

SPATIAL AND TEMPORAL VARIATION OF GROUNDWATER CHEMISTRY IN PETTYJOHNS CAVE, NORTHWEST GEORGIA, USA

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A longitudinal study of water chemistry in Pettyjohns Cave, Georgia, reveals a wide range of major ion water chemistry at different sampling points within the cave, and pronounced seasonal water-chemistry variations at some locations. The cave occurs in the Mississippian Bangor Limestone on the east side of Pigeon Mountain in the Appalachian Plateaus physiographic province of northwest Georgia, USA. Four sampling points within the cave were monitored at approximately 2- to 3-month intervals for 22 months: a major conduit stream; a small conduit tributary; water dripping into the cave through a small fracture; and water dripping from active speleothems. Other waters, including surface water, were sampled as available. Samples were analyzed for temperature, pH, specific conductance, alkalinity, and major ions. Most spatial water chemistry trends within the cave appear to be the result of rock-water interaction along distinct subsurface flowpaths. Temporal variations, most pronounced in conduit streams, result primarily from mixing of distinct waters in varying ratios, although seasonal changes in CO₂ partial pressure may account for some variation. Results illustrate the inherent spatial and temporal variability of water chemistry in karst aquifers and point to the need to design sampling programs carefully.

Karst aquifers are difficult to characterize because of their inherent heterogeneity. Water chemistry, for example, can vary tremendously over very short distances depending upon whether a sample is drawn from an actively flowing conduit or from rock matrix (Quinlan & Ewers 1985). Water chemistry also varies over time in response to seasonal changes in recharge and dilution effects of individual storms (Hess & White 1988). Along subsurface flowpaths, waters can be modified by CO₂ outgassing, mineral dissolution and/or precipitation, and mixing (Dreybrodt, 1981; Herman & Lorah, 1986; Holland *et al.* 1964;). Finally, karst aquifers typically possess several chemically distinct recharge sources including internal runoff, sinking streams that originate in adjacent borderlands, and diffuse infiltration (Drake & Harmon 1973). Much karst water variability results from mixing among these recharge sources and from rock-water interaction.

This study demonstrates spatial and temporal variability of groundwater chemistry within a relatively small portion of a karst aquifer, and identifies mechanisms responsible for the observed variation. These results provide a detailed look at karst aquifer flowpaths and water types that are not normally resolved separately. Understanding such small-scale variability of karst water is important for understanding sources of large-scale water chemistry variability in karst systems. The study highlights the complexity of karst aquifers and underscores the importance of designing karst water sampling programs carefully.

Waters analyzed in this study were collected in and around Pettyjohns Cave, northwest Georgia, USA. They are derived from surface and subsurface water sources and many apparently distinct flowpaths. Water samples were collected over a 22-month period and, thus, also capture seasonal water-chem-

istry fluctuations. The study was prompted by observations of the many and varied water sources within Pettyjohns Cave, and the obvious role of the cave as a capture and mixing zone for these waters. As is the case in many caves, it is possible in Pettyjohns Cave to stand ankle-deep in one conduit stream within sight of one or more tributary streams, while watching water trickle into the cave through fractures, vertical shafts, and/or ceiling formations. Within the cave, chemically distinct waters from these varied sources mix and ultimately discharge via springs at the conduit terminus. The amount and proportion of different waters entering the cave varies with seasonal precipitation. Thus, waters that owe their composition to mixing of different input sources will reflect these changes. An initial hypothesis was that most temporal and spatial trends in the cave, especially those in the main conduit, could be explained by mixing of two endmember waters. During times of low flow, water composition appeared to shift toward a slowly infiltrating, concentrated endmember; during times of high flow, waters appeared to be diluted by a rapidly-infiltrating, fresh-water endmember. Although this scenario appears to be true for conduit waters, there are important deviations from a simple mixing model.

Objectives of the study are to characterize major-ion water chemistry within Pettyjohns Cave and to identify spatial and temporal trends in water composition. Questions addressed include: 1) To what extent does mixing of chemically distinct input waters control water chemistry variations within Pettyjohns Cave? 2) If mixing is important, what endmember waters are involved? 3) In addition to mixing, what other processes control chemical composition of cave waters? 4) Are there significant temporal variations in water chemistry? The main hypotheses argued in this paper are: 1) most observed

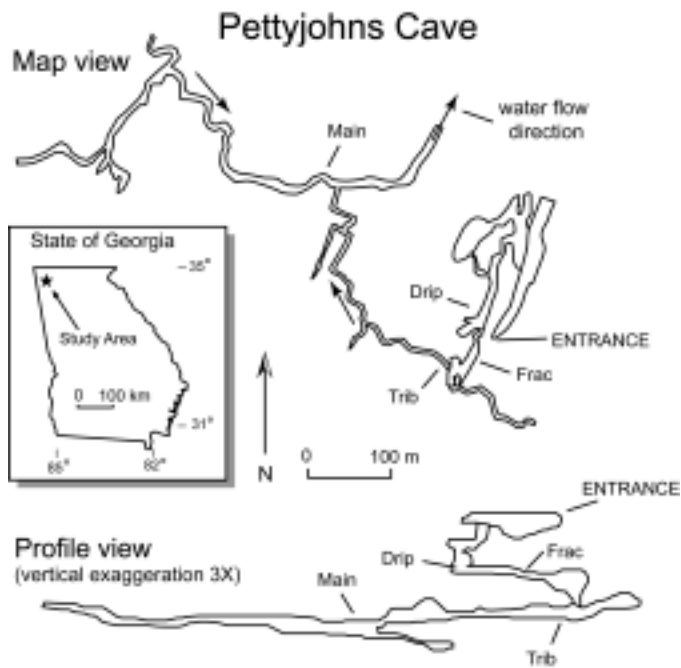


Figure 1. Map and profile of studied portion of Pettyjohns Cave (map after Schreiber, 1985; profile after Crowell, 1993).

spatial water chemistry trends within the cave are the result of rock-water interaction along distinct subsurface flowpaths (some separated only by a few meters); and 2) temporal variations result primarily from mixing of chemically distinct waters.

LOCATION

Pettyjohns Cave (Fig. 1) is on the southeastern margin of the Appalachian Plateaus physiographic province of northwest Georgia (Hack 1986) and contains more than 9750 m of surveyed passage (Schreiber *et al.* 1985). The cave lies on the east side of Pigeon Mountain within the Mississippian Bangor Limestone, and is overlain by Mississippian and Pennsylvanian shale and sandstone (Cressler 1964). Pettyjohns Cave is an excellent setting in which to study karst water chemistry because of the many and varied water sources within the cave. Several trunk passages possess perennial streams that converge within the cave, along with countless smaller rivulets derived from small conduits and shafts; slowly infiltrating water drips into the cave from numerous small fractures and actively growing speleothems. There appear to be two major sources of recharge to the cave. One is a series of surface streams that originate on sandstones and shales atop Pigeon Mountain, and infiltrate through streambed fractures where streams cross from clastic rock units onto underlying limestone rocks. The second source is diffuse infiltration that falls as precipitation both on sandstone-capped uplands and on limestone and alluvium of valley bottoms. There is little or no

direct surface runoff into the cave through large conduits or sinkholes. Thus, water levels in the cave do not fluctuate rapidly, and all water entering the cave undergoes at least moderate rock-water interaction in the subsurface. The discharge point for cave waters is Dickson Spring, a large conduit spring ~1600 m south of the cave entrance (A. Padgett, personal communication, 1999).

METHODS

Major-ion water chemistry was assessed at numerous points within the cave and in surface streams above the cave. In the field, samples were analyzed for pH, temperature, and specific conductance. Samples collected in the cave in 250 ml polyethylene bottles were transferred to a cooler at the surface and transported to the laboratory. Subsamples for major ion analysis were filtered through 0.45 μm membrane filters. Cation samples were acidified to pH <2.0 with trace-metal grade nitric acid. Processed samples were stored in polyethylene bottles and refrigerated. Bicarbonate concentration was determined by alkalinity titration of unfiltered sample with 0.1 N HCl to an assumed bicarbonate endpoint of pH 4.5. Titrations were completed within 24 hours of sample collection. Alkalinity was also determined with potentiometric titration on a sample subset. However, titration to a fixed endpoint yielded results within experimental error and was used for routine alkalinity determination in this study. Major cation composition was determined by inductively coupled plasma-atomic emission spectrometry. Major anion composition was determined by ion chromatography. Total dissolved ion (TDI) concentration was determined by summing concentrations of major ions reported in Table 1. Carbon dioxide partial pressure and calcite saturation indices were calculated using the computer code WATEQF (Plummer *et al.* 1976). Analysis and quality control procedures followed standard methods (American Public Health Association 1995). Analyses for which charge-balance error exceeded 5% were eliminated from the dataset.

Waters were analyzed on an approximately bimonthly basis from January 1997 through October 1998. Conditions permitting, three sites within the cave were sampled on each visit (Fig. 1): water dripping from a small fracture (frac); a tributary to the main cave conduit stream (trib); the main cave conduit stream (main) upstream from confluence with tributary. In addition, numerous other points were sampled as available according to flow conditions and accessibility, including other points along cave streams, water infiltrating rapidly into the cave through large fractures and shafts, water dripping from actively growing speleothems (drip), and surface waters above the cave (sfc).

RESULTS

MAJOR ION CHEMISTRY

Cave waters are very similar in overall composition (Fig. 2;

Table 1. Water chemistry data used in this study.

Date	Station	T (°C)	pH	HCO ₃ (mg/L)	Mg (mg/L)	Ca (mg/L)	Na (mg/L)	K (mg/L)	Si (mg/L)	Cl (mg/L)	NO ₃ (mg/L)	SO ₄ (mg/L)	TDI (mg/L)	log pCO ₂	log SI Cal
01/20/97	main	10.4	7.4	27.30	0.75	8.80	0.51	*	2.32	1.26	*	3.38	44.32	-3.03	-1.75
01/20/97	trib	13.6	7.7	88.14	1.64	30.22	0.76	0.74	2.96	1.49	1.22	3.13	124.47	-2.82	-0.41
01/20/97	wall	11.2	7.7	72.96	1.63	26.31	0.61	0.62	1.89	1.18	0.08	8.72	114.01	-2.91	-0.58
01/20/97	frac	13.0	7.8	142.13	2.35	45.70	0.82	0.38	3.44	2.68	*	3.47	201.00	-2.67	-0.01
070/1/97	trib	**	7.4	93.60	1.62	30.33	0.57	0.30	2.81	1.71	*	2.04	132.98	-2.50	-0.68
07/01/97	main	**	7.4	57.60	1.30	17.06	0.64	0.40	2.96	1.35	0.12	3.03	84.46	-2.69	-1.11
09/16/97	frac	13.6	7.6	122.80	1.98	40.80	0.82	0.16	3.67	2.31	*	3.18	175.72	-2.58	-0.25
09/16/97	trib	13.8	7.5	101.30	1.89	33.04	0.57	0.16	2.89	1.65	1.41	1.95	144.86	-2.56	-0.51
09/16/97	main	14.1	7.7	94.90	2.44	29.87	1.00	*	3.22	1.92	0.41	3.72	137.56	-2.78	-0.38
11/08/97	trib	13.5	7.2	106.90	1.99	34.64	0.54	0.11	2.90	1.67	2.14	2.24	153.14	-2.23	-0.77
11/08/97	main	13.9	7.5	73.40	1.96	22.87	0.82	*	3.02	1.23	*	3.51	106.88	-2.69	-0.79
11/08/97	frac	13.0	7.9	122.00	1.99	39.20	0.54	*	3.53	2.15	*	3.52	172.96	-2.88	0.01
01/03/98	frac	13.0	7.7	162.50	2.63	51.80	0.70	0.46	3.54	2.58	1.15	3.80	229.16	-2.56	0.04
01/03/98	trib	13.0	7.9	103.70	1.84	34.54	0.54	0.52	2.96	1.60	1.54	2.80	150.05	-2.95	-0.10
01/03/98	main	12.0	7.6	35.60	1.10	11.50	0.64	0.38	2.66	1.17	*	3.33	56.38	-3.11	-1.30
01/03/98	infiltr	12.5	7.6	92.70	2.29	34.36	0.61	0.58	2.04	1.32	0.32	13.05	147.27	-2.70	-0.46
01/03/98	conduit	11.5	7.2	30.50	0.97	10.18	0.54	0.42	2.056	1.55	*	4.55	51.28	-2.78	-1.83
02/15/98	drip C	12.0	8.2	204.50	2.19	70.69	0.61	0.38	2.26	2.59	1.24	13.50	297.96	-2.98	0.73
02/15/98	frac	13.0	8.2	133.20	2.01	43.86	0.61	0.51	3.44	2.52	*	3.04	189.19	-3.15	0.39
02/15/98	trib	10.0	7.2	22.70	0.67	8.83	0.42	0.40	1.93	1.20	0.10	3.29	39.54	-2.91	-2.03
02/15/98	main	10.5	7.4	29.50	0.80	10.51	0.51	0.40	2.23	1.11	*	3.17	48.23	-3.00	-1.64
02/15/98	drip A	13.0	8.2	153.70	2.42	49.01	0.70	0.45	2.57	2.26	0.46	6.97	218.54	-3.09	0.48
02/15/98	sfc lower	9.0	2.9	0.49	0.43	1.05	0.39	*	1.85	1.04	0.03	3.45	8.81	-3.27	-5.90
02/15/98	sfc upper	7.0	5.7	0.25	0.44	0.62	0.42	0.39	1.96	1.26	*	3.17	8.51	-3.38	-6.68
04/07/98	frac	13.0	7.5	135.00	1.92	42.28	0.64	0.13	3.31	2.28	0.51	2.56	188.63	-2.44	-0.31
04/07/98	trib	11.0	7.0	20.30	0.57	6.96	0.39	*	2.05	0.97	0.26	3.06	34.64	-2.75	-2.36
04/07/98	trib B	11.0	6.8	13.40	0.55	4.58	0.42	*	1.91	0.93	0.11	3.34	25.24		
04/07/98	drip A	13.0	7.8	164.10	2.56	54.78	0.73	0.17	2.81	2.14	0.39	6.39	234.07	-2.66	0.16
05/31/98	frac	12.9	7.4	118.40	1.73	38.11	0.57	*	3.30	2.26	0.88	3.12	168.37	-2.39	-0.50
05/31/98	trib	12.5	7.4	95.20	1.56	30.42	0.51	*	2.74	1.76	1.85	1.52	135.60	-2.49	-0.69
05/31/98	main	13.2	7.6	69.60	1.54	21.66	0.76	0.13	2.78	1.20	0.48	2.67	100.82	-2.82	-0.75
09/20/98	frac	13.0	7.3	123.30	1.98	39.62	0.57	0.32	4.01	2.22	1.36	3.10	176.61	-2.28	-0.57
09/20/98	trib	13.0	7.3	97.90	1.83	31.42	0.54	0.56	2.73	1.60	1.95	2.20	140.76	-2.37	-0.76
09/20/98	wall	12.5	7.3	83.5	1.41	26.50	0.54	0.48	3.15	1.34	0.99	2.34	120.25		
09/20/98	main	13.0	7.4	96.70	2.41	29.49	0.94	0.60	3.19	1.35	0.99	3.37	139.04	-2.48	-0.69
09/20/98	drip B	13.0	7.5	141.10	2.25	45.77	0.70	0.79	3.02	1.98	3.43	4.95	203.99	-2.42	-0.26
10/04/98	frac	13.0	7.1	122.80	1.90	39.11	0.54	0.32	3.67	2.12	1.04	2.87	174.41	-2.08	-0.78
10/04/98	trib	13.0	7.1	102.50	1.79	30.83	0.54	0.55	2.83	1.50	1.99	2.19	144.77	-2.15	-0.95
10/04/98	main	13.0	7.0	98.10	2.40	29.40	0.97	0.43	3.14	1.37	1.19	3.33	140.33	-2.07	-1.08
10/04/98	drip B	13.0	7.4	143.50	2.13	44.15	0.76	0.65	3.02	1.90	4.16	4.81	205.08	-2.31	-0.37

* below detection limit ** not recorded due to equipment malfunction

Table 1). Dominant ions are calcium and bicarbonate; magnesium, sulfate, chloride, sodium, silica and potassium are also present above detection limits in most waters. Most variation among cave waters consists of differences in TDI concentrations—ion relative abundances are similar. Cave conduit streams are generally lower in TDI concentration than other cave waters, especially during winter months. Cave streams during periods of high flow are significantly more dilute than other cave waters, but always contain much higher TDI concentrations, and significantly more calcium and bicarbonate than surface waters. Surface waters, as well as being much lower in TDI concentrations than cave waters, are also deficient in calcium, magnesium and bicarbonate.

TOTAL DISSOLVED ION CONCENTRATION

Although the entire sample suite spans a large range of TDI concentration, samples collected from individual locations are fairly consistent (Fig 3; Table 1). Surface waters range from 8.5-8.8 mg/L TDI. The main cave stream shows more variability than other locations, ranging from 40-140 mg/L TDI. The tributary stream also varies widely, but it does so in a strongly bimodal fashion. During the late summer and fall when rainfall, surface stream flow, and cave stream flow are at their lowest levels, TDI concentration ranges from 124-153 mg/L. During exceptionally high flows after prolonged winter and spring rains, TDI concentration ranges from 34-40 mg/L. Fracture water ranges from 168-230 mg/L TDI. Drip water varies between 204 and 298 mg/L TDI.

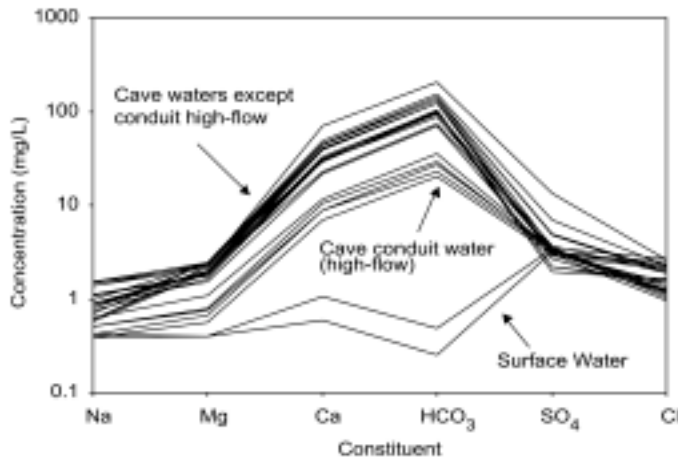


Figure 2. Major ion chemistry of cave and surface waters. Surface waters are very dilute and relatively deficient in calcium, magnesium and bicarbonate compared to cave waters. Cave conduit waters are more dilute than other cave waters but maintain similar ionic composition.

SCATTER PLOTS

Figure 4 shows plots of magnesium, sodium, sulfate and chloride vs. TDI. Total dissolved ion concentration is assumed to indicate extent of reaction with bedrock minerals and, thus, is a rough indicator of aquifer residence time. The extent to which points diverge with increasing TDI concentration reflects the extent to which flow histories of waters differ. Figure 4 reveals subtle differences in major-ion composition between sample sites, and underscores the consistency of water chemistry from individual subsurface sources. Using one or more of the plotted ions, it is possible to distinguish between all of the major water sources of this study. For example, main stream waters during low-flow conditions, when they are most concentrated, are similar in ionic composition and TDI concentration to tributary conduit waters. However, main stream waters are distinguishable from other waters based on their higher concentrations of magnesium and sodium. Similarly, there is significant TDI overlap between fracture and drip waters, but they are easily distinguishable based on sulfate and chloride concentrations.

CALCITE SATURATION INDEX, pCO₂

Surface waters are strongly undersaturated with respect to calcite. Conduit waters are undersaturated but span a wide range of SI values. Fracture and drip waters range from slightly undersaturated to slightly oversaturated with respect to calcite (Fig. 5). There is a weak positive correlation between calculated pCO₂ and TDI with considerable data scatter. Carbon dioxide partial pressure varies from 10^{-2.1} to 10^{-3.4} atm and individual sample locations show relatively large variations in pCO₂. Distinguishing between samples based on pCO₂ is dif-

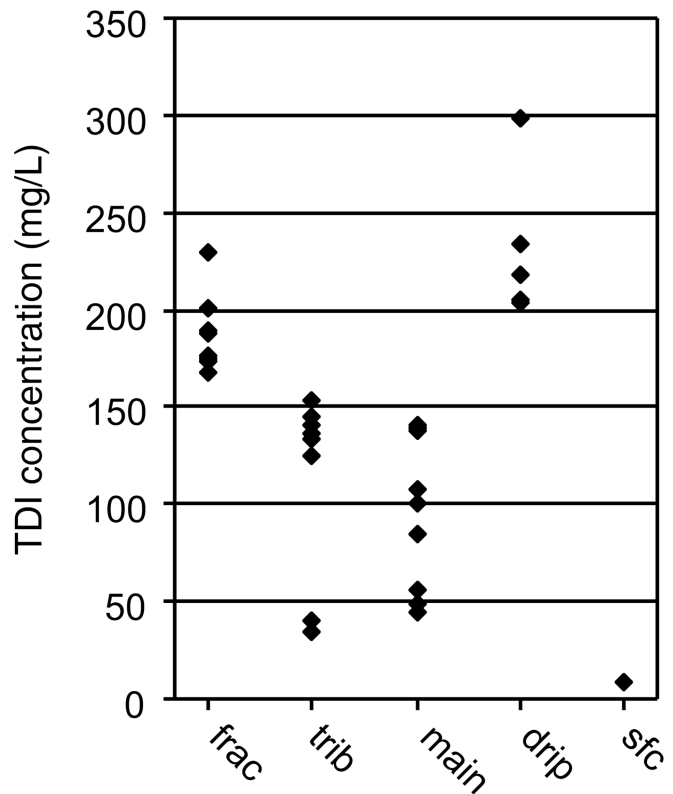


Figure 3. Total dissolved ion (TDI) concentrations of major water types in this study. Surface waters are the most dilute, drip waters most concentrated. Conduit and conduit tributary waters show most variability. TDI is defined as the sum of major ions analyzed in this study as reported in Table 1. Key: frac=fracture seep, trib=conduit tributary, main=main conduit stream, drip=soda straw drip, sfc=surface stream.

ficult or impossible. However, at least some of the pCO₂ variation apparent in Figure 5 is probably an artifact of sample collection techniques, as outlined in the discussion section below.

TEMPORAL TRENDS

Water chemistry variability reflected in the scatter plots of figure 4 is not random. Rather, there are clear temporal trends. In figure 6, TDI concentrations are plotted as a function of time for three cave waters: main conduit, tributary conduit, and fracture drip waters. Temporal variations of TDI concentration in main stream water follow seasonal flow volume variations. Although flow volume was not quantified, relative streamflow estimates clearly show that the main stream reaches maximum discharge during winter and spring months, declines through the summer, and reaches a minimum during the late summer or autumn. TDI concentration varies inversely with this trend, reaching a maximum during low-flow periods. Individual ions show clear temporal trends similar to TDI concentration trends.

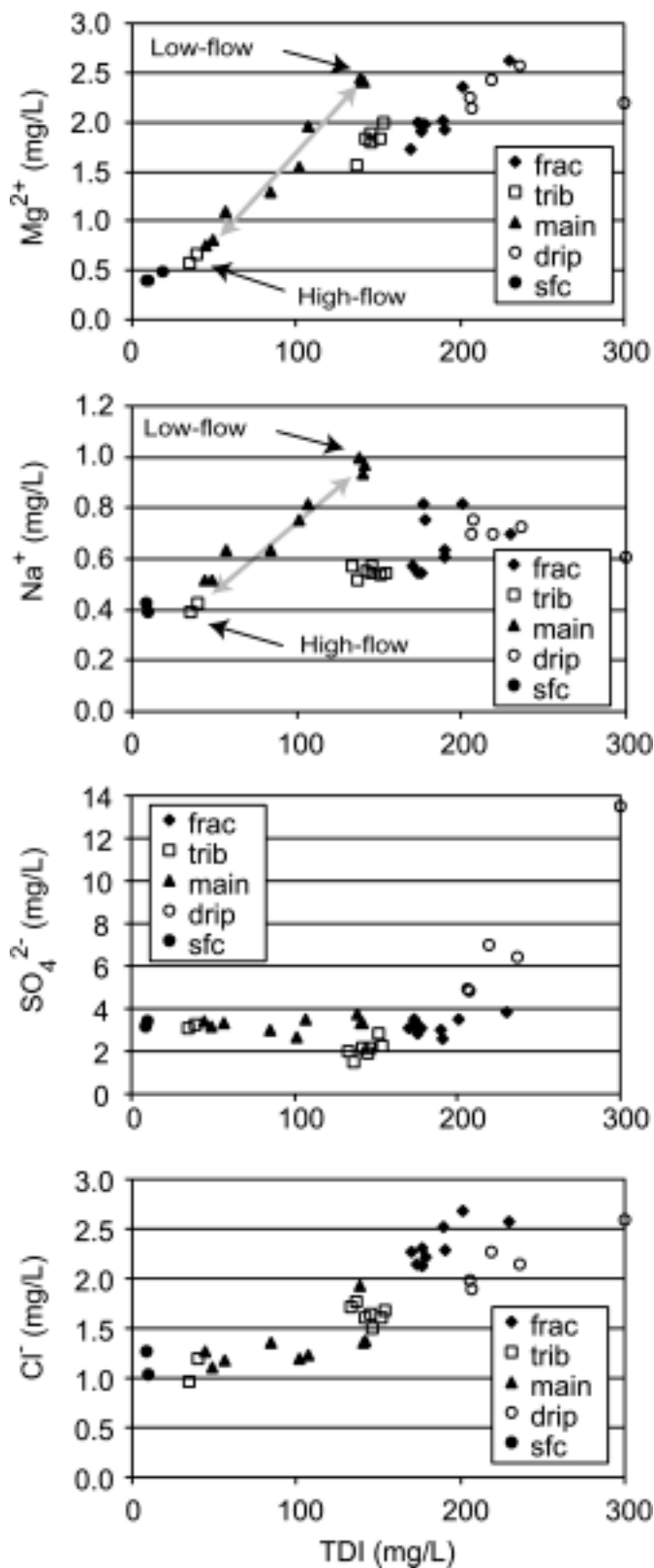
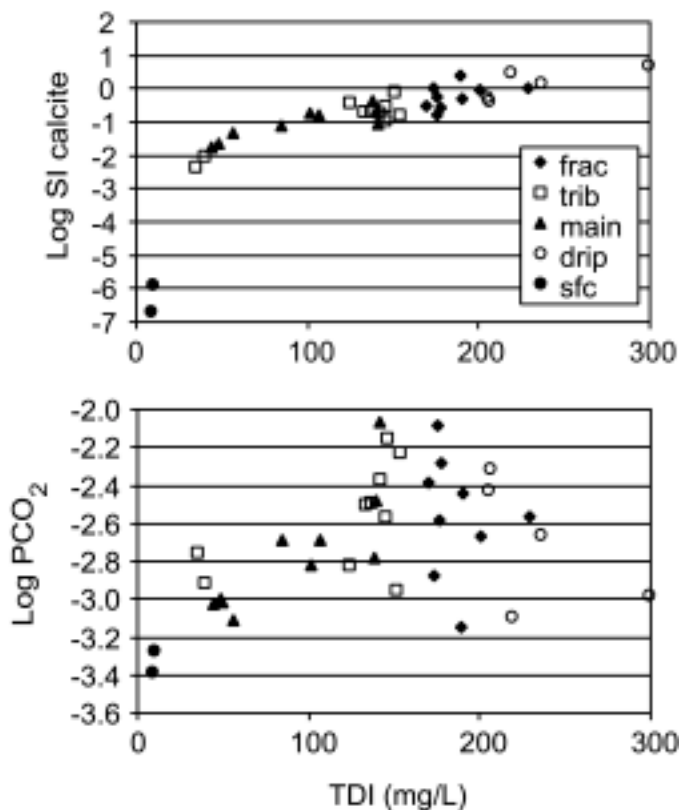


Figure 4 (left). Mg²⁺, Na⁺, SO₄²⁻, and Cl⁻ concentrations vs. TDI concentration. Plots illustrate consistency of individual water sources and subtle differences among different water sources. See text for explanation of figure annotation.

Figure 5 (below). Calcite saturation index and calculated carbon dioxide partial pressure vs. TDI concentration.



However, during months of exceptionally high flow volume (late winter, early spring) it is nearly indistinguishable from main conduit waters.

DISCUSSION

WATER CHEMISTRY CONTROLS

Spatial variation of groundwater composition in Pettyjohns Cave is controlled primarily by rock-water interaction along distinct subsurface flowpaths. Temporal variation is controlled by mixing—primarily dilution during wet periods. It is possible that seasonal variations of pCO₂ also play a role in temporal variation. Calcium, bicarbonate, and magnesium are derived from carbonate dissolution. The relatively low concentrations of magnesium indicate dissolution of very magnesium-poor calcite. Silica is derived either from dissolution of siliceous microfossils that are abundant within carbonate rocks surrounding the cave, or from weathering of silicates in overlying soils and clastic units. Sodium and potassium are prob-

Also apparent in figure 6 is the bimodal behavior of the tributary conduit stream (trib). It is generally intermediate in composition between main conduit and fracture water.

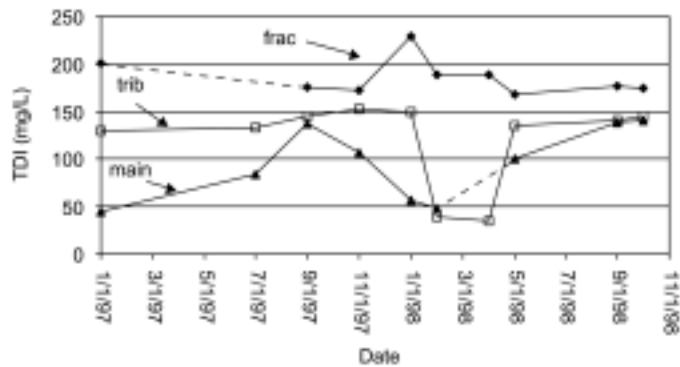


Figure 6. Temporal water chemistry variation of fracture (frac), conduit tributary (trib), and main conduit (main) waters. Main stream water was inaccessible on the April 1998 trip due to high water levels. Fracture water from the July 1997 trip was not sampled due to logistical problems.

ably derived from atmospheric inputs plus ion-exchange in soils and clastic rock units. Chloride is probably derived solely from atmospheric inputs. Sulfate is likely derived from atmospheric inputs, pyrite oxidation, or dissolution of minor gypsum fracture fillings that occur in drier parts of Pettyjohns Cave and presumably in similar settings throughout the aquifer. Nitrate is likely derived from human and animal wastes deposited in and above the cave. Because the cave and associated groundwater recharge area lie mostly on undeveloped land of a wildlife preserve, local pollution is probably not a significant source of other ions.

SPATIAL WATER CHEMISTRY VARIATION

Waters sampled in this study can be distinguished from each other based on TDI concentration and subtle differences in major ion composition. Fracture and drip waters show remarkably little variation over the course of the study. Conduit waters vary in composition over well-defined ranges that do not significantly overlap with other water types. For a calcite-undersaturated water in contact with a predominantly limestone aquifer, concentrations of calcium and bicarbonate will tend to increase through time as the water approaches thermodynamic equilibrium (Jacobson & Langmuir 1970). Therefore, differences in TDI concentration in a karst aquifer are due largely to differences in residence time within the aquifer. Furthermore, residence time is primarily a function of flowpath—waters entering the cave through large fractures and conduits flow faster and have much shorter residence times than waters percolating through small fractures or limestone matrix. Thus, the persistent differences in water composition between different locations in Pettyjohns Cave are likely caused by differences in aquifer residence time, which in turn result from different subsurface flowpaths. This is also suggested by casual observation of cave hydrology: rapidly flowing conduit waters contain low TDI concentrations and are strongly undersaturated with respect to calcite; slowly perco-

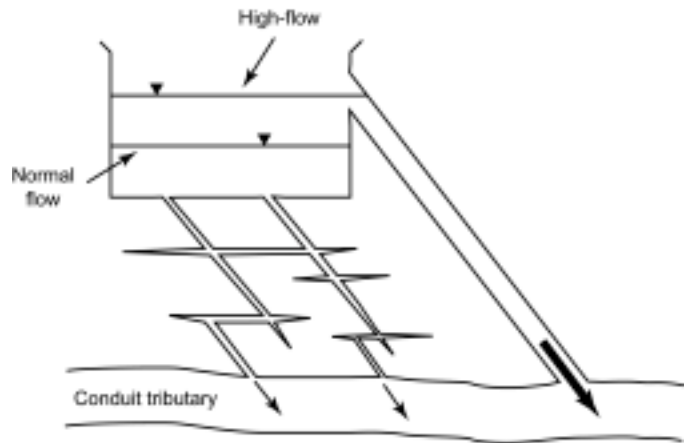


Figure 7. Conceptual model to explain bimodal behavior of conduit tributary stream. During normal flow conditions, water reaches the conduit only after significant contact with bedrock in narrow fracture network. During high flows, water reaches the conduit by a much more direct route and much less bedrock contact.

lating drip water is saturated with respect to calcite, and contains the highest concentrations of dissolved ions.

TEMPORAL WATER CHEMISTRY VARIATION

Water chemistry of the main conduit stream is controlled largely by mixing of two endmember waters: a rapidly infiltrating, dilute endmember that dominates conduit water chemistry during high-flow conditions of winter and spring, and a slowly infiltrating, concentrated endmember that dominates during low-flow conditions of late summer and autumn. Mixing of two endmember waters is indicated by the linear trend of main conduit data points on scatter plots of figure 4 (Mazor 1997, p. 115). Note in particular the magnesium and sodium vs. TDI plots. These plots clearly show the linear mixing trend between concentrated and dilute endmembers and key differences in water chemistry between conduit waters and other cave and surface waters. In particular, as TDI concentration increases, magnesium and sodium concentrations increase much more in conduit waters than in other waters. Preliminary results had suggested that the dilute conduit water endmember was surface water and that the concentrated endmember was drip water. Total dissolved ion concentrations and casual observation of mixing within the cave supported this hypothesis. However, further analysis showed both of these proposed endmembers to be incorrect. Surface water lies significantly off of the mixing lines identified in figure 4. Therefore, the dilute endmember is not unaltered surface water. Instead, the dilute endmember is probably surface water that dissolves a moderate amount of carbonate rock as it percolates through fractures connecting surface streams to the cave. This is suggested by a significantly higher TDI concentration and elevated concentrations of calcium and bicarbonate in the dilute endmember relative to surface water. The dilute

conduit endmember appears to be represented by the most dilute conduit tributary samples, which lie at the low-concentration end of mixing lines defined by main conduit waters.

The concentrated endmember of the conduit mixing system has a slightly lower TDI concentration than fracture drip waters and approximately the same TDI concentration as most conduit tributary waters. Subtle differences in major ion composition, however, show that main conduit waters are distinct from other cave waters. Most notably, they are relatively enriched in magnesium and sodium (Fig. 4). Thus, the source of main conduit baseflow is different from that of conduit tributary and drip waters. There are two obvious source possibilities for this endmember. It may originate well upstream from sample points within the cave, or it may react with different stratigraphic horizons than other cave waters. In either case this would allow interaction with different strata and subsequent evolution of distinct water chemistry.

The strongly bimodal behavior exhibited by the conduit tributary stream suggests different water sources in wet versus dry periods. During high-flow, tributary waters are very similar in composition to the most dilute main conduit waters. Conduit tributary behavior can be grossly conceptualized as in figure 7. During all but the highest flows, water percolates through a network of small fractures to eventually emerge in the conduit tributary. Such a flowpath would allow significant contact with carbonate bedrock and subsequent carbonate dissolution. During times of high recharge rates, however, the fracture system cannot transmit all available water and some bypasses the fractures by a more direct route to reach the conduit after significantly less contact with bedrock. Many other plumbing arrangements could also lead to the observed bimodal behavior. The important point is that there is a separate infiltration mechanism during high-flow conditions.

Carbon dioxide is an important control of carbonate dissolution. Some of the variation apparent in TDI concentration in this study may result from seasonal variations of soil CO₂ concentration. The rough positive correlation between calculated pCO₂ and TDI concentration in figure 5 may be, in part, due to the increased availability of CO₂ during summer months and a corresponding increase in the ability of summer infiltration to dissolve carbonate rock. However, much of the variation in pCO₂ shown by fracture and drip water is likely an artifact of sample collection techniques. For example, fracture water was withdrawn from a small depression at the base of a narrow fracture on the cave wall. During summer and autumn—times during which pCO₂ would be expected to be at a maximum—flow rates reach their minimum levels. Water issuing from the fracture therefore remains in the depression for a relatively much longer time, where it might equilibrate with cave atmospheric CO₂. Likewise, soda straw drip water hangs exposed to cave air at the cave ceiling much longer during low-flow periods than during high-flow periods, and probably loses much CO₂ to the cave atmosphere. Thus, some of the relatively low pCO₂ values for fracture and drip water of figure 5 probably do

not accurately reflect aquifer conditions, but rather are caused by CO₂ outgassing during low-flow conditions.

CONCLUSION

Water chemistry trends within Pettyjohns Cave, Georgia and in adjacent surface streams reveal a wide range of water chemistry. Depending on which water source is sampled, and when it is sampled, cave waters range from 34-298 mg/L TDI and are dominated by calcium and bicarbonate. Surface streams vary between 8 and 9 mg/L TDI and are very deficient in calcium and bicarbonate compared to cave waters. In general, water composition from a given source is remarkably consistent. As may be expected, conduit waters exhibit the most temporal variability.

Important processes that control groundwater chemistry in Pettyjohns Cave include evolution via carbonate dissolution along subsurface flowpaths, mixing, and seasonal variations in pCO₂ in overlying soil. Although all processes contribute to a certain degree to each water source, it appears that a subsurface flowpath is by far the most important factor. The importance of a subsurface flowpath is demonstrated by the persistent, subtle differences in water chemistry documented at numerous cave sampling points at all times of the year and under a wide range of flow conditions. Even conduit water, which is also strongly influenced by mixing of two endmember waters, is discernible from other cave water sources at all times of the year, regardless of which endmember dominates.

The greatest variation in water chemistry occurs in the main cave stream. This variation appears to be the result of mixing between two endmember waters: a baseflow component that is diluted during wet periods with a rapidly infiltrating, dilute water. The dilute endmember is most likely surface water that has reacted with limestone bedrock during infiltration from losing streams. Interestingly, the relatively high-TDI baseflow endmember is not composed of the high-TDI waters identified in this study: fracture and drip waters. The baseflow component is relatively enriched in magnesium and sodium compared to other high-TDI cave waters and may originate in the upstream reaches of the conduit system or in a different stratigraphic horizon. Results illustrate the fine-scale complexity of karst aquifers and reinforce the notion that karst water sampling programs must be carefully designed and executed.

The most pronounced seasonal variations in water chemistry occur in conduits and appear to be the result of mixing between two endmembers—a dilute, rapidly infiltrating water, and a more concentrated, slowly infiltrating water. The dilute endmember appears to be surface stream water that has experienced moderate rock-water interaction. The concentrated endmember is distinct from local fracture and drip infiltration and may originate in the upstream portion of the main conduit stream. Some seasonal water-chemistry variation may also result from seasonal variations in soil CO₂ partial pressure.

ACKNOWLEDGMENTS

I wish to thank State University of West Georgia students James Burgess and Eric Crisp for introducing me to caving and to the caves of TAG, and for their assistance with various stages of this project. Thanks to Dr. Richard Sanders, State University of West Georgia for running water samples on the Geology Department ICP. The manuscript benefited from editorial comments of Barb Mahler (U.S.G.S., Austin, Texas), George Moore (Oregon State University), and an anonymous reviewer. Work was supported by State University of West Georgia Faculty Research Grant #10-21-1-14-122-000.

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