

# GEOCHEMICAL TRENDS IN SELECTED LECHUGUILLA CAVE POOLS

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**Abstract:** Lechuguilla Cave is the deepest known limestone cave in the United States, with a surveyed length in excess of 185 km, and hosts some of the world's most exemplary speleogenetic features. Since its discovery in 1986, Lechuguilla Cave has provided researchers with a unique location to study speleogenesis, geology, microbiology, and geochemistry. Although approximately 200 water samples were collected by numerous researchers between 1989 and 1999, subsequently little water quality monitoring has occurred. The primary objective of this study was to collect recent major ion chemical data from pools which either have experienced chemical changes in the past, or which have been designated as drinking-water sources for cavers, and to use those results in conjunction with previous data to evaluate historical trends. The study locations consisted of Lake Lechuguilla, and three pools designated as drinking-water supply (Lake Louise, Pearlsian Gulf Water Supply, and Tower Place Water Supply). In conjunction with sampling for general chemistry, the oxidation-reduction (redox) states of the pools were also assessed by conducting additional measurements for dissolved oxygen, dissolved organic carbon, redox potential (Eh), ferrous iron (Fe<sup>2+</sup>), total dissolved iron, manganese, and nitrogen (NH<sub>3</sub>-N and NO<sub>3</sub>-N). Although Lake Lechuguilla experienced unexplained increases in nitrate and sulfate between 1988 and 1990, the major ion chemistry has apparently returned to baseline conditions. Results also show that between 1988 and 2006, the major ion chemistry of Lake Louise, Pearlsian Gulf, and Tower Place has remained relatively constant. Evaluation of redox status in these pools between 2005 and 2006 indicate an oxic (aerobic) environment, with dissolved oxygen levels in equilibrium with the atmosphere, and concentrations of dissolved organic carbon, NH<sub>3</sub>-N, iron, and manganese below detection limits.

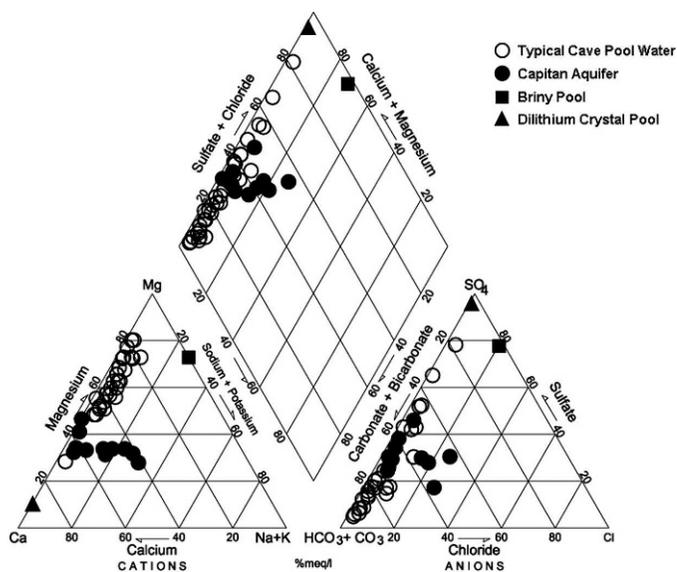
## INTRODUCTION

Lechuguilla Cave, located within Carlsbad Caverns National Park in the Guadalupe Mountains of southeastern New Mexico, is currently the fifth longest cave in the world and the deepest limestone cave in the United States. Lechuguilla Cave, Carlsbad Cavern, and numerous other Guadalupe Mountain caves were formed during the late Miocene through early Pliocene (12 to 4 Ma) through a unique process of speleogenesis whereby sulfuric acid (H<sub>2</sub>SO<sub>4</sub>), derived from oil and gas accumulations in the Delaware Basin, dissolved limestones and dolostones of the Capitan Reef Complex (Hill, 2000; Jagnow et al., 2000). As a result, Lechuguilla Cave contains a vast array of unusual speleogenetic by-products, examples of which include massive gypsum (CaSO<sub>4</sub>·2H<sub>2</sub>O) blocks and rinds, native sulfur, and minerals such as the alunite [KAl<sub>3</sub>(SO<sub>4</sub>)<sub>2</sub>(OH)<sub>6</sub>] group (alunite, jarosite, and natroalunite), hydrated halloysite or endellite [Al<sub>2</sub>Si<sub>2</sub>O<sub>5</sub>(OH)<sub>4</sub>·2H<sub>2</sub>O], and uranium-bearing minerals such as tyuyamunite [Ca(UO<sub>2</sub>)<sub>2</sub>V<sub>2</sub>O<sub>8</sub>·5-8H<sub>2</sub>O] (Polyak and Provencio, 2001). Lechuguilla Cave is renowned for hosting some of the world's most outstanding secondary speleogenetic features, including gypsum glaciers, sulfur masses, gypsum chandeliers, gypsum hairs, subaqueous helictites, hydromagnesite

fronds, and corrosion residue (Davis, 2000; Hill and Forti, 1997).

Operating under the stewardship of the National Park Service (NPS) since breakthrough in May 1986, the exploration and scientific study of Lechuguilla Cave is still ongoing. Since that time, Lechuguilla has provided researchers with a unique natural laboratory for many important studies in the fields of speleogenesis, geology, geochemistry, and microbiology (e.g., DuChene, 2000; Polyak and Provencio, 2000; Polyak and Provencio, 2001; Hill, 2000; Northup et al., 2000). On the day following the initial breakthrough into inner Lechuguilla Cave, explorers discovered a small lake near the entrance which they named Lake Lechuguilla (Reames et al., 1999). As exploration continued, it became apparent that a large number of isolated pools existed throughout the cave. The first pool samples were collected from Lechuguilla Cave during June 1986, and since that time over 200 pool and drip samples have been collected and analyzed for a variety of major ions and trace elements.

Major ion chemical data collected from Lechuguilla Cave pools by various researchers between 1986 and 1999 were eventually compiled and published by Turin and Plummer (2000). Evaluation of these data show that the chemistry of most Lechuguilla pools is dominated by



**Figure 1.** Trilinear diagram illustrating the major ion compositions of the four categories of Lechuguilla Cave water described by Turin and Plummer (2000): (1) Typical Cave Pool water, (2) Capitan Aquifer water, (3) Briny Pool water, and (4) Dilithium Crystal Pool water.

calcium, magnesium, bicarbonate, and sulfate due to interaction of ground water with calcite ( $\text{CaCO}_3$ ), dolomite [ $\text{CaMg}(\text{CO}_3)_2$ ], and massive gypsum deposits within the cave. Supersaturation with respect to calcite and dolomite occurs as a result of carbon dioxide [ $\text{CO}_2(\text{g})$ ] outgassing, the degree of which is largely controlled by the partial pressure of carbon dioxide [ $P_{\text{CO}_2}(\text{g})$ ] in the cave atmosphere. Pools in both Lechuguilla Cave and Carlsbad Cavern are recharged through flowstone seepage and ceiling drips originating from the overlying vadose zone; water can also be lost from the cave pools by processes such as overflow, evaporation, and leakage. Consequently, pools display a range in chemical composition due to a combination of factors such as variations in bedrock mineralogy along recharge flow paths, differences in localized evaporation rates, and residence times of water in the pools (Forbes, 2000; Turin and Plummer, 2000).

Based upon their evaluation of the 1986–1999 pool chemistry data, Turin and Plummer (2000) identified four types of water in Lechuguilla Cave: (1) Typical Cave Pool water, (2) Capitan Aquifer water, (3) Briny Pool water, and (4) Dilithium Crystal Pool water (Fig. 1). Typical Cave Pool water has a pH between 7.5 and 8.5, a magnesium to calcium (Mg:Ca) molar ratio greater than 1.0, a  $P_{\text{CO}_2}$  greater than atmospheric ( $10^{-3.5}$  atm), and is oversaturated with respect to calcite and dolomite. Capitan Aquifer water is similar in composition, but is characterized by a higher  $P_{\text{CO}_2}$ , a lower Mg:Ca molar ratio, and has been shown to contain detectable concentrations of dissolved iron (0.2 to  $0.9 \text{ mg L}^{-1}$ ) indicating that reducing conditions can exist in the regional aquifer (Turin and Plummer, 2000). The

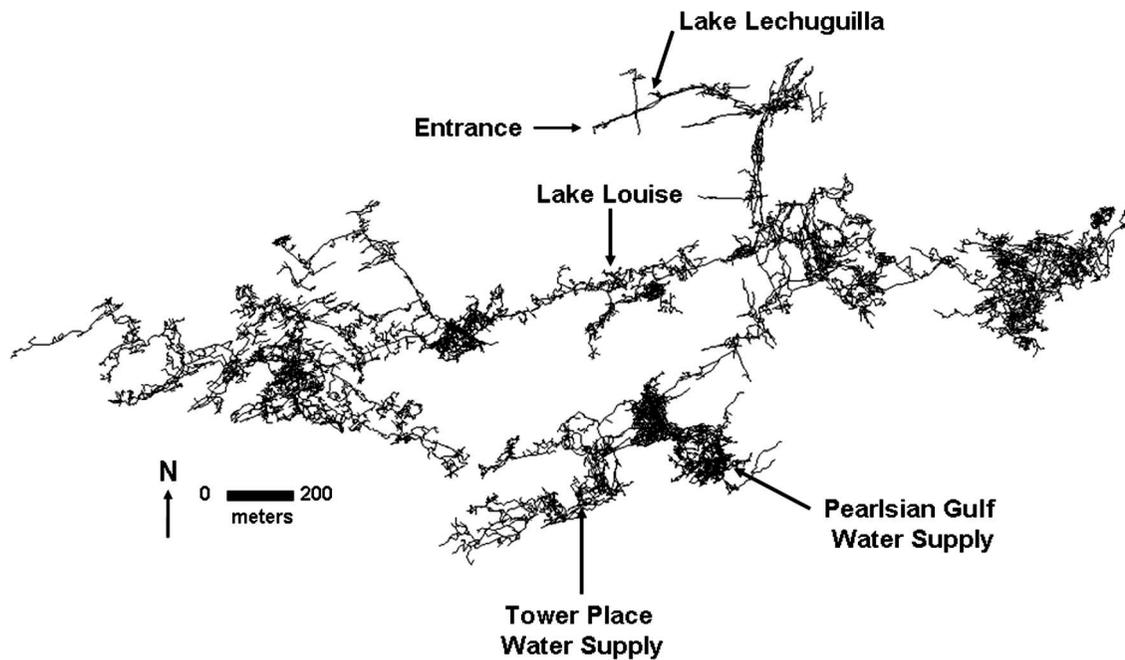
Briny Pool and Dilithium Crystal Pool represent two chemical extremes of unique composition when compared to most Lechuguilla Cave water. The Briny Pool water contains higher proportions of sodium and chloride when compared to Typical Cave Pool water (Fig. 1) and is apparently extremely evapoconcentrated, with a total dissolved solids (TDS) concentration of approximately  $45,000 \text{ mg L}^{-1}$ . The Dilithium Crystal Pool (TDS approximately  $2,500 \text{ mg L}^{-1}$ ) contains the highest proportions of calcium and sulfate for any water sampled in the cave (Fig. 1), and is the only pool yet identified which is oversaturated with respect to gypsum.

Repeated sampling and analysis of certain Lechuguilla Cave pools has shown that individual pools tend to maintain fairly consistent chemistry. Lake Lechuguilla, however, experienced significant increases in the concentrations of sulfate and nitrate between 1986 and 1990. Turin and Plummer (2000) noted that these changes may be an indication of variations in local precipitation chemistry, or anthropogenic contamination due to proximity to the cave entrance, and suggested continued monitoring in Lake Lechuguilla. A number of other pools in Lechuguilla Cave also have the potential to be affected by human activities because of their proximity to designated camps and their continued use as drinking-water supply by scientists and explorers for 20 years. For example, coliform bacteria, a potential indicator of human fecal contamination, have been identified in a number of Lechuguilla Cave pools (Hunter et al., 2004; Barton and Pace, 2005), prompting closure of the Red Lake Camp in the Western Branch by the NPS until further notice.

The current study presents the first major ion chemical data that have been collected in eight years from Lake Lechuguilla and over 15 years from three other designated drinking-water sources in Lechuguilla Cave (Lake Louise, Pearlsian Gulf, and Tower Place). The primary objective of this study was to collect additional pool samples and characterize current chemical conditions in selected Lechuguilla Cave pools to better evaluate historical major ion trends and potential impacts to water quality from human activities. Although hundreds of samples have previously been collected and analyzed from Lechuguilla Cave pools, few data exist to evaluate the oxidation-reduction (redox) status of the pools. Therefore, a secondary objective was to evaluate the redox status of the pools by characterizing dissolved oxygen (DO), dissolved organic carbon (DOC), oxidation-reduction potential (Eh), and concentrations of redox-sensitive elements such as iron, manganese, and the forms of inorganic nitrogen ( $\text{NH}_3\text{-N}$  and  $\text{NO}_3\text{-N}$ ).

## STUDY LOCATIONS

Water samples were collected during 2005 and 2006 from selected pools located in various branches of Lechuguilla Cave. The general areas of sample collection are shown on Figure 2 and include: (1) Lake Lechuguilla



**Figure 2.** Map of Lechuguilla Cave (plan) showing the cave entrance and general locations of the pools sampled during this study (survey data provided by Carlsbad Caverns National Park, July 13, 2006).

(Entrance), (2) Lake Louise (Western Branch), (3) Pearlsian Gulf Water Supply (Southwestern Branch), and (4) Tower Place Water Supply (Southwestern Branch). Lake Lechuguilla is relatively close to the cave entrance and is located approximately 55.5 m below the entrance elevation (−55.5 m). Water levels in Lake Lechuguilla exhibit rapid responses to surface precipitation, and pool levels have decreased significantly over the past decade. Lake Lechuguilla is not a designated drinking-water supply for cavers, but the chemical trends in Lake Lechuguilla are of interest due to its proximity to both the main route of travel and the ground surface. Lake Louise is located in the Western Branch at approximately −307 m and is the designated drinking water supply for Deep Seas Camp. The Pearlsian Gulf Water Supply (−233 m) is the designated drinking-water supply for Big Sky Camp, and consists of a small pool near the Pearlsian Gulf in the Southwest Branch. The Tower Place Water Supply (−130 m) consists of a small pool located near the handline for the entrance to Tower Place and was only sampled once in 2005 during this study.

#### MATERIALS AND METHODS

Field measurements of pH, temperature, and electrical conductivity (EC, corrected to 25 °C) were made using a combination HACH® (Loveland, CO) ion-selective electrode instrument, calibrated using standard pH and EC solutions prior to each use. Field measurement of ferrous iron ( $\text{Fe}^{2+}$ ) and dissolved oxygen ( $\text{O}_2$ ) were conducted using a HACH® DR-850 colorimeter. Redox potential (Eh) was measured using a combination Pt/Ag-

AgCl electrode and standardized to the Standard Hydrogen Electrode using Zobell Solution (Eaton et al., 2005).

Water-sample collection followed the standard procedures for sampling and preservation of natural waters (Eaton et al., 2005). Pool samples were collected from the water surface using a sterilized plastic syringe and filtered through a 0.45  $\mu\text{m}$  pore-size syringe filter and split into: (1) a hydrochloric-acid (HCl)-preserved sample for analysis of DOC, (2) a nitric-acid ( $\text{HNO}_3$ )-preserved sample for analysis of manganese plus total iron ( $\text{Fe}^{2+} + \text{Fe}^{3+}$ ), (3) a sulfuric-acid ( $\text{H}_2\text{SO}_4$ )-preserved sample for determination of both ammonia-nitrogen ( $\text{NH}_3\text{-N}$ ) and nitrate plus nitrite-nitrogen ( $\text{NO}_3+\text{NO}_2\text{-N}$ ), and (4) an unpreserved sample for analysis of major dissolved cations and anions. Two field cave blanks (2005 and 2006) were also prepared by preserving and filtering analytical-grade distilled water into clean sample containers containing the appropriate preservative while in-cave to evaluate the presence of potential sample contaminants. Both cave blanks were prepared at Lake Lechuguilla.

Within one hour of exiting the cave, the water samples were stored under refrigeration and maintained at 4 °C or less during shipping to SVL Analytical, Inc. (Kellogg, ID) for chemical analysis. Chemical analyses were conducted using standard methods of the United States Environmental Protection Agency (USEPA, 1983): Dissolved organic carbon (Method 415.1), chloride (Method 300.0), dissolved calcium, potassium, magnesium, sodium, iron, manganese, silicon (Method 200.7), ammonia-nitrogen ( $\text{NH}_3\text{-N}$ , Method 350.1), carbonate alkalinity (Method 2020B), sulfate (Method 300.0), and nitrate+nitrite-nitrogen ( $\text{NO}_3+\text{NO}_2\text{-N}$ ).

N, Method 353.2) (in this study,  $\text{NO}_3+\text{NO}_2\text{-N}$  concentrations are assumed to equal  $\text{NO}_3\text{-N}$  concentrations due to the instability of  $\text{NO}_2\text{-N}$  in the ambient aerobic environment). Laboratory quality assurance/quality control (QA/QC) samples included duplicates, matrix spikes, and laboratory control samples.

The analytical results were reviewed for QA/QC and chemical trends were evaluated in conjunction with historical pool chemistry data previously collected from the same locations (Turin and Plummer, 2000). The data were input into the geochemical speciation model PHREEQC (Parkhurst and Appelo, 1999), which uses the Debye-Hückel equation for ion activity calculations, to calculate  $P_{\text{CO}_2}$  values and mineral saturation states for the various carbonate, sulfate, and silicate minerals. The saturation index (*SI*) for a solid mineral phase is defined as:

$$SI = \log\left(\frac{IAP}{K_{sp}}\right) \quad (1)$$

where:

*IAP* = ion activity product observed in solution  
*K<sub>sp</sub>* = theoretical solubility product at field temperature

A positive *SI* indicates that the solution is oversaturated with respect to a given solid phase and that precipitation of the respective phase is thermodynamically favorable. A negative *SI* indicates that the solution is undersaturated and will dissolve the solid phase. When *SI* = 0, the solution and solid phases are in apparent equilibrium. In this study, apparent equilibrium is defined when *SI* values are between -0.50 and +0.50 due to inherent uncertainties in the thermodynamic data.

## RESULTS AND DISCUSSION

### QUALITY ASSURANCE/QUALITY CONTROL

Analytical results from the two cave blanks (2005 and 2006) were below detection for all constituents except for low levels of calcium (0.085 to 0.235 mg L<sup>-1</sup>), chloride (0.23 to 1.24 mg L<sup>-1</sup>), and  $\text{NH}_3\text{-N}$  (0.04 mg L<sup>-1</sup> in 2006). Cation-anion balances for all samples were within 5%. Percent recovery for laboratory control samples ranged from 95.3% to 108%, while percent recovery from matrix spikes ranged from 92% to 116%. Relative percent differences ranged from 0% to 8% for laboratory duplicate samples. All values for the laboratory control samples, matrix spikes, and laboratory duplicates were within acceptable limits (USEPA, 1994).

### FIELD AND LABORATORY RESULTS

The results for field and laboratory parameters collected from Lechuguilla Cave pools during the 2005 and 2006 study are provided in Table 1. The data are shown in conjunction with results from previous investigators for the

Pearlsian Gulf and Tower Place water supply locations to demonstrate historical trends. Historical major ion chemistry for Lake Lechuguilla and Lake Louise (Turin and Plummer, 2000) are presented graphically and discussed in the following section, and therefore those data are not tabulated in Table 1. The discussion of field and laboratory results in this section pertains only to water samples collected during 2005 and 2006.

The field and laboratory results for selected Lechuguilla Cave pools studied during 2005-2006 are consistent with those of Typical Cave Pool water discussed by Turin and Plummer (2000). Field results show ranges in pH from 7.58 to 8.06, EC from 397 to 517  $\mu\text{S cm}^{-1}$ , and temperature from 18.4 to 20.4 °C (Table 1). Dissolved oxygen ranged from 7.9 to 9.3 mg L<sup>-1</sup> indicating the presence of aerobic conditions in the pools. The measured Eh values ranged from 416 to 466 mV and dissolved ferrous iron concentrations were <0.03 mg L<sup>-1</sup> in all samples.

Laboratory results for the major cations and anions were used to generate a trilinear diagram illustrating the overall chemical composition of the pools (Fig. 3). The pool water compositions are predominantly Ca-Mg-HCO<sub>3</sub> waters, consistent with those of Typical Pool water (Turin and Plummer, 2000). The data indicate that each pool maintained consistent chemistry between 2005 and 2006, but there were slight differences in major ion composition between the pools. Lake Louise and the Pearlsian Gulf Water Supply contained higher proportions of calcium and sulfate when compared to Lake Lechuguilla and the Tower Place Water Supply (Fig. 3), perhaps due to a higher abundance of gypsum in these areas. Calculated total dissolved solids (TDS) concentrations ranged from 331 to 383 mg L<sup>-1</sup> and were slightly higher in the Pearlsian Gulf and Tower Place water supplies when compared to Lake Lechuguilla and Lake Louise. As a result of preferential calcite precipitation over dolomite, the Mg:Ca molar ratios are greater than unity (Table 1), consistent with the majority of Lechuguilla Cave pools (Turin and Plummer, 2000).

### Oxidation-Reduction (Redox) State

The redox state of the pools was evaluated by direct measurement of Eh and DO in conjunction with the concentrations of redox-sensitive elements (Table 1). The high DO concentrations indicate that the pools are in equilibrium with atmospheric oxygen. Consequently, the concentrations of both DOC and redox-sensitive metals (ferrous iron, total iron, and manganese) are below detection, and inorganic nitrogen is mainly present as the oxidized nitrate ( $\text{NO}_3\text{-N}$ ) species rather than ammonia ( $\text{NH}_3\text{-N}$ ) (Table 1). While the Eh measurements typically reflect oxidizing conditions, obtaining thermodynamically-meaningful Eh measurements when using a platinum electrode is not possible if the dominant redox-sensitive elements are carbon, nitrogen, oxygen, hydrogen, and oxidized sulfur (sulfate). These observations led to the development of a simplified redox classification scheme

**Table 1. Recent (2005–2006) and historic chemical data for selected Lechuguilla Cave pools (mg L<sup>-1</sup> unless otherwise indicated).**

Parameter	Lake Lechuguilla Survey Station A10		Lake Louise Survey Station EC58		Pearlsian Gulf Water Supply Survey Station FUX9				Tower Place Water Supply Survey Station sFLVV2	
	6/17/05	6/17/06	6/13/05	6/12/06	4/2/90 <sup>b</sup>	6/9/96 <sup>c</sup>	6/15/05	6/15/06	5/29/89 <sup>b</sup>	6/16/05
Depth Below Entrance (m)	-55.5		-307		-233				-130	
Approx. Pool Volume (m <sup>3</sup> )	Variable <sup>a</sup>		8.7		1.6				2.6	
Sampling Date	6/17/05	6/17/06	6/13/05	6/12/06	4/2/90 <sup>b</sup>	6/9/96 <sup>c</sup>	6/15/05	6/15/06	5/29/89 <sup>b</sup>	6/16/05
<b>Field Parameters</b>										
pH	8.06	8.03	7.66	7.62	7.80	7.58	7.62	7.63	7.90	7.62
Temperature (°C)	18.4	19.0	19.9	20.4	NR	NR	18.9	20.3	NR	18.9
Elect. Cond. (µs cm <sup>-1</sup> )	413	397	425	420	460	NR	517	476	430	517
Dissolved Oxygen	NM	7.9	7.9	8.4	NR	NR	9.3	7.9	NR	9.3
Eh (mV)	NM	416	455	451	NR	NR	442	466	NR	442
Fe <sup>2+</sup>	< 0.03	< 0.03	< 0.03	< 0.03	NR	NR	< 0.03	< 0.03	NR	< 0.03
<b>Laboratory Parameters</b>										
Alkalinity (mg CaCO <sub>3</sub> L <sup>-1</sup> )	180	183	126	135	152	270	134	141	200	195
HN <sub>3</sub> -N	< 0.03	< 0.03	0.04	0.05	NR	NR	< 0.03	0.04	NR	< 0.03
Ca	35.1	31.1	44.2	39.9	43.8	NR	48.3	43.7	31.7	29.7
Cl	3.4	3.65	3.02	4.16	2.3	NR	2.03	3.06	3.4	3.11
Dissolved Organic Carbon	< 1	< 1	< 1	< 1	NR	NR	< 1	< 1	NR	1.7
Fe	< 0.06	< 0.06	< 0.06	< 0.06	< 0.02	NR	< 0.06	< 0.06	< 0.02	< 0.06
Mg	32.8	32.7	27.8	27.6	33	NR	34.1	34.0	38.8	40.6
Mn	< 0.004	< 0.004	< 0.004	< 0.004	< 0.02	NR	< 0.004	< 0.004	< 0.02	< 0.004
NO <sub>3</sub> -N	1.90	1.65	1.53	1.49	1.5	1.2	1.03	1.05	1.3	0.740
K	0.89	0.84	0.59	0.53	0.6	NR	0.73	0.65	1.1	0.74
Na	2.77	2.76	3.62	3.29	2.4	NR	2.52	2.26	3.0	2.92
Si	5.09	5.61	5.23	5.33	4.49	NR	4.91	4.95	4.81	4.95
SO <sub>4</sub>	28.2	34.7	79.8	84.4	92	99.8	108	112	28	29.5
Total Dissolved Solids	342	348	331	342	376	NC	374	383	366	360
Mg:Ca Molar Ratio	1.54	1.74	1.04	1.14	1.24	NC	1.16	1.28	2.02	2.25

<sup>a</sup> 2.2 m<sup>3</sup> (June 2005) and 0.64 m<sup>3</sup> (June 2006).

<sup>b</sup> Collected by Gregg Oelker (Oelker, 1990).

<sup>c</sup> Collected by Helen Dawson (Turin and Plummer, 2000).

NR – not reported in cited study.

NM – not measured in current study.

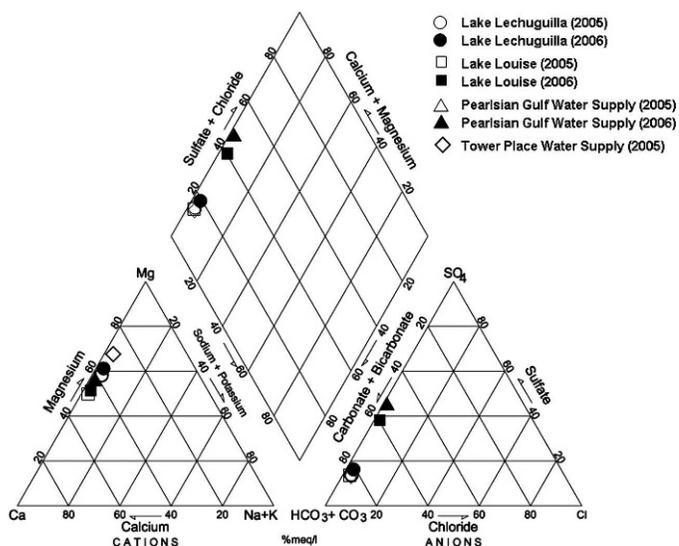
NC – not calculated due to incomplete data.

which is broadly-based on the presence or absence of oxygen, organic carbon, iron, and manganese; according to the redox classification, the Lechuguilla Cave pool samples indicate an oxic environment (Langmuir, 1997).

#### GEOCHEMICAL MODELING

The results of geochemical modeling using PHREEQC (Table 2) indicate that the pool waters are generally in equilibrium with respect to calcite, (CaCO<sub>3</sub>), dolomite, and magnesite (MgCO<sub>3</sub>). High degrees of gypsum undersaturation were calculated, and silica concentrations in the waters

appear to be controlled by chalcedony (SiO<sub>2</sub>), as *SI* values were close to zero for this mineral. Calculated *P*<sub>CO<sub>2</sub></sub> values were up to 12 times higher than atmospheric (10<sup>-3.5</sup> atm). The lowest calculated *P*<sub>CO<sub>2</sub></sub> value (10<sup>-2.80</sup> atm) was for Lake Lechuguilla, while the highest calculated values (10<sup>-2.39</sup> atm) were for the Pearlsian Gulf and Tower Place water-supply locations. The low calculated ionic strength values (0.0062 to 0.0077 *M*) demonstrate that samples are within the range of ionic strength values considered valid for calculation of ion activities when using the Debye-Hückel equation (Langmuir, 1997).



**Figure 3.** Trilinear diagram illustrating the major ion compositions for selected Lechuguilla Cave pools sampled during 2005 and 2006.

#### HISTORICAL TRENDS IN MAJOR ION CHEMISTRY

Pool chemistry data collected during 2005 and 2006 were used in conjunction with the data compiled by Turin and Plummer (2000) to examine historical major ion trends for selected Lechuguilla Cave pools. Between 1988 and 1990, Lake Lechuguilla reportedly experienced considerable increases in sulfate and nitrate concentrations, balanced by increases in calcium, magnesium, potassium and a decrease in bicarbonate (Fig. 4). During the same period, the concentrations of TDS also increased by  $260 \text{ mg L}^{-1}$ , although pH remained in the range between 7.4 and 8.4. The increases in sulfate and nitrate cannot be attributed to evapoconcentration because the associated increases in chloride were relatively small (Fig. 4) and the area has been shown to maintain a relative humidity  $> 95\%$  year-round (Burger, 2005). Since 1996, the concentra-

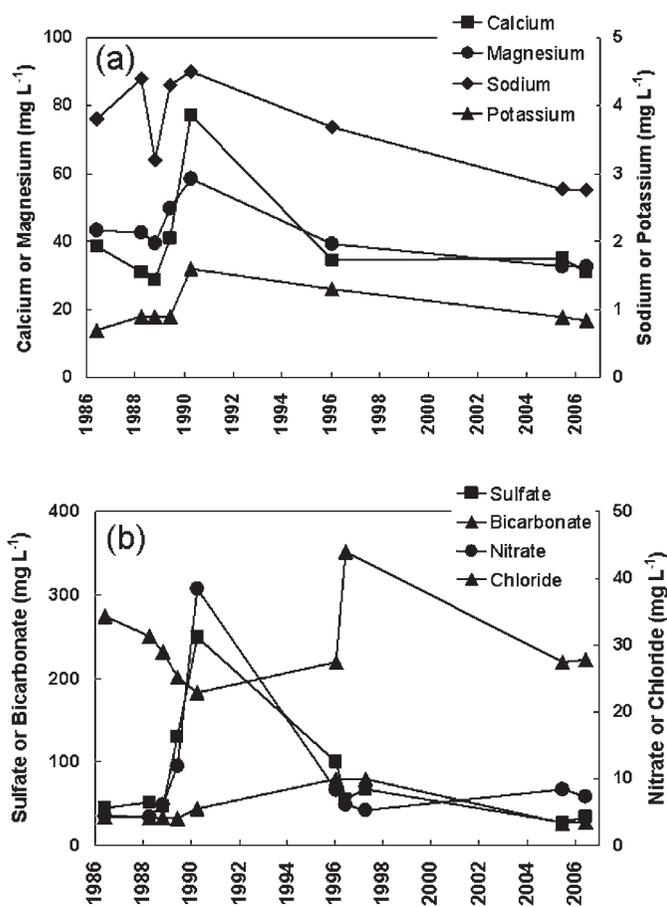
tions of sulfate, nitrate, and TDS have been decreasing, and the recent data collected during 2005 and 2006 indicate that Lake Lechuguilla has returned to baseline (pre-1989) chemical conditions (Fig. 4).

Water-level data have been collected from a staff gauge installed in Lake Lechuguilla since 1997. The relationship between precipitation and water level demonstrates the rapid hydrologic response of Lake Lechuguilla to precipitation, especially when water levels are closely monitored as demonstrated during 2004 and 2005 (Fig. 5). Above-average precipitation in 2004 produced considerable increases in Lake Lechuguilla water levels which declined rapidly thereafter. Major ion chemistry and lake level data collected during these recent fluctuations show that while water volumes changed considerably between June 2005 and June 2006 (from  $2.2$  to  $0.64 \text{ m}^3$ ), the EC, TDS, and chloride concentrations remained constant (Table 1, Fig. 4). Together with observed rapid hydrologic responses to precipitation events at the surface, the absence of chemical concentration increases between 2005 and 2006 indicates that leakage, rather than evaporation, is the primary mechanism of water loss from Lake Lechuguilla.

Other possible explanations for the observed increases in nitrate and sulfate in cave pools are atmospheric deposition and either natural or anthropogenic biological activity (Turin and Plummer, 2000). Precipitation-weighted mean concentrations calculated using data from the National Atmospheric Deposition Program for Guadalupe Mountains National Park (Station TX22) (1986 through 1991) were  $0.83 \text{ mg L}^{-1}$  for nitrate,  $0.17 \text{ mg L}^{-1}$  for ammonium ( $\text{NH}_4^+$ ), and  $1.4 \text{ mg L}^{-1}$  for sulfate. These concentrations do not explain the observed increases in nitrate or sulfate, however, when considering the enrichment factors ( $\text{EF} = \text{pool}:\text{precipitation}$ ) calculated for nitrate ( $\text{EF} = 9$ ) and sulfate ( $\text{EF} = 38$ ) in Lechuguilla Cave pools (Turin and Plummer, 2000). It is interesting to note, however, that the maximum precipitation-weighted mean values for nitrate ( $3.17 \text{ mg L}^{-1}$ ) and sulfate ( $7.1 \text{ mg L}^{-1}$ ) occurred in 1989, corresponding to the time

**Table 2.** Mineral saturation index (*SI*),  $P_{\text{CO}_2}$ , and ionic strength (*I*) values for selected samples calculated using PHREEQC (Parkhurst and Appelo, 1999).

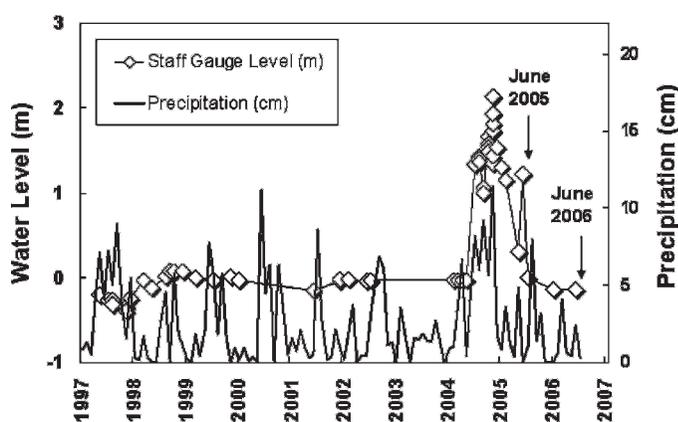
Mineral Phase	Lake Lechuguilla (6/17/06)	Lake Louise (6/12/06)	Pearlsian Gulf Water Supply (6/15/06)	Tower Place Water Supply (6/16/05)
Calcite ( $\text{CaCO}_3$ )	0.20	-0.19	-0.17	-0.17
Dolomite [ $\text{CaMg}(\text{CO}_3)_2$ ]	0.64	-0.32	-0.17	0.01
Magnesite ( $\text{MgCO}_3$ )	-0.06	-0.62	-0.52	-0.32
Gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ )	-2.35	-1.88	-2.45	-2.45
Chalcedony ( $\text{SiO}_2$ )	-0.11	-0.15	-0.16	-0.16
Quartz ( $\alpha\text{-SiO}_2$ )	0.40	0.36	0.35	0.35
$\text{SiO}_2$ (amorphous)	-0.93	-0.97	-0.67	-0.67
$P_{\text{CO}_2}$ (atm)	-2.80	-2.54	-2.39	-2.39
Ionic Strength ( <i>M</i> )	0.0062	0.0066	0.0077	0.0077



**Figure 4.** Historical trends in major ion chemistry for Lake Lechuguilla (1986–2006): (a) cation concentrations and (b) anion concentrations. The 2005 and 2006 data are from the present study.

when historical nitrate and sulfate concentrations began to increase (Fig. 4).

Lake Lechuguilla is in close proximity to the main trail, and therefore the potential also exists for anthropogenic contamination of the lake. The trail is narrow and steeply-sloping toward the lake, and therefore it is conceivable that disturbance and sloughing of rocks, mud, or other debris from the heavily-traveled route past Lake Lechuguilla could release constituents into the water. Anthropogenic contamination could also have resulted from dropping of food or foreign objects into the water, or tracking of bat guano on boots from the cave entrance, which was released to the water and slowly mineralized or dissolved over several years to produce the observed trends (Fig. 4). Nonetheless, simple mass balance calculations indicate that significant mass would have to be added to produce the observed concentration increases. For example, mineralization of the nitrogen contained in bat guano to produce a 30 mg L<sup>-1</sup> increase in nitrate concentrations in Lake Lechuguilla, assuming a pre-1990 volume of 4 m<sup>3</sup>, would require approximately 900 g of guano. It seems unlikely that the mass of guano or other foreign matter required to

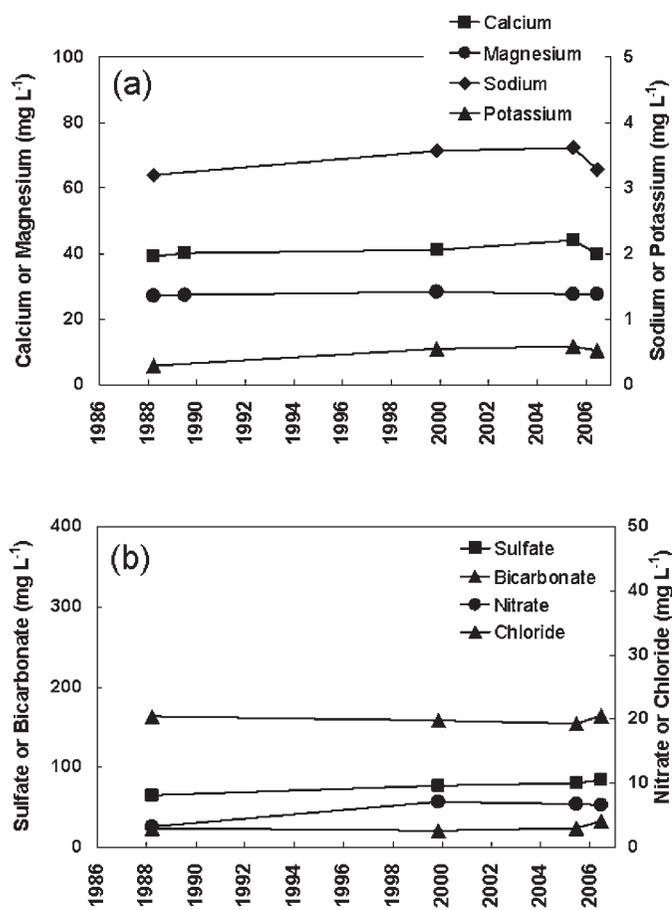


**Figure 5.** Lake Lechuguilla water levels and precipitation hydrograph for Carlsbad Caverns National Park for the period 1997–2006.

produce the observed concentration increases in Lake Lechuguilla could have been introduced into Lake Lechuguilla by human activities.

The increase in nitrate and sulfate concentrations in Lake Lechuguilla was relatively gradual and occurred over a period several years (Fig. 4), yet monitoring has shown that Lake Lechuguilla water volumes respond rapidly to surface precipitation events. Gradual changes in water quality would not be expected in such a dynamic system if anthropogenic contamination had occurred. Rather, the chemical trends are probably natural and related to a combination of variation in factors such as climate (chemistry, duration, and intensity of local precipitation events), soil biological activity, and the degree of water-soil-rock interaction of water percolating through the overlying vadose zone. Between 1990 and 2006, nitrate concentrations in seepage entering the Entrance Series near Lake Lechuguilla (Liberty Bell Room) ranged from 2.2 to 21.7 mg L<sup>-1</sup>. The maximum concentrations of nitrate in seepage (21.7 mg L<sup>-1</sup>) and in Lake Lechuguilla (38.5 mg L<sup>-1</sup>) were both measured in 1990 and are of the same magnitude. Sulfate concentrations in seepage have varied from 11.5 to 29 mg L<sup>-1</sup> but are generally an order of magnitude less than Lake Lechuguilla and other Entrance Series pools (Turin and Plummer, 2000). These observations indicate that nitrate concentrations in Lake Lechuguilla may be more closely related to those of vadose-zone seepage, whereas enrichment of sulfate in pools occurs to varying degrees due to chemical and mineralogical variations along cave seepage flow paths.

Historical trends in major ion concentrations for Lake Louise indicate minimal variation between 1988 and 2006 (Fig. 6). The consistent chemistry of Lake Louise (-307 m) in comparison to Lake Lechuguilla (-55.5 m) could reflect isolation from near-surface hydrologic processes, a lower degree of anthropogenic disturbance, or the longer flow path of water through the cave which results in chemically-consistent inflow to the pool. Examination of



**Figure 6. Historical trends in major ion chemistry for Lake Louise (1988–2006): (a) cation concentrations and (b) anion concentrations. The 2005 and 2006 data are from the present study.**

both the historic and current major ion chemistry for Pearlsian Gulf and Tower Place Water Supply also indicates that the major cation and anion compositions of these waters have not changed significantly since they were first sampled and analyzed (Table 1).

### CONCLUSIONS

Recent major ion chemistry data collected during 2005 and 2006 were used to supplement previous data collected from Lechuguilla Cave pools to evaluate historical trends in water chemistry. Lake Lechuguilla experienced unexplained increases in sulfate and nitrate between 1988 and 1990, but the major ion chemistry has returned to pre-1990 conditions. Evaluation of the historical chemical trends and hydrologic properties of Lake Lechuguilla indicate that the increases in sulfate and nitrate probably represent natural variations in the chemistry of vadose zone water and cave seepage near the surface. Both historical and recent major ion analyses from three other significantly deeper pools designated as drinking-water sources for

cavers (Lake Louise, Tower Place/Pearlsian Gulf water supplies) indicates that their major ion chemistry has remained relatively constant since the first water samples were collected over 15 years ago. The pools were close to equilibrium with calcite, dolomite, and chalcedony, and calculated  $P_{\text{CO}_2}$  were 10 to 12 times greater than atmospheric. Evaluation of pool redox status indicates an oxic environment, with dissolved oxygen levels in equilibrium with the ambient atmosphere, and concentrations of DOC,  $\text{NH}_3\text{-N}$ , iron, and manganese below detection limits. Because the major ion composition of most Lechuguilla Cave pools generally remains stable, routine monitoring for inorganic constituents in Lechuguilla Cave pools is not necessary. However, current and future researchers are encouraged to incorporate general inorganic water-quality characterization into their research when appropriate, because periodic monitoring could possibly identify chemical variations which could occur from natural climatic, anthropogenic, or biological activities.

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### REFERENCES

- Barton, H.A., and Pace, N.R., 2005, Discussion: Persistent coliform contamination in Lechuguilla Cave pools: *Journal of Cave and Karst Studies*, v. 67, p. 55–57.
- Burger, P., 2005, Lechuguilla Newsletter, Issue 1, January: Carlsbad Caverns National Park.
- Davis, D., 2000, Extraordinary features of Lechuguilla Cave, Guadalupe Mountains, New Mexico: *Journal of Cave and Karst Studies*, v. 62, p. 147–157.
- DuChene, H.R., 2000, Bedrock features of Lechuguilla Cave, Guadalupe Mountains, New Mexico: *Journal of Cave and Karst Studies*, v. 62, p. 109–119.
- Eaton, A.E., Clasceri, L.S., Rice, E.W., Greenberg, A.E., and Franson, M.A.J., eds., 2005, Standard methods for the examination of water and wastewater: Washington, D.C., American Public Health Association, 1368 p.
- Forbes, J.R., 2000, Geochemistry of Carlsbad Cavern Pool Waters, Guadalupe Mountains, New Mexico: *Journal of Cave and Karst Studies*, v. 62, p. 127–134.
- Hill, C.A., 2000, Overview of the geologic history of cave development in the Guadalupe Mountains, New Mexico: *Journal of Cave and Karst Studies*, v. 62, p. 60–71.

- Hill, C., and Forti, P., 1997, *Cave Minerals of the World*, 2<sup>nd</sup> Edition: Huntsville, Ala., National Speleological Society, 463 p.
- Hunter, A.J., Northup, D.E., Dahm, C.N., and Boston, P.J., 2004, Persistent coliform contamination in Lechuguilla Cave pools: *Journal of Cave and Karst Studies*, v. 66, p. 102–110.
- Jagnow, D.H., Hill, C.A., Davis, D.G., DuChene, H.R., Northup, D.E., and Queen, J.M., 2000, History of the sulfuric acid theory of speleogenesis in the Guadalupe Mountains, New Mexico: *Journal of Cave and Karst Studies*, v. 62, p. 54–59.
- Langmuir, D.L., 1997, *Aqueous Environmental Chemistry*: Englewood Cliffs, N.J., Prentice Hall, 600 p.
- Northup, D.E., Dahm, C.N., Melim, L.A., Spilde, M.N., Crossey, L.J., Lavoie, K.H., Mallory, L.M., Boston, P.J., Cunningham, K.I., and Barns, S.M., 2000, Evidence for geomicrobiological interactions in Guadalupe caves: *Journal of Cave and Karst Studies*, v. 62, p. 80–90.
- Oelker, G.L., 1990, *The Lechuguilla Cave Water Quality Study*, Unpublished Report, Carlsbad Caverns National Park files.
- Parkhurst, D.L., and Appelo, C.A.J., 1999, *User's Guide to PHREEQC (Version 2.0)*, A Computer Program for Speciation, Batch-Reaction, One-Dimensional Transport, and Inverse Geochemical Calculations, U.S. Geological Survey Water-Resources Investigations Report 99-4259, 312 p.
- Polyak, V.J., and Provencio, P., 2000, Summary of timing of sulfuric-acid speleogenesis for Guadalupe caves based on ages of alunite: *Journal of Cave and Karst Studies*, v. 62, p. 72–74.
- Polyak, V.J., and Provencio, P., 2001, By-product materials related to H<sub>2</sub>S-H<sub>2</sub>SO<sub>4</sub> influenced speleogenesis of Carlsbad, Lechuguilla, and other caves of the Guadalupe Mountains, New Mexico: *Journal of Cave and Karst Studies*, v. 63, p. 23–32.
- Reames, S., Fish, L., Burger, P., and Kambesis, P., 1999, *Deep Secrets: The Discovery and Exploration of Lechuguilla Cave*: St. Louis, Mo, Cave Books, 381 p.
- Turin, H.J., and Plummer, M.A., 2000, Lechuguilla Cave Pool Chemistry, 1986–1999: *Journal of Cave and Karst Studies*, v. 62, p. 135–143.
- USEPA, 1983, *Methods for Chemical Analysis of Water and Wastes*, EPA-6-4-79-20, U.S. Environmental Protection Agency, Washington, D.C., 552 p.
- USEPA, 1994, *USEPA Contract Laboratory Program (CLP) National Functional Guidelines for Inorganic Data Review*, 143 p.