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GEOCHEMISTRY OF CARLSBAD CAVERN POOL WATERS, GUADALUPE MOUNTAINS, NEW MEXICO

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Water samples collected from 13 pools in Carlsbad Cavern were analyzed to determine the concentrations of major ions. Air temperature, relative humidity, and carbon dioxide concentration of the cave atmosphere were also measured. Large differences in water quality exist among different cave pools, with some pools containing very fresh water, while others are brackish, with total dissolved solids concentrations up to 5000 mg/L. Brackish water pools appear to be associated with those portions of the cave where evaporation rates are high and/or soluble minerals are present. Geochemical speciation modeling showed that some pools are close to saturation with respect to the common cave minerals aragonite, calcite, gypsum, and hydromagnesite.

A tracer test was performed using a non-toxic bromide salt to estimate the leakage rates of selected pools. Pool volumes calculated based on dilution of the bromide tracer were up to 550 m³. The tracer test results were used to calculate mean residence times for the water in each pool. Calculated mean residence times based on bromide tracer loss rates ranged from less than a year for Rookery Pool and Devil's Spring to 16 years for Lake of the Clouds. Calculated pool leakage rates ranged from 2 L/day to over 100 L/day. The pools with the highest leakage rates appear to be Rookery Pool, Green Lake, and Lake of the Clouds.

The long residence times indicated by the tracer tests suggest that the pools evaporate more water than they leak. However, evaporation should result in an accumulation of dissolved chloride and other solutes in the pools, which for most pools does not appear to be the case. Taken together, these observations suggest that the pools are recharged primarily by infrequent precipitation events, separated by long periods of slow evaporation and minimal leakage.

Carlsbad Cavern, located in southeastern New Mexico, U.S.A., contains numerous pools of standing water ranging from small shallow puddles to Lake of the Clouds, with an estimated volume of approximately 550 m³. This report summarizes the results of a two-year water chemistry study of 13 of the pools selected throughout the cave (Fig. 1). The main objectives of the study were to determine how pool water quality varies from one pool to another, and to track water quality changes in a particular pool over time.

The cave pools in Carlsbad Cavern are recharged by drip water that enters through the cave ceiling. Water is lost from the pools by a combination of evaporation from the pool surface, leakage from the bottom, and overflow from the perimeter. Flowing streams are not observed in the cave, except possibly following infrequent intense precipitation events. Detailed geologic information and maps of Carlsbad Cavern and the surrounding Guadalupe Mountains can be found in Jagnow (1977) and Hill (1987).

The pools investigated during this study lie at depths ranging from approximately 150 m to 316 m below the main entrance. Lake of the Clouds is the deepest known point in the cave. All of the pools in Carlsbad Cavern are perched, and dripwater moving downward accumulates in each pool as a result of the low permeability of the pool bottom. The elevation of the regional groundwater table is believed to be some 30 m below the lake level at Lake of the Clouds (Hill 1987).

Some of the pools sampled during this study have been affected by human activities. For example, there are reports that some pools (e.g. Mirror Lake, Longfellows Bathtub) were refilled in the past with water from the Park drinking water supply, which is obtained from Rattlesnake Springs located 8 km to the southwest (Bowen 1998). Furthermore, Caldwell (1991) reported that hypochlorite bleach was used in past restoration activities around some of the pools. Therefore, the data reported here serve primarily to document current condi-

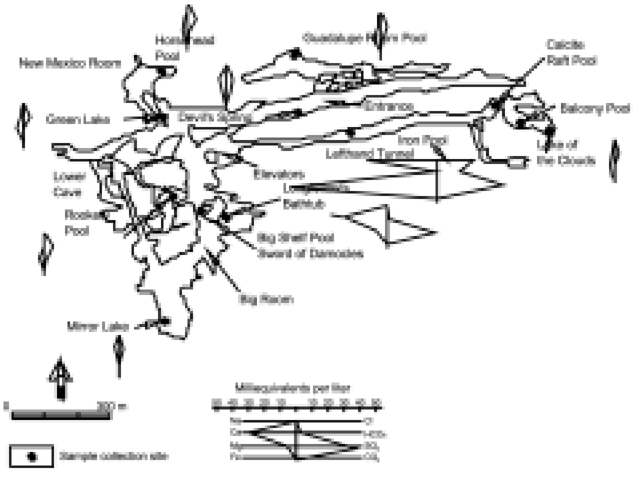

Figure 1. Sample locations in Carlsbad Cavern.

Table 1. Summary of Carlsbad Cavern Pool Water Quality.

NM = not measured

***TDS too low and charge balance error too high, possibly due to presence of ions that were not analyzed.**

Sample Location	Date	Air Temp (C)	Air RH (%)	Air CO2 (ppm)	Water pH	Water Temp (C)	EC (µS/cm @ 25C)
Balcony Pool	1/22/95	19.4	95	NM	8.19	18.5	795
Big Shelf Pool	4/8/95	NM	NM	NM	NM	14.4	1680
	9/24/95	12.6	NM	NM	NM	14.7	1710
	11/12/95	NM	NM	NM	NM	14.6	1710
Calcite Raft Pool	1/22/95	18.9	95	530	8.27	18.3	1150
	4/9/95	18.6	97	NM	8.34	18.1	1150
	9/25/95	18.2	NM	NM	7.64	18.2	1125
	11/12/95	NM	NM	NM	NM	18.0	1120
Devils Spring	8/6/94	13.3	95	NM	7.87	11.0	770
	10/8/94	13.6	92	750	8.11	12.6	755
	1/21/95	10.7	71	NM	8.50	9.5	740
	4/8/95	12.2	91	NM	8.72	10.7	760
	9/24/95	NM	NM	NM	7.86	12.1	760
	11/12/95	NM	NM	NM	NM	11.0	760
Green Lake	8/6/94	13.9	97	NM	8.12	13.5	505
	10/8/94	14.2	97	1000	8.01	13.6	520
	1/21/95	13.6	88	330	8.62	13.3	480
	4/8/95	13.9	92	NM	9.14	13.1	485
	9/24/95	NM	NM	NM	8.04	13.5	490
	11/12/95	NM	NM	NM	NM	13.5	485
Guadalupe Rm	8/6/94	NM	NM	NM	NM	NM	520
Horsehead Pool	8/6/94	16.1	97	NM	8.33	15.5	420
	10/8/94	16.4	97	1000	7.92	16.0	415
	1/21/95	16.1	98	570	8.46	15.9	400
	4/8/95	16.4	97	NM	8.38	15.7	400
Iron Pool	3/12/94	16.3	NM	NM	8.67	NM	11300
	8/7/94	16.4	92	NM	8.84	15.5	11100
	10/9/94	16.1	92	800	8.34	15.8	9440
	1/22/95	16.1	90	400	8.64	15.7	9830
	4/9/95	16.4	97	NM	8.78	15.6	10800
	9/25/95	NM	NM	NM	8.30	15.7	9340
	11/12/95	NM	NM	NM	NM	15.6	10000
Lake of Clouds	8/7/94	19.4	95	NM	NM	18.5	405
	10/9/94	19.6	96	800	7.72	19.2	400
	1/22/95	19.7	95	670	8.45	19.0	385
	4/9/95	19.4	95	600	8.71	19.0	385
	11/12/95	NM	NM	NM	NM	19.0	392
Longfellows Bathtub	8/7/94	15.3	94	NM	NM	14.0	2630
	10/8/94	15.3	92	1000	7.46	14.6	2590
	1/21/95	14.7	89	370	7.91	14.1	2440
	4/8/95	14.7	92	NM	8.01	13.9	2570
	9/24/95	13.0	NM	NM	7.23	14.4	2560
	11/12/95	NM	NM	NM	NM	14.2	2550
Mirror Lake	10/8/94	15.6	94	1200	7.64	15.3	335
	1/21/95	15.3	95	330	8.44	14.9	315
	4/8/95	15.0	97	NM	8.38	14.7	345
	9/24/95	13.2	NM	NM	7.59	14.8	355
	11/12/95	NM	NM	NM	NM	14.8	355
Rookery Pool	8/7/94	14.3	95	NM	NM	13.0	475
	10/9/94	14.2	97	900	8.09	14.0	420
	1/21/95	13.9	96	400	8.69	13.6	435
	4/9/95	14.4	94	NM	8.40	13.4	450
	9/24/95	12.4	NM	NM	8.27	13.7	475
	11/12/95	NM	NM	NM	NM	13.8	525
Sword of Damocles Pool	4/8/95	NM	NM	NM	NM	13.5	1550
	9/24/95	12.0	NM	NM	NM	14.0	1580
	11/12/95	NM	NM	NM	NM	13.8	1540

tions, but do not necessarily reflect pool water quality prior to anthropogenic impacts.

Previous Studies

Several prior studies of water quality have been done in Carlsbad Cavern. As part of his PhD dissertation, Thrailkill (1965, 1971) performed a thorough investigation of speleothem precipitation based primarily on chemical analysis of drip and seep water samples collected along flow paths. He reported major ion concentrations from about 50 sample locations throughout the cave, including one-time sampling of several of the same pools investigated here (Mirror Lake, Green Lake, and Rookery Pool). Thrailkill's field assistant, Boyer (1964), wrote an excellent report on drip and pool water chemistry as it pertains to carbonate mineral precipitation.

Two studies by McLean (1971, 1976) were done to determine the potential causes of the drying of cave pools in Carlsbad Cavern. In addition to measurements of air temperature and air flow, pool water-level hydrographs were prepared,

TDS	Calcium	Magnesium	Sodium	Potassium	Chloride	Sulfate	Bicarbonate	Chg. Bal. Error (%)	Ionic Strength (molal)
			(All concentrations in mg/L)						
NM	70	39	NM	NM	7	25	135	NM	NM
NM	NM	NM	NM	NM	NM	NM	NM	NM	NM
NM	NM	NM	NM	NM	NM	NM	NM	NM	NM
NM	NM	NM	NM	NM	NM	NM	NM	NM	NM
NM	94	60	NM	NM	16	45	135	NM	NM
NM	NM	NM	NM	NM	NM	NM	NM	NM	NM
NM	NM	NM	NM	NM	NM	NM	NM	NM	NM
NM	NM	NM	NM	NM	NM	NM	NM	NM	NM
630	87	45	24	1.8	30	140	305	1.8	0.013
571	84	29	21	1.8	30	145	260	-4.0	0.011
NM	76	39	NM	NM	30	160	270	NM	NM
NM	NM	NM	NM	NM	NM	NM	NM	NM	NM
NM	NM	NM	NM	NM	NM	NM	NM	NM	NM
NM	NM	NM	NM	NM	NM	NM	NM	NM	NM
447	31	48	8	0.4	10	22	325	-1.7	0.008
420	30	46	8	0.4	10	24	305	-1.2	0.008
NM	30	46	NM	NM	9	22	275	NM	NM
NM	NM	NM	NM	NM	NM	NM	NM	NM	NM
NM	NM	NM	NM	NM	NM	NM	NM	NM	NM
NM	NM	NM	NM	NM	NM	NM	NM	NM	NM
439	25	52	15	0.7	20	48	280	0.4	0.009
406	25	45	7	0.5	10	17	305	-3.3	0.008
379	24	42	7	0.4	10	17	275	-1.7	0.007
NM	24	35	NM	NM	7	19	240	NM	NM
NM	NM	NM	NM	NM	NM	NM	NM	NM	NM
NM	15	440	NM	NM	840	2500	665	NM	NM
5971	25	1140	910	220	820	2000	860	28.0	0.14
4390	24	860	820	200	670	1040	775	36.0	0.11
NM	24	795	NM	NM	500	1650	665	NM	NM
NM	NM	NM	NM	NM	NM	NM	NM	NM	NM
NM	NM	NM	NM	NM	NM	NM	NM	NM	NM
NM	NM	NM	NM	NM	NM	NM	NM	NM	NM
327	37	38	5	1.1	15	13	220	9.7	0.007
305	30	32	5	1.1	10	10	220	3.3	0.006
NM	30	32	NM	NM	7	12	220	NM	NM
NM	NM	NM	NM	NM	NM	NM	NM	NM	NM
NM	NM	NM	NM	NM	NM	NM	NM	NM	NM
2671	608	67	9	1.1	15	1850	120	-6.0	0.051
2277	516	70	9	1.1	10	1520	150	-3.7	0.045
NM	516	58	NM	NM	14	1750	110	NM	NM
NM	NM	NM	NM	NM	NM	NM	NM	NM	NM
NM	NM	NM	NM	NM	NM	NM	NM	NM	NM
NM	NM	NM	NM	NM	NM	NM	NM	NM	NM
298	47	14	6	0.5	10	27	195	-3.4	0.006
NM	47	7	NM	NM	7	29	150	NM	NM
NM	NM	NM	NM	NM	NM	NM	NM	NM	NM
NM	NM	NM	NM	NM	NM	NM	NM	NM	NM
NM	NM	NM	NM	NM	NM	NM	NM	NM	NM
392	31	49	NM	NM	10	NM	305	NM	NM
411	30	46	5	0.4	10	18	305	-1.3	0.008
NM	24	42	NM	NM	7	17	240	NM	NM
NM	NM	NM	NM	NM	NM	NM	NM	NM	NM
NM	NM	NM	NM	NM	NM	NM	NM	NM	NM
NM	NM	NM	NM	NM	NM	NM	NM	NM	NM
NM	NM	NM	NM	NM	NM	NM	NM	NM	NM
NM	NM	NM	NM	NM	NM	NM	NM	NM	NM
NM	NM	NM	NM	NM	NM	NM	NM	NM	NM

and limited water quality data were also reported. McLean showed that the primary cause of excessive pool evaporation was the unrestricted air flow up the elevator shafts during winter. In response to McLean's work, revolving doors were installed at the bottom of each elevator shaft in 1972 to reduce the convective air flow, and drying of the cave pools.

Williams (1983) correlated rainfall patterns at Carlsbad Cavern with pool water levels and drip rates in the cave. Drip rates into some cave pools (e.g. Green Lake) increased significantly following storm events, but the drip response was found to lag from 2 to 5 weeks behind the associated precipitation event. Pool water levels showed similar responses and lags of 6 to 14 weeks. The lag times were taken as evidence of considerable water storage in the vadose zone.

Ingraham *et al.* (1990) and Chapman *et al.* (1992) investigated the stable isotopic composition and tritium activity of water samples collected from drips and pools in Carlsbad Cavern, including some of the same pools sampled during this study (Horsehead Pool, Rookery Pool, Lake of the Clouds). Their data indicate that the pools investigated leak more water than they evaporate, and that the travel time for water through the vadose zone from the surface to the main cave level range between 17 and 36 years. S.J. Lambert (pers. comm.) also performed extensive stable isotopic analyses of drip and pool water samples from Carlsbad Cavern, but reached the quite different conclusion that vadose zone travel times may be as little as 3 weeks to 3 months, depending on the intensity of precipitation events.

Caldwell (1991) reported the results of chemical and microbiological tests performed on pool water samples collected throughout Carlsbad Cavern in 1981. The main focus of this study was to compare the water quality of pools affected by visitor activities with those that had not been affected. The report concluded that oranges and other organic debris deposited in particular cave pools by visitors had created anoxic conditions that altered the natural microbiology of these pools.

Brooke (1996) performed a water quality study in Carlsbad Cavern to identify anthropogenic impacts on cave water quality, with an emphasis on correlating such impacts with specific surface sources (e.g. sewer, parking lot, visitor center, etc.). For example, elevated dissolved nitrate concentrations in the eastern portion of the cave (Left Hand Tunnel) were attributed to some combination of sewerline leaks and bat guano from overlying portions of the cave. Van der Heijde *et al.* (1997) summarized Brooke's work, and attempted to identify areas of the cave most susceptible to impacts by release of contaminants at the surface.

METHODS

Water samples from 13 pools throughout Carlsbad Cavern (Fig. 1) were collected and analyzed periodically for pH, temperature, electrical conductivity (EC), alkalinity, and the concentrations of major and trace inorganic solutes. The temperature, relative humidity, and carbon dioxide concentration of the cave air adjacent to each of the pools was also measured. Water temperature (±0.1°C) and pH (±0.01 unit) were measured in the cave using an Orion 250A pH meter, and EC was determined using a Horiba ES-12 conductivity meter (±2 percent). EC values were corrected from field temperature to 25°C by applying a 2 percent per degree C temperature coefficient, as described in APHA (1992). Wet and dry bulb air temperatures were determined to the nearest 0.1°C using a research-grade sling psychrometer, and percent relative humidity (RH) was calculated from these values. The precision of RH values is approximately ±1 percent up to a maximum of 95 percent RH, above which the sling psychrometer becomes unreliable. Absolute barometric pressure was measured to the nearest 5 mbar using a Casio watch barometer. Carbon dioxide concentrations in the cave air were measured using Draeger colorimetric tubes (Draeger 1992).

Analysis of water samples was performed as follows. Total alkalinity was determined in the cave by acid titration using a Hach kit to the bromcresol green-methyl red colorimetric endpoint. Concentrations of calcium, magnesium, and chloride were determined later on clear, unfiltered water samples by colorimetric titration. Calcium and magnesium were titrated using CalVer colorimetric indicator chloride was titrated using a silver nitrate endpoint indicator and sulfate was determined turbidimetrically with barium chloride (Hach 1992). Bromide was determined by ion-selective electrode (ISE), with selected samples verified using ion chromatography. Sodium and potassium concentrations were determined by flame atomic emission spectroscopy. The precision of the major ion analyses is approximately ±10 percent. For samples for which all major ions were determined, total dissolved solids (TDS) concentrations were calculated as the sum of dissolved ions.

The geochemical equilibrium speciation code PCWATEQ (Plummer *et al.* 1976) was used to determine the distribution of dissolved species in the pool waters, as well as the saturation indices of common cave minerals. The Davies equation option was used in the model runs, and the ionic strengths of the pool waters (Table 1) were low enough (<0.2) to be successfully handled by the code. Input data included field temperature, pH, and the concentrations of the major ions as determined in the laboratory. The code also calculates CO_2 partial pressure in the water, which provides a useful comparison to CO_2 concentrations determined in the cave air.

A tracer test was performed using a non-toxic bromide salt to estimate the leakage rates of selected pools. Crystalline NaBr was oven-dried at 105°C for 24 hours. Based on the estimated volume of each pool, an aliquot of NaBr (weighed to 0.1g) was added such that the resulting bromide ion concentration in the pool would be approximately 10 mg/L, assuming zero initial Br concentration. Based on ISE analyses of pool water samples collected prior to addition of the tracer, this assumption is valid, as initial Br concentrations were all less than 0.1 mg/L. For each pool, the weighed quantity of NaBr was dissolved in approximately 500 mL of deionized water. The concentrated solution was poured into the pool, and the water mixed using a canoe paddle. Water samples were collected periodically over time and analyzed for bromide ion concentrations to monitor the disappearance of the tracer resulting from leakage or overflow of the pool. The dissolved bromide ion is generally believed to behave as a "conservative tracer" in water, meaning that it travels unretarded with the water, and that its concentration varies only as a result of simple dilution or evaporation processes.

RESULTS

Table 1 shows the results of field and laboratory tests performed on water samples collected from the various cave pools in Carlsbad Cavern. For samples with complete major ion analyses, charge balance errors expressed as percentages were calculated as:

$$CBE = 100\ (meq_{cations} - meq_{anions}) / (meq_{cations} + meq_{anions})$$

Charge balance errors were generally within acceptable ranges (<5%), with the exception of a few saline samples from Iron Pool.

POOL WATER QUALITY

The concentrations of major ions were found to vary significantly among the pools. Most of the pool waters can be classified as very fresh water (TDS 200 to 500 mg/L) of the calcium-magnesium-bicarbonate type. Fresh water pools include Devils Spring, Green Lake, Horsehead Pool, Lake of the Clouds, Mirror Lake, and Rookery Pool. Stiff water quality diagrams were prepared to illustrate differences in water types among the different pools (Fig. 1).

Values of pH ranged between 7 and 9, with most values being close to 8.5. For a particular pool, the lowest pH values generally occur during late summer or early autumn, which corresponds to the period of maximum stagnation of the cave atmosphere, and hence the highest carbon dioxide concentrations in the cave air (McLean 1971).

Somewhat unusual is the observation that in some pools, magnesium concentrations equal or exceed those of calcium (e.g. Lake of the Clouds, Rookery Pool). This situation is probably attributable both to the high magnesium content of the dolomitic rocks in which the cave is developed, as well as the tendency for the magnesium/calcium ratio to increase in the cave waters as a result of evaporation and precipitation of calcite (Thrailkill 1971).

Two of the pools (Longfellows Bathtub and Iron Pool) were found to contain much higher concentrations of dissolved ions. Longfellows Bathtub contained elevated concentrations of calcium and sulfate, with calculated TDS concentrations of about 2500 mg/L. These observations are consistent with the dissolution of gypsum, which is present nearby in the cave (Hill 1987; her sheet 2).

Iron Pool is a small, but interesting, yellow-green-colored pool in Left Hand Tunnel. Iron Pool contains the most saline water of any of the pools studied. The water in this pool is a magnesium-sulfate type brine, with calculated TDS values ranging between 4000 and 6000 mg/L. Although only about 0.5 m deep, the water in Iron Pool is chemically stratified, with less dense, less saline water near the surface, and more saline water at the bottom. The elevated magnesium concentrations are probably at least partially attributable to dissolution of hydromagnesite “moonmilk”, which is abundant in this portion of Left Hand Tunnel (Thrailkill 1971). Evaporation appears to be responsible for the high concentrations of other major ions measured in Iron Pool (e.g. sodium, potassium, chloride). It is not known what gives Iron Pool its characteristic color, but the color cannot be due to dissolved iron, which was below detection limits. The unacceptably high positive charge balance error for samples from the Iron Pool suggests the presence of another major anion that was not determined during this study (probably nitrate), although poor analytical precision for these samples may also be a factor.

The TDS of the pool waters does not correlate with depth beneath the land surface. In fact, the pool at the lowest elevation in the cave (Lake of the Clouds) is among the pools containing the lowest concentrations of dissolved solutes. The locations of brackish or saline pools appears instead to correlate with those locations in the cave where evaporation rates are high and/or soluble minerals are present, such as gypsum or hydromagnesite.

Based on the similarity of EC measurements for successive monitoring dates at a particular pool (Table 1), only very small changes in water quality were observed during the course of this study. This, in turn, suggests that any water quality changes during the 1994-95 study period were occurring quite slowly. However, it is quite possible that more rapid changes in pool water quality could occur in response to unusually heavy precipitation events. Indeed, rapid filling of cave pools has been reported following periods of heavy rainfall (McLean 1994). Comparing the major ion concentrations determined in this study with those reported previously by Thrailkill (1965) and Caldwell (1991), the results for particular pools appear quite similar. This suggests, but does not prove, that large changes in water quality have not occurred in most of the pools over a period of three decades.

The chloride concentration of most of the pool waters is surprisingly low, generally between 5 and 20 mg/L. If pool water evaporates slowly over time, but the pool does not leak, then a gradual increase in chloride concentration over time should be expected. The only pool that contains elevated chloride concentrations is Iron Pool (Cl^- = 840 mg/L). Because all other pools contain relatively low chloride levels, this suggests that chloride and other solutes are being carried away from the pools, either by leakage through pool bottoms, or overflow along the edges. This conclusion is supported by previous data reported by Thrailkill (1965) for some of the same pools (Mirror Lake, Green Lake), which indicates only minor change in chloride concentration over the past 30 years.

The chloride and bromide concentrations in Rookery Pool (4.3 and 0.06 mg/L) and in the nearby drip water that recharges the pool (5.2 and 0.07 mg/L) were similar, indicating little evaporative concentration of solutes in the pool. Given that the relative humidity above the pool is ~92 percent, and, thus, evaporation is occurring, we can infer that the evaporation rate from the pool surface is small compared with the leakage rate of water through its bottom, as discussed below.

GEOCHEMICAL MODELING

Table 2 shows calculated mineral saturation indices for selected minerals and water samples. Values greater than zero indicate mineral supersaturation, whereas values less than zero indicate undersaturation. The model results indicate that most of the pools are saturated or slightly supersaturated with respect to calcite and aragonite. The water in Longfellows Bathtub is at saturation with respect to gypsum, which is not surprising given the presence of this mineral. Based on the model results, the water in Iron Pool is somewhat supersaturated with respect to hydromagnesite, which is reasonable

Table 2. Mineral Saturation Index Calculated Using PCWATEQ

Location	Sample Date	Calculated Log PCO_2 (dissolved, in atm)	$SI_{aragonite}$	$SI_{calcite}$	SI_{gypsum}	$SI_{hydromagnesite}$
Devils Spring	8/6/94	-2.5	+0.38	+0.53	-1.4	-11.
Green Lake	8/6/94	-2.7	+0.31	+0.46	-2.6	-8.5
Horsehead Pool	8/6/94	-2.9	+0.43	+0.58	-2.7	-7.2
Iron Pool	8/7/94	-3.3	+0.70	+0.85	-1.5	+1.8
Lake of the Clouds	10/9/94	-2.4	-0.14	+0.01	-2.9	-11.
Longfellows Bathtub	10/8/94	-2.4	+0.22	+0.37	0.0	-14.
Mirror Lake	10/8/94	-2.4	-0.13	+0.02	-2.2	-14.
Rookery Pool	10/9/94	-2.7	+0.25	+0.40	-2.6	-8.8

given the abundance of this mineral in the moonmilk that lines the floor of this portion of Left Hand Tunnel.

CAVE ATMOSPHERE

The carbon dioxide concentration of the cave atmosphere above the pools ranges from that of fresh outside air ($10^{-3.5}$ atm = 350 ppm) to approximately 5 times greater than atmospheric. The lowest carbon dioxide concentrations in cave air are observed during the winter months when cold dense outside air sinks into the natural entrance, thereby freshening the cave atmosphere (McLean 1971). Based on the geochemical modeling, the partial pressures of carbon dioxide in the pool waters themselves are 2 to 10 times greater than those of the cave atmosphere (Table 2), suggesting that the pools represent a continuous source of carbon dioxide to the cave air. This is in accordance with previous observations by McLean (1971). Relative humidity (RH) of the cave air follows similar seasonal trends, with the lowest RH values occurring in winter, when pulses of cold, dense, dry air sink into the Natural Entrance.

TRACER TEST

The results of the bromide tracer test are shown in table 3. Pool volumes calculated from dilution of the bromide tracer ranged from <1 m³ for Sword of Damocles Pool to 550 m³ for Lake of the Clouds. The volume of Lake of the Clouds was undoubtedly even larger in the past, as evidenced by the large subaqueous mammillary concretions (clouds) that are now exposed far above lake level (Hill 1987). Calculated volumes for most of the other pools are in the range of 10 to 50 m³.

Mean residence times were calculated from the bromide tracer test results for each pool. The residence time may be thought of as the average time that a water molecule spends in the pool, assuming steady state conditions. Steady state implies that pool volume remains constant over time, or stated differently, inflow equals outflow.

Mean residence times were calculated using the loss of bromide over time (Table 3). Residence times ranged from less than a year for Rookery Pool and Devils Spring to 16 years for Lake of the Clouds. Figure 2 shows an example plot of the bromide tracer data for Devils Spring. In this plot, C/C_0 represents the ratio of the bromide concentration in the pool at any given time to its initial (or highest) concentration following addition of the bromide tracer. When the natural log of C/C_0 is plotted versus time, a straight line should result whose slope is proportional to the mean residence time. The time required for loss of half of the tracer initially present ($C/C_0 = 0.5$ or $\ln C/C_0 = -0.69$) is equivalent to the mean residence time.

In general, the calculated residence times were much longer than expected. In addition, some of the pools showed anomalous tracer test results that appeared puzzling at first. For example, bromide concentrations at Lake of the Clouds climbed steadily for the first 100 days following introduction of the tracer, then declined slowly thereafter. This was due to our inability to achieve thorough initial mixing of the tracer in this large lake. Instead, the bromide tracer slowly diffused throughout Lake of the Clouds, effectively delaying the onset of the test.

For any reservoir in steady state, it can be shown that the mean residence time is equal to the turnover time (T_0), which is defined as the ratio of the volume of the reservoir to its flux rate into or out of the reservoir:

$T_0 = V/Q$
where: V is pool volume (L)
Q is inflow rate or outflow rate (L/s)

Because we have calculated the pool volumes based on the initial dilution of the bromide tracer, it is possible to estimate the inflow rate (or outflow rate) by solving for Q in the equa-

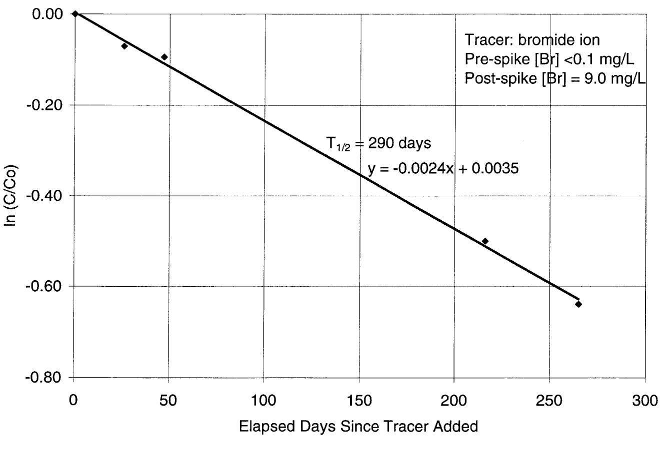

Figure 2. Plot of bromide tracer data for Devils Spring.

Table 3. Bromide Tracer Test Results.

Pool Name	Mass NaBr (g)	Date Tracer Introduced	Sample Date	Elapsed Days	Br Conc. (mg/L)	C/Co	ln(C/Co)	Est. Pool Volume (m3)	Br Loss Rate (yr-1)	Mean Res. Time (yrs)	Est. Leakage Rate (L/day)
Big Shelf Pool	75	2/19/95	2/23/95	3	12.4	1.00	0.00	6	0.07	9.3	2
			2/26/95	6	12.3	0.99	-0.01				
			3/5/95	13	12	0.97	-0.03				
			4/8/95	47	11.9	0.96	-0.04				
			9/24/95	216	11.6	0.94	-0.07				
			11/12/95	265	11.6	0.94	-0.07				
Devils Spring	200	2/19/95	2/20/95	0	8.9	1.00	0.00	22	0.9	0.8	75
			3/18/95	26	8.3	0.93	-0.07				
			4/8/95	47	8.1	0.91	-0.09				
			9/24/95	216	5.4	0.61	-0.50				
			11/12/95	265	4.7	0.53	-0.64				
Green Lake	340	2/19/95	2/23/95	3	7.8	1.00	0.00	44	0.6	1.2	100
			2/26/95	6	7.7	0.99	-0.01				
			3/5/95	13	7.9	1.01	0.01				
			3/18/95	26	7.7	0.99	-0.01				
			4/8/95	47	7.7	0.99	-0.01				
			9/24/95	216	5.9	0.76	-0.28				
			11/12/95	265	5.1	0.65	-0.42				
Lake of the Clouds	1200	4/9/95	4/9/95	0	0.2	0.09	-2.40	550	0.04	16	94
			4/17/95	8	0.7	0.32	-1.15				
			4/23/95	14	1	0.45	-0.79				
			5/6/95	27	1.4	0.64	-0.45				
			5/29/95	50	1.9	0.86	-0.15				
			11/12/95	217	2.2	1.00	0.00				
			12/8/96	609	2.1	0.95	-0.05				
Longfellows Bathtub	300	2/19/95	2/20/95	0	17.8	1.00	0.00	17	NM	NM	NM
			2/23/95	3	18.6	1.04	0.04				
			2/26/95	6	19	1.07	0.07				
			3/5/95	13	20.5	1.15	0.14				
			3/18/95	26	21	1.18	0.17				
			4/8/95	47	21.1	1.19	0.17				
			9/24/95	216	20.5	1.15	0.14				
			11/12/95	265	17.4	0.98	-0.02				
Mirror Lake	150	2/19/95	2/23/95	3	14.9	1.00	0.00	10	0.3	2.3	12
			2/26/95	6	14.2	0.95	-0.05				
			3/5/95	13	14.3	0.96	-0.04				
			9/24/95	216	12.6	0.85	-0.17				
			11/12/95	265	11.7	0.79	-0.24				
Rookery Pool	400	2/19/95	2/23/95	3	12.2	0.91	-0.09	30	1	0.7	117
			2/26/95	6	12.4	0.93	-0.08				
			3/5/95	13	13.4	1.00	0.00				
			4/8/95	47	12.6	0.94	-0.06				
			9/24/95	216	7.6	0.57	-0.57				
			11/12/95	265	6.3	0.47	-0.75				
Sword of Damocles Pool	13	2/19/95	2/23/95	3	16.5	1.00	0.00	0.8	0.9	0.8	3
			2/26/95	6	16.2	0.98	-0.02				
			3/5/95	13	14.9	0.90	-0.10				
			4/8/95	47	13.6	0.82	-0.19				
			9/24/95	216	10.7	0.65	-0.43				
			11/12/95	265	8.5	0.52	-0.66				

tion above. Leakage rate values calculated in this manner for each pool are shown in table 3, and range from 2 L/day to over 100 L/day. The pools with the highest leakage rates appear to be Rookery Pool, Green Lake, and Lake of the Clouds. Given its large volume, however, the leakage rate of Lake of the Clouds is remarkably low, possibly attributable to sealing of the pool bottom by precipitation of subaqueous calcite.

The long residence times indicated by the tracer tests would suggest that the pools evaporate more water than they leak. However, evaporation should result in an accumulation of dissolved chloride and other solutes in the pools, making them progressively more saline with time. Except for Iron Pool, this does not appear to be the case, and most of the pools contain very fresh water, with no buildup of salts. This is consistent with the stable isotopic composition of the water, which indicates little evaporative concentration of heavy isotopes (Ingraham *et al.* 1990; Chapman *et al.* 1992). Taken together, these observations suggest that the pools are recharged primarily by infrequent precipitation events, separated by long quiescent periods of slow evaporation and minimal leakage.

CONCLUSIONS

Chemical analysis of water samples collected from pools in Carlsbad Cavern reveals large differences in water quality among the different pools sampled, but little change in water quality for a particular pool during the two-year study period during 1994-95. While most pools contain fresh water of the calcium-magnesium-bicarbonate type, brackish water is found in some pools where evaporation rates are high and/or soluble evaporite minerals are present. Bromide tracer tests suggest mean water residence times in the pools ranging from less than one year to 16 years. The relatively long residence times for some pools indicate that leakage rates are slow. However, the low concentrations of dissolved ions observed in most of the pools demonstrate that leakage or overflow rates are sufficient to prevent evaporative buildup of solutes in these pools over time.

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REFERENCES

American Public Health Association (APHA) (1992). Standard methods for the analysis of waste and wastewater. Method 2510 (Electrical Conductivity): 2-43 to 2-47.

Bowen, E. (1998). Hydrogeology of Rattlesnake Springs, independent study paper as partial fulfillment of MS degree in Hydrology, New Mexico Tech, Socorro: 171 pp.

Boyer, P. S. (1964). Analysis of cave waters from Carlsbad Caverns. Senior thesis, Dept. of Geology, Princeton University, May 1, 1964: 58 pp.

Brooke, M. (1996). *Infiltration pathways at Carlsbad Cavern National Park determined by hydrogeologic and hydrochemical characterization and analysis.* MS thesis, Colorado School of Mines.

Caldwell, D. E. (1991). Limnological survey of cavern pools. Unpublished report to Carlsbad Caverns National Park: 31 pp.

Chapman, J.B., Ingraham, N.L. and Hess, J.W. (1992). Isotopic investigation of infiltration and unsaturated zone flow processes at Carlsbad Cavern, New Mexico. *Journal of Hydrology 133*:343-363.

Draeger Company (1992). Draeger Detector Tube Handbook, 8th Edition, National Draeger, Inc.: 318 pp.

Hach Company (1992). *Water Analysis Handbook, 2nd Edition*: 831 pp.

Hill, C.A. (1987). Geology of Carlsbad Cavern & other caves in the Guadalupe Mountains, New Mexico and Texas. *New Mexico Bureau of Mines & Mineral Resources, Bulletin 117*: 150 pp.

Ingraham, N.L., Chapman, J.B. and Hess, J.W. (1990). Stable isotopes in cave pool systems: Carlsbad Cavern, New Mexico, U.S.A. *Chemical Geology 86*:65-74.

Jagnow, D.H. (1977). Geologic factors influencing speleogenesis in the Capitan Reef complex, New Mexico & Texas. MS thesis, University of New Mexico: 197 pp.

McLean, J.S. (1971). The microclimate of Carlsbad Caverns. *U.S. Geological Survey Open-File Rept. 71-198:* 67 pp.

McLean, J.S. (1976). Factors altering the microclimate in Carlsbad Caverns. *U.S. Geological Survey Open-File Rept. 76-171:* 55 pp.

Plummer, L.N., Jones, B.F., and Truesdell, A.H. (1976 revised 1978, 1984). WATEQF, a FORTRAN IV version of WATEQ, a computer program for calculating chemical equilibria of natural waters. U.S. Geological Survey Water Resources Investigations paper 76-13.

Thrailkill, J.V. (1965). *Studies of the excavation of limestone caves and the deposition of speleothems, Pt. 2: Water chemistry and carbonate speleothem relationships in Carlsbad Caverns, New Mexico*. PhD dissertation, Princeton University: 193 pp.

Thrailkill, J.V. (1971). Carbonate deposition in Carlsbad Caverns. *Journal of Geology 79:*683-695.

Van der Heijde, Paul K.M., Kolm, K.E., Dawson, H., and Brooke, M. (1997). Determining water infiltration routes from structures located above Carlsbad Cavern, Carlsbad Caverns National Park, New Mexico, International Ground Water Modeling Center Rept. GWMI 97-01: 88 p.

Williams, P.W. (1983). The role of the subcutaneous zone in karst hydrology. *Journal of Hydrology 61:*45-67.