for unit base flow (Quinlan and Ray, 1995), derived from preliminary data for the autogenic recharge area of the Graham Springs Basin (Joe Ray, Kentucky Division of

Water, personal communication, 2005), this discharge corresponds to an estimated recharge area for the waterfall of about 2 ha. Estimates of three epikarst spring recharge areas at other sites in Kentucky range from 4-8 ha (Ray and Idstein, 2004). Although the rainfall data after 25 March (storms 2-4) are from 9.5 km away, they show close correlation to the cave signals when there was a response.

Responses of the cave parameters show a varying behavior following the different storm events and thus provide information on flow and storage within the aquifer system. Flow in the waterfall, initially under relatively dry conditions, began to increase within 2.3 hours of the onset of significant rainfall measured above the cave system, and showed a clear flow increase of about 120% that returned to the original condition within about 1.5 days. However, there was no systematic change in the spC signal following this rainfall, as explained later.

About three days later a more intense storm occurred with obvious differences in the cave response. While the timing of the flow increase was similar to the first storm (though rain data for this storm are from the NPS station), flow rates stayed more than twice as high as the initial condition for more than four days without significant rainfall, rather than returning quickly to pre-storm levels. The spC signal from relatively dilute rainfall quickly moving through the system was also clear and corresponded to rainfall intensity, reaching a low of about 160 μS cm^{-1}, or about 70% of pre-storm levels, after an intense thunderstorm cell in which rainfall intensity exceeded 5 cm hr^{-1}. We lost data on peak waterfall flow rate because the flow exceeded the limits of the tipping bucket mechanism, but later modified the equipment to accommodate higher flows.

The next storm, about four days later, was different from the first two with respect to both signals. Flow rates continued at a similarly high level without an appreciable increase, while spC dropped again in very clear relation to rainfall. In contrast to the second storm, however, spC took more than seven days to rise to the same level that had taken

only two days after the previous rainfall, even though starting at a higher minimum level.

Finally, a small storm about five days later, which began with waterfall flow rates at a similarly high rate and spC still uniformly rising through time to pre-storm three levels, had little or no impact on waterfall behavior.

Spatial Water Quality Variations

Significant variations in water quality were observed between the three waterfalls (Figure 6). Both Ca and Mg were significantly higher in waterfall 2 and this is consistent with higher alkalinity and spC values at this location. The average Ca concentration for waterfall 2 was 50.7 mg L^{-1} compared to 32.1 mg L^{-1} and 33.4 mg L^{-1} for waterfalls 1 and 3, respectively (Figure 6A). Similarly, the average concentration of Mg in waterfall 2 was 8.57 mg L^{-1} compared to 5.93 mg L^{-1} for waterfall 1 and 5.02 mg L^{-1} for waterfall 3 (Figure 6B). Alkalinity and spC were also highest in waterfall 2. Mean alkalinity for waterfall 2 was 106 mg $CaCO_3$ L^{-1} and for waterfalls 1 and 3 the mean concentrations were 73.3 mg $CaCO_3$ L^{-1} and 60.0 mg $CaCO_3$ L^{-1}, respectively (Figure 6C). Mean spC was 328 µs cm^{-1} for waterfall 2, 236 µs cm^{-1} for waterfall 1, and 238 µs cm^{-1} for waterfall 3. Differences between waterfall 2 and waterfalls 1 and 3 were statistically significant at the 99% confidence level (Figure 6D).

As was the case with Ca, Mg, spC, and alkalinity, PO_4 was significantly higher in waterfall 2 (p < 0.001) compared to waterfalls 1 and 3 (Figure 6E). PO_4 concentrations averaged 0.204 mg L^{-1} in waterfall 2 whereas mean concentrations were only 0.063 mg L^{-1} and 0.047 mg L^{-1} for waterfalls 1 and 3, respectively. NO_3, on the other hand, was highest in waterfall 3 and lowest in waterfall 1 (Figure 6F). The average concentrations of NO_3-N were 10.4 mg L^{-1}, 8.19 mg L^{-1}, and 5.60 mg L^{-1} for waterfalls 1, 2, and 3, respectively. (For reference, the EPA NO_3-N Maximum Contaminant Level for drinking water is 10 mg L^{-1}) Statistical analysis on log-transformed NO_3-N data indicated that concentrations between the three waterfalls were significantly different (p < 0.001). NH_4 concentrations were at or below detection limit (0.02 mg L^{-1}) for all sampling times at each location.

DISCUSSION

Although the three waterfalls are separated laterally by a total of only about 160 m and at about the same depth underground, within a groundwater basin of over 315 km^2 (Ray and Currens, 1998), statistically significant differences occur in water chemistry between the three sites. These appear to result from a combination of different land use types and subsurface flow path conditions. Differences between parameters expected to result from dissolution of limestone, including Ca, Mg, alkalinity (closely related to bicarbonate concentrations), and spC, appear to indicate a difference in residence times for the flow paths leading to these waterfalls. Increased residence times may be due to greater flow path lengths and/or slower rates of movement through the epikarst and sections of the vadose zone below. Waterfall 2, for example (Figures 6A-6D), shows significantly higher concentrations than waterfalls 1 and 3 with respect to each of these four parameters.

The elevated concentrations of NO_3 and PO_4 measured in the waterfalls, particularly in waterfalls 2 and 3, suggest impact from agricultural land use in the cave's recharge zone. Although we currently lack data to discriminate the individual waterfall recharge zones (tracer testing is in progress to evaluate these), there are three different patterns in the concentrations of these compounds (Figures 6E and 6F) and indeed three general types of land use above the cave (Figure 1). Above and south of the first 90 m of the cave entrance (Figure 1, parcel A) is residential, the area to the north over the next 200 m (parcel B) had row crops (wheat) during the sampling period, and the area across the road to the east (parcel C) had cattle production. The row crops had both animal waste and chemical fertilizers applied before and during the study, while no chemicals were applied to either parcel A or C during or before sampling. While somewhat speculative until more data become available, a hypothesis consistent with the results so far might indicate that waterfalls 1, 2,
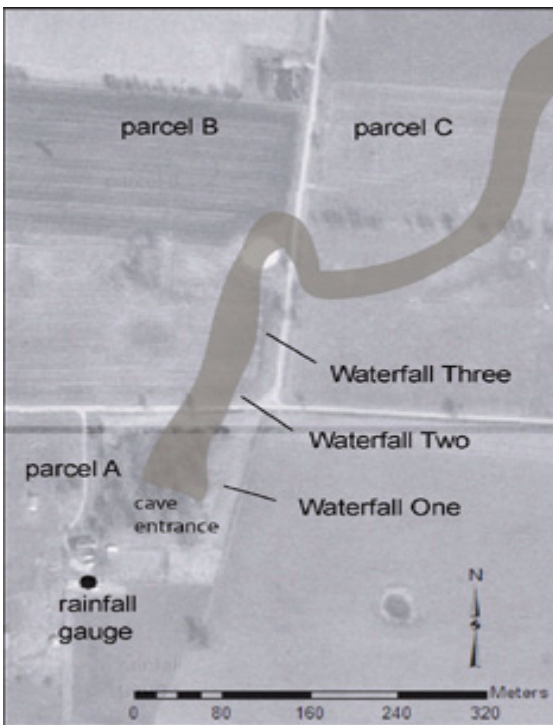
Figure 1. Map of the entrance area to Cave Spring Caverns showing sampling locations in relation to surface.

Figure 2. Weather station for recharge measurements, showing typical surface landscape above the cave system.
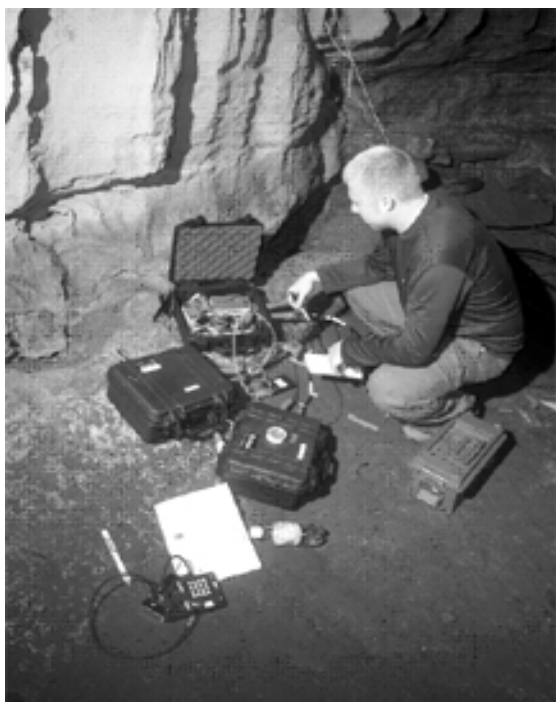

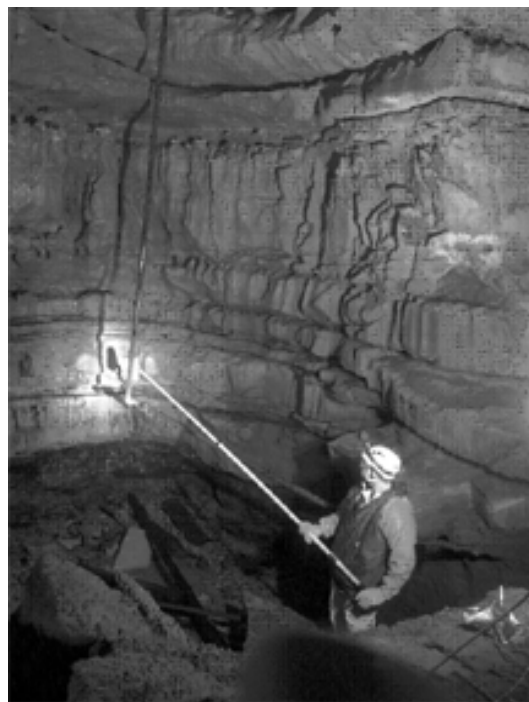Figure 3. Triplicate Data logger system at Waterfall One.

Figure 4. Water sampling at Waterfall Three using remote device to avoid a shower while sampling.

and 3 have at least partial recharge zones in parcels A, B, and C, respectively. This is indicated by water relatively low in both NO_3 and PO_4 from A (residential), higher in both from B (animal and chemical fertilizers), and from C where NO_3 is high from cattle waste but PO_4 is low because no fertilizer was applied. As the rocks within which the cave has formed are dipping to the west, it is feasible that some parts of the waterfall recharge zones could be located to the east in parcel C.

Comparison between rainfall and flow and spC at waterfall 1 (Figure 6) reveals significant storage within the soil/epikarst above the cave, as well as slow and rapid flow paths through the epikarst whose functions depend on recharge rates and antecedent moisture. The spC signal at the onset of the record (~220 mS cm^{-1}) represents water that has reached an approximate chemical equilibrium with the soil/epikarst system. This signal is at times diluted by rainfall that has a typical spC of 10-15 mS cm^{-1} as measured at the NPS Atmospheric Monitoring Station (Bob Carson, National Park Service, personal communication).

While the flow conditions clearly responded to the input from the first rainfall (~day 81) the fact that spC did not change suggests that no dilute rainwater reached the probes, and that the storm input altered the hydraulic gradients within the epikarst in a way that pushed through a slug of previously-stored water, which drained through in about 1.5 days. While another possibility is that rainwater did indeed come through quickly but had within a short period developed the chemical characteristics of the epikarst storage, consideration of later storms, discussed below, makes this unlikely.

The intense rainfall beginning on day 86 was sufficient to impact the waterfall's spC indicating a relatively rapid transport of rainwater through the system within about one-half day, although it is impossible to measure this timing more accurately as these rainfall data came from 9.5 km away. Once this flow had been established, water from a large, very intense thunderstorm cell (occurring over the cave at about the same time as the more distant rain

gauge, based on observations at the cave) caused a precipitous drop in spC within hours. While the spC returned to within 5% of its pre-storm values with less than eight hours after the spC minimum, the fact that flow remained high instead points to a significant epikarst storage reservoir. We interpret the differences in these two storms to suggest that this reservoir was relatively depleted during the dry antecedent conditions prior to the first storm, but was "replenished" during the large recharge event of storm 2. Differences in the three-dimensional head distributions within the epikarst water between the filled and depleted reservoir conditions account for differences in the responses. The more gradual return to prestorm spC conditions over the next several days reflects both mixing of storage and rainfall waters, as well as chemical reactions (limestone dissolution, for example) that increase the ionic strength of recharge water. The storm 2 response also suggests a recharge intensity threshold above which a rapid flow path is established, in addition to the more diffuse flow paths continually present.

These interpretations are consistent with the response from the third storm (day 92), which was intense but occurred under antecedent conditions with relatively full epikarst storage. The return to pre-storm chemical conditions is more gradual than in the previous storm, however, reflecting the greater proportion of storm to chemically equilibrated water within the reservoir. These two responses also indicate that the timescale for chemical mixing/ equilibration for these waters is on the order of several or more days, confirming that the slug of water pushed through during the first storm was already in the aquifer prior to that storm's onset.

Using flow and isotope measurements of rainfall and spring water, as well as underground streams leading to the spring, Perrin and others (2003) concluded that the soil/epikarst system forms an important mixing reservoir and were able to discriminate waters contributed by diffuse and rapid flow through the epikarst reservoir, the latter operating when a threshold recharge rate has been exceeded. These findings are similar to those obtained in the present study, and taken together, the
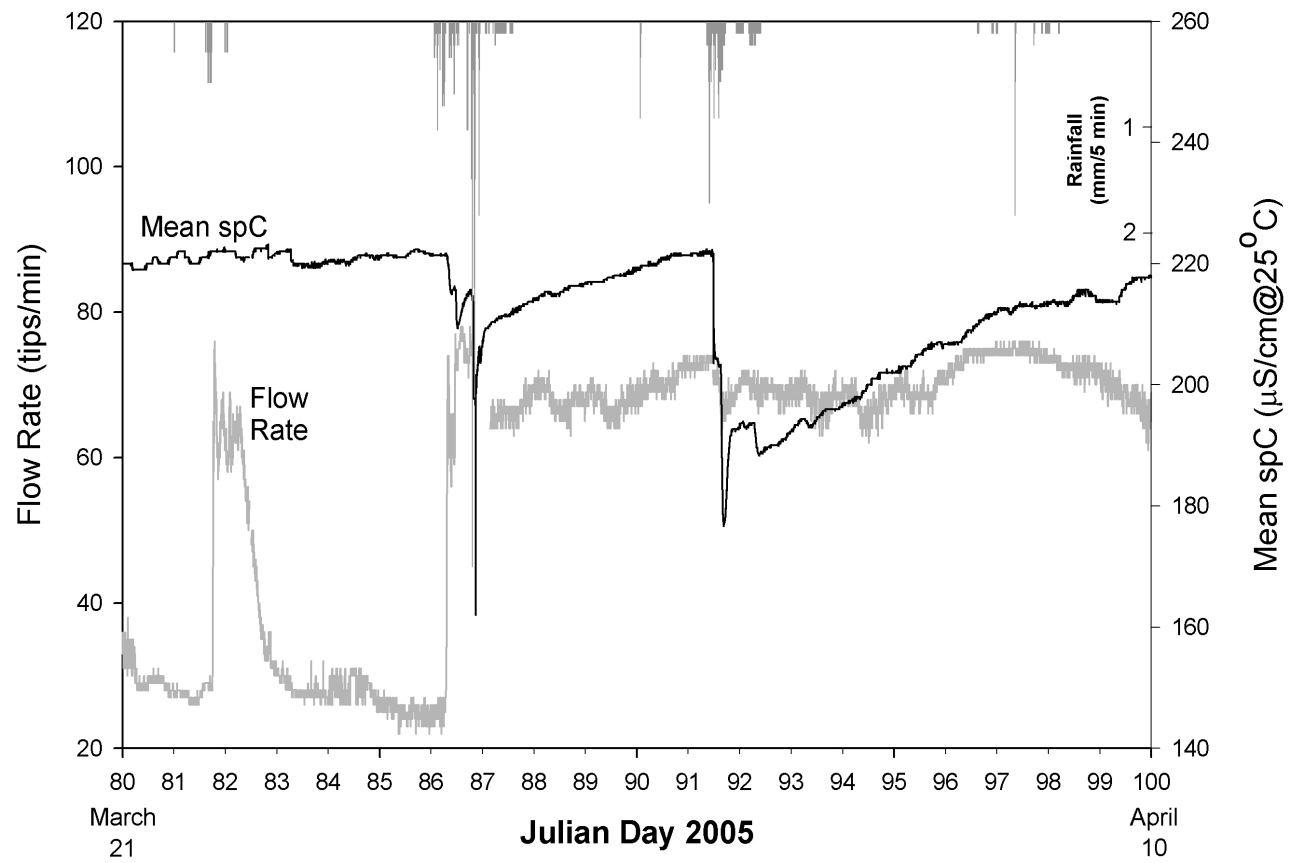
Figure 5. Plots of flow rate and mean specific conductance for waterfall 1 in Cave Spring Caverns, along with rainfall above the cave.
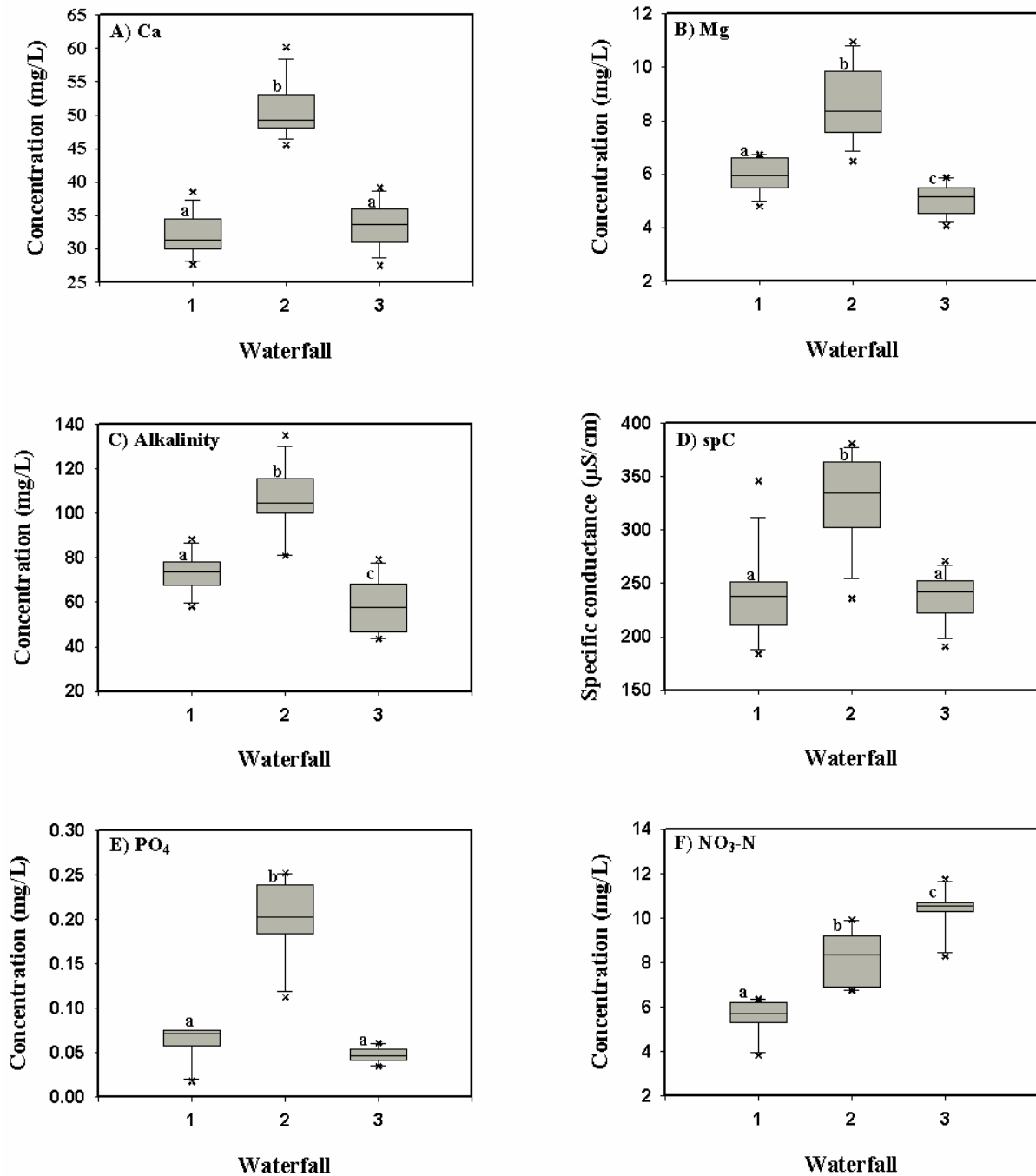
Figure 6. Boxplots of (A) calcium (mg L^{-1}), (B) magnesium (mg L^{-1}), (C) alkalinity as CaCO$_3$ (mg L^{-1}), (D) specific conductance (μS cm^{-1}), (E) phosphate (mg L^{-1}), and (F) nitrate-N (mg L^{-1}). Boxes with same letter are not significantly different based on Fisher's t-test on means of transformed (ca, Mg, Spc, NO$_3$, and PO$_4$) and untransformed data (alkalinity).

two studies provide quantitative evidence to strengthen the hypothesis that vadose zone storage plays a key role influencing flow and transport within a variety of karst aquifer systems.

ACKNOWLEDGMENTS

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Comparison of Water Chemistry in Spring and Well Samples from Selected Carbonate Aquifers in the United States

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ABSTRACT

Water chemistry in samples from 226 wells and 176 springs were assessed to determine if samples from springs and wells have similar concentrations of selected properties such as dissolved solids, dissolved oxygen, nitrate, and calcite and dolomite saturation indices. Samples were collected in seven carbonate aquifers–Edwards-Trinity, Floridan, Mississippian, Basin and Range, Valley and Ridge, Springfield Plateau, and Ozark. Comparisons were made between concentrations of inorganic constituents in water samples from springs and from wells within the same aquifer. Results were variable, but showed that concentrations were not significantly different between samples from springs and wells for most properties. Nitrate and dissolved solids concentrations were only significantly different between spring and well samples in one or two of the seven aquifers; however, dissolved oxygen concentrations were significantly different between well and spring samples in four of the seven aquifers. Median calcite and dolomite saturation index values were significantly different between well and spring samples in three of the seven aquifers. Spring samples probably represent water from shallower parts of the aquifer flow systems and thus represent parts of the flow system that are most susceptible to contamination from land-use practices. These results indicate that the collection of water from springs should be considered critical to adequately characterize water quality in carbonate aquifers.

INTRODUCTION

About 20 percent of the ground water withdrawn for drinking water in the United States is from carbonate aquifer systems (M.A. Maupin, U.S. Geological Survey, written commun., 2004). Understanding the factors that control water quality in these systems requires information on water chemistry from the aquifer matrix, fractures, and from secondary porosity features (e.g., solution conduits). Comprehensive monitoring strategies that include the sampling of both springs and wells (Quinlan, 1989) have been used to interpret geochemical variability that arises from ground-water flow through different parts of a carbonate aquifer system (Scanlon, 1990; Adamski, 2000).

Water samples were collected from 226 wells and 176 springs in seven carbonate aquifers from 1993 through 2003 as part of the U.S. Geological Survey's National Water-Quality Assessment Pro-gram. This number of samples from carbonate aquifers around the United States represents an opportunity to explore the differences in major-ion chemistry between samples collected from wells and from springs. Limestone and dolomite units were sampled within the following aquifers: Edwards-Trinity, Floridan, Mississippian, Basin and Range, Valley and Ridge, Springfield Plateau, and Ozark (fig. 1). These limestone and dolomite units range in age from Cambrian to Quaternary (Adamski, 2000; Miller, 1990; Maclay, 1995) and some are interlayered with sandstone or chert layers (Dettinger and others, 1995; Johnson, 2002; Kingsbury and Shelton, 2002).

COMPARISON OF SAMPLES FROM SPRINGS AND WELLS WITHIN SELECTED AQUIFERS

Spring and well water samples were collected from seven aquifers—Edwards-Trinity, Floridan, Mississippian, Valley and Ridge, Basin and Range,
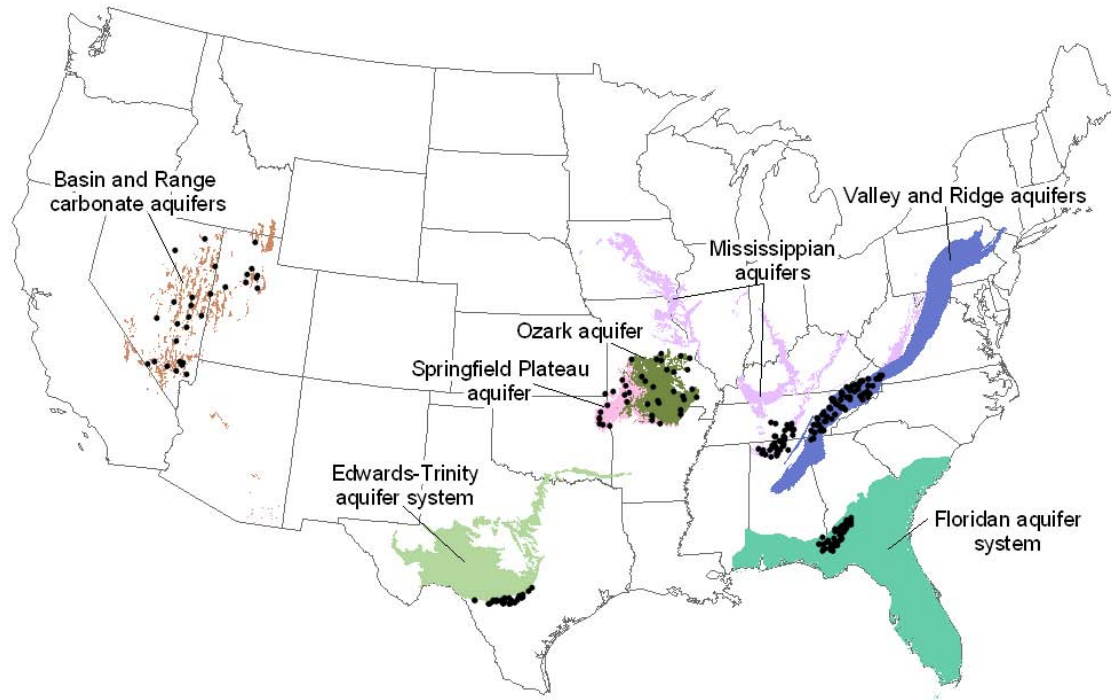
Figure 1. Location of spring and well sites sampled from 1993-2003.

Springfield Plateau, and Ozark. Within each aquifer, the number of water samples collected from springs ranged from 6 to 58 samples and the number of samples from wells ranged from 18 to 57 (fig. 2). In the Floridan aquifer system, samples were collected exclusively from the Upper Floridan aquifer, thus Upper Floridan will be used for the remainder of this discussion. Comparisons were made only between
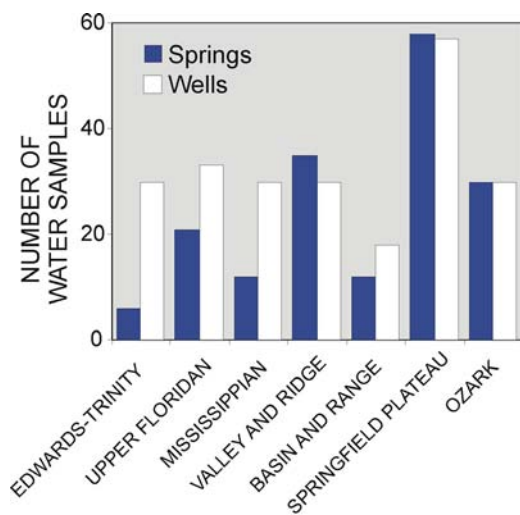

Figure 2. Number of spring and well samples collected from selected aquifers.

the water samples from springs and wells within a given hydrogeologic setting in each aquifer.

For example, in the Upper Floridan aquifer, samples were collected from throughout the extent of the aquifer, but spring water samples were collected only in southwestern Georgia; thus, these spring water samples were compared only to well samples collected in the same hydrogeologic setting in southwestern Georgia. The nonparametric Wilcoxon rank-sum test (Helsel and Hirsch, 1992) was used to determine if concentrations of constituents were significantly different (level of significance 0.05) between water samples collected from wells and springs.

Major Dissolved Species

Calcium-bicarbonate is the dominant water type for all of the aquifers and aquifer systems; however, the chemical composition of water samples from the springs and wells in the Basin and Range aquifer system was highly variable. In most aquifers, fewer than half of the 14 inorganic constituents examined showed significant differences in

Table 1. Summary of p-values from Wilcoxon rank-sum test comparing concentrations between samples from springs and wells.

[P-values lower than the level of significance, 0.05, are shaded gray; <, less than]

Aquifer	Calcium	Magnesium	Sodium	Potassium	Iron	Manganese	Bicarbonate	Sulfate	Chloride	Nitrate	Silica	pH	Dissolved oxygen	Dissolved solids
Edwards-Trinity	0.20	0.78	0.46	0.36	1.00	0.51	0.01	0.63	0.52	0.98	0.75	0.98	0.63	0.38
Upper Floridan	0.68	0.69	0.58	0.59	0.01	0.01	0.45	0.37	1.00	0.16	0.80	<0.01	0.12	0.52
Mississippian	0.70	0.61	0.05	0.72	0.14	0.44	0.74	0.38	0.08	0.36	0.18	0.11	<0.01	0.40
Valley and Ridge	0.36	0.18	0.17	0.06	<0.01	<0.01	0.16	0.01	0.29	0.09	0.10	0.08	<0.01	0.05
Basin and Range	0.08	0.85	0.25	0.44	<0.01	<0.01	0.25	0.24	0.92	0.98	1.00	0.09	0.66	0.25
Springfield Plateau	0.34	0.08	0.54	<0.01	0.33	0.10	<0.01	0.16	<0.01	<0.01	<0.01	<0.01	<0.01	0.05
Ozark	<0.01	<0.01	0.04	0.51	0.45	0.09	0.05	0.12	0.23	0.95	0.94	0.05	<0.01	<0.01

concentrations between springs and well samples (table 1). The greatest number of inorganic constituents with significant differences in concentration was seven in the Springfield Plateau aquifer. In three aquifers—Edwards-Trinity, Mississippian and Basin and Range—significant differences in concentrations were noted for only one or two properties, indicating that samples collected from springs and wells were collected from ground water from similar locations within the aquifer flow systems.

The range in dissolved solids concentrations among the seven aquifers provides some information about the relative residence times and flow path lengths in the aquifers. Aquifers with greatest median dissolved solids concentrations in spring and well samples, the Edwards-Trinity aquifer (322 and 294 milligrams per liter (mg/L), respectively) and the Basin and Range aquifer (410 and 364 mg/L, respectively), also had the greatest median well depths—1,270 feet (Edwards-Trinity) and 940 feet (Basin and Range). The median well depths for wells in the other aquifers ranged from 87 to 227 feet. Water from the deeper wells with greater dissolved solids concentrations may indicate that longer flow paths and older ground water are being sampled in these aquifers. Dissolved solids concentrations were only significantly different between spring and well samples in the Valley and Ridge and Ozark aquifers (fig. 3).

Median dissolved oxygen concentrations ranged from 2.5 mg/L in water samples from the Basin and Range aquifer wells to about 8 mg/L for springs in several of the aquifers (fig. 4). In four of the seven aquifers, dissolved oxygen concentrations were significantly different between samples from springs and wells (fig. 4). In each aquifer where significant differences in dissolved oxygen were noted, the spring samples have the greater dissolved oxygen concentrations, indicating generally younger waters and more dynamic flow systems. The median dissolved oxygen concentration in water samples from wells was greater than that for springs in the Edwards-Trinity aquifer. Deeper, more regional circulation of ground water may account for lower dissolved oxygen concentrations in some springs in the Edwards-Trinity aquifer.
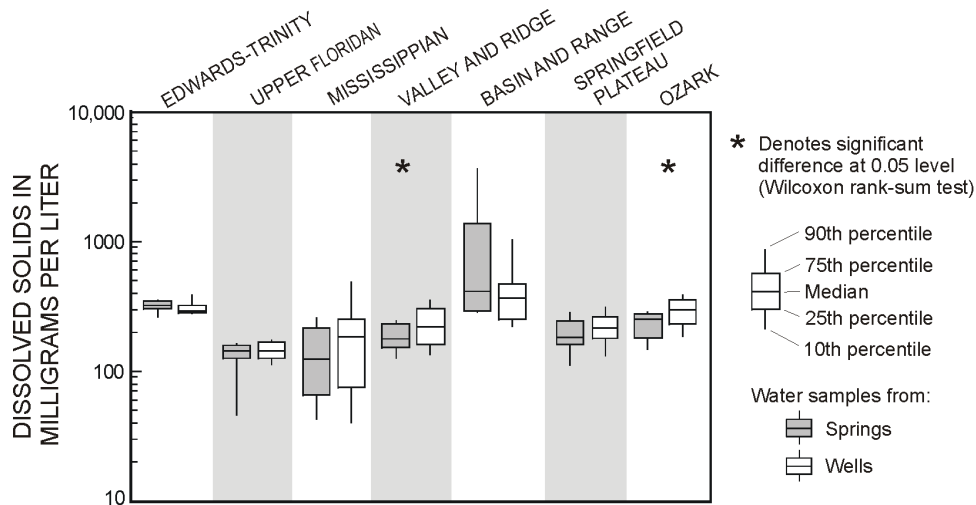
Figure 3. Distribution of dissolved solids concentrations in samples from springs and wells.
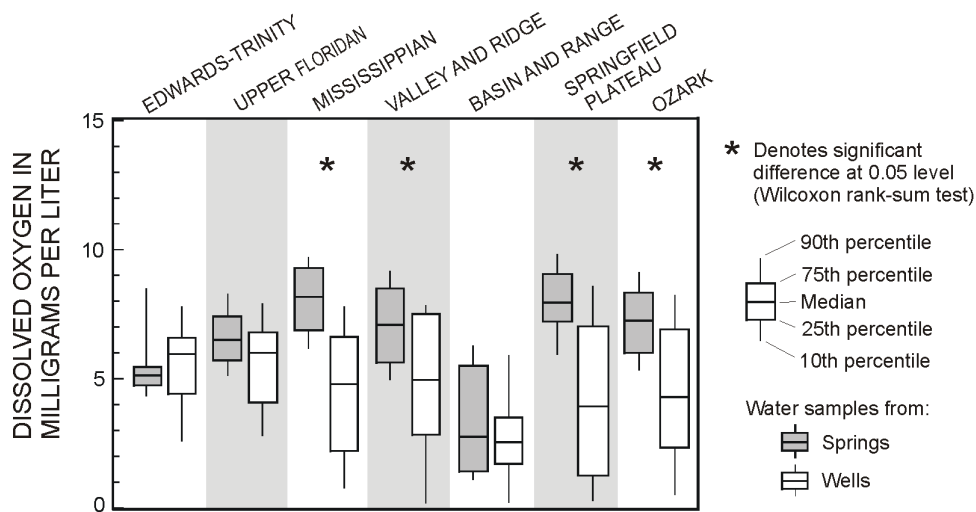

Figure 4. Distribution of dissolved oxygen concentrations in samples from springs and wells.

Saturation Indices with Respect to Calcite and Dolomite

Saturation indices were calculated for calcite and dolomite using the program PHREEQC (Parkhurst and Appelo, 1999). In most aquifers, the calcite saturation index values for the spring and well samples were at or near equilibrium (values of 0 +/- 0.2 are considered to represent equilibrium) (fig 5a). Most water samples were undersaturated with respect to calcite (values less than -0.2) for the Mississippian aquifer. Minerals in these aquifer materials may be less soluble than the aquifer materials in most of the other carbonate aquifers sampled.

Calcite saturation index values were significantly different between water samples from springs and wells in three of the seven aquifers—Upper Floridan, Springfield Plateau Ozark aquifers (fig. 5a). In each aquifer where the calcite saturation index values were significantly different (and in three of the other aquifers where significant differences were not noted), the significantly lower values were in the spring samples, indicating waters from
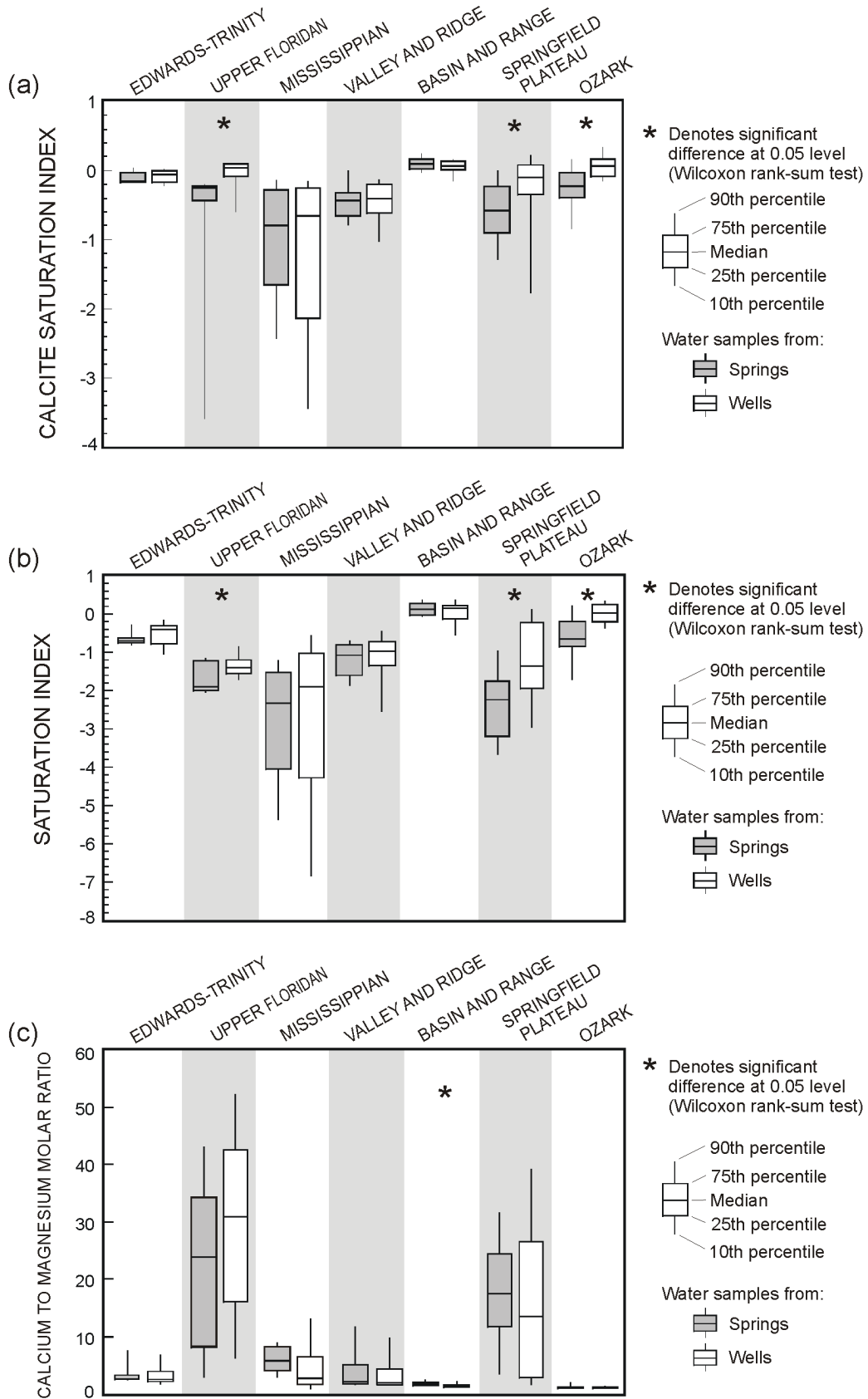
Figure 5. Distribution values for (a) calcite saturation index, (b) dolomite saturation index, and (c) calcium to magnesium molar ratio in samples from springs and wells.

springs were more undersaturated with respect to calcite than water from wells. The lower calcite saturation index values also indicate that spring waters may originate from shallower parts of the flow systems than the water withdrawn from wells.

Spring and well water samples for most of the aquifers were undersaturated with respect to dolomite (fig 5b). Only spring and well samples from the Basin and Range aquifer and well samples from the Ozark aquifer were at or near equilibrium with respect to dolomite (values mostly between -0.2 to 0.2) (fig 5b). Dolomite saturation index values for the spring and well samples were significantly different in three of the seven aquifers—Upper Floridan, Springfield Plateau, and Ozark (fig. 5b)—the same three aquifers where significant differences were noted for calcite saturation index values. In each of the three aquifers where dolomite saturation index values were significantly different (and in the four aquifers where significant differences were not noted), the significantly lower values were in the spring samples indicating that the spring samples were more undersaturated with respect to dolomite than the samples from wells.

The molar ratio of calcium to magnesium was calculated for each sample to determine if this ratio correlates with the relative amount of dolomite in the carbonate aquifers. Results show that in five of the aquifers, calcium-magnesium molar ratios were

less than about 5, and are consistent with the reported mineralogy for the Edwards-Trinity, Mississippian, Valley and Ridge, Basin and Range, and Ozark aquifers (fig. 5c) (Maclay, 1995, Kingsbury and Shelton, 2002, Johnson, 2002, Dettinger and others, 1995, and Adamski, 2000). The three aquifers where the most dolomite is indicated (where the calcium-magnesium ratios were lowest), Edwards-Trinity, Basin and Range and Ozark aquifers, were also the aquifers where dolomite saturation index values were highest (greater than -1.0) (figs. 5b and 5c).

Nitrate

Median nitrate concentrations in the seven aquifers ranged from 0.32 to 2.5 mg/L (fig. 6). Median concentrations were lowest (less than 1.0 mg/L) in the spring and well water samples from the Basin and Range and the Ozark aquifers. Although median nitrate concentrations did not exceed the maximum contaminant level of 10 mg/L, several median nitrate concentrations ranged from 1 to 4 mg/L, which may indicate anthropogenic inputs. Nitrate concentrations were only significantly different between spring and wells samples in the Springfield Plateau aquifer. The significantly higher concentrations in nitrate in water samples from springs relative to wells in the Springfield Plateau was noted by Adamski (2000) who attributed the higher nitrate concentrations to the greater susceptibility of
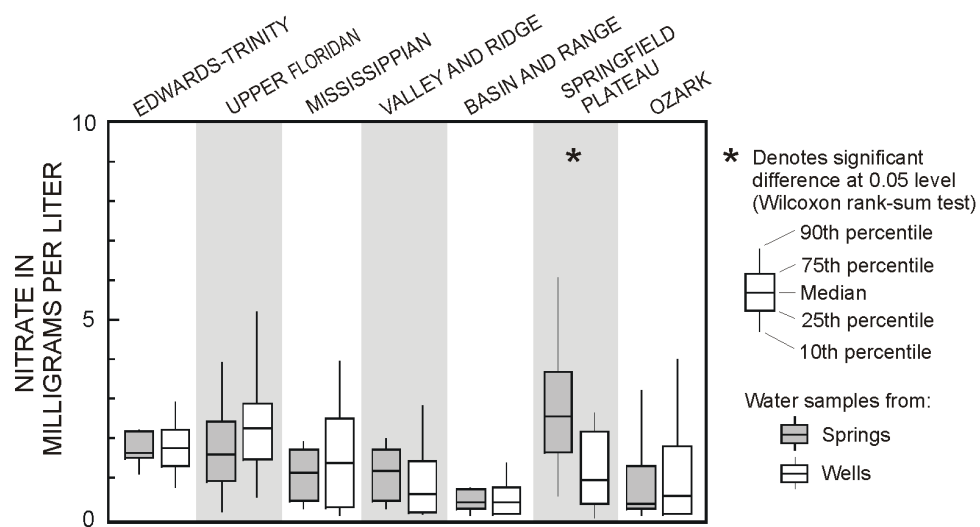

Figure 6. Distribution of nitrate concentrations in samples from springs and wells.

springs to surface sources of contamination. The land use in the area overlying the Springfield Plateau aquifer is predominantly agriculture (Adamski, 1996).

IMPLICATIONS FOR USE OF SPRINGS IN THE CHARACTERIZATION OF WATER QUALITY IN CARBONATE AQUIFERS

Differences in chemistry between spring waters and well water reflect ground-water movement in distinct parts of the flow system. Higher dissolved oxygen concentrations, lower saturation indices with respect to calcite and dolomite, and lower dissolved solids concentrations relative to water from wells, indicate that springs discharge ground water mainly from shallow parts of most of the studied aquifer systems. Exceptions are the Basin and Range and the Edwards-Trinity aquifers, where deeper circulation of ground water may occur prior to discharge from springs. Chemical differences between water from springs or wells also are related to the hydrologic conditions at the time of sampling. Rainfall patterns should be evaluated along with spring discharge at the time of sampling to characterize the contribution of recent recharge to the aquifer and its impact on ground-water chemistry.

There were no consistent patterns when comparing nitrate concentrations in spring waters and well water. Nitrate concentrations were significantly higher in spring water than in ground water in the Springfield Plateau aquifer, but not in the adjacent Ozark aquifer. Nitrate concentrations were higher in spring waters than in well waters from the Valley and Ridge aquifer, but nitrate concentrations in spring waters were similar or lower than nitrate concentrations in well waters from the Edwards-Trinity, Upper Floridan, Mississipian, and Ozark aquifers. These differences likely reflect the complex relation between nitrate concentrations in ground water and various nitrogen sources, and include past and present land-use and waste-management practices, and hydrologic and climatic variability.

Spring samples most likely represent water from shallower parts of the aquifer flow systems, and flow through large solution openings in carbonate aquifer systems. These parts of the flow system are also the parts of the aquifer systems most susceptible to contamination from land-use practices. For these reasons, obtaining water samples from springs, in addition to wells, may be necessary for adequate characterization of water quality in carbonate aquifers and for addressing their susceptibility to contamination.

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