STUDY OF A KARST-GEOCHEMICAL DATA SET FROM A MARBLE CAVE: OREGON CAVES NATIONAL MONUMENT

Mary Schubert
38 Champagne Drive
Lake St. Louis, Missouri 63367
choclt3376@centurytel.net
314-324-7191

Abstract

Oregon Caves National Monument (ORCA) is situated in the Applegate group, a formation in the Western Triassic-Paleozoic tectonostratigraphic terrane of the Siskiyou Mountains in southwest Oregon. This cave is unusual because it occurs in marble, most dissolution caves are formed in limestone or dolomite. The U.S. National Park Service (NPS) has over 3,900 caves, but only Oregon Caves National Monument, Kings Canyon, and Great Basin National Parks have caves formed in marble. Though much has been written about karst water chemistry in limestone, little has been written about marble.

A water-chemistry data set for Oregon Caves National Monument was compiled by the National Park Service between late 1991 and fall 1995 from both drip water and cave streams. Seventeen months of data were selected for this study, covering the period May 1992 through October 1993 from six sampling sites within the cave and one surface stream. Along with pH and temperature, major ions and total organic carbon concentrations were recorded. This study showed that water from most of the sites was supersaturated with respect to calcite, and levels of $P\text{co}_2$ were up to two orders of magnitude higher than atmospheric. Distinct similarities in ionic composition were observed for sites with similar source-water travel histories. The data indicate that karst water chemistry varies more as a function of passage geometry, soil type, rock chemical composition, and source water than of differences in texture (marble vs. limestone).

Key words: Oregon Caves National Monument, geochemistry, marble caves, Pettyjohns Cave, Georgia, Lilburn Cave, Sequoia and Kings Canyon National Park, California

Introduction

Oregon Caves National Monument (ORCA), in southwest Oregon (Figure 1), was dedicated in 1909. The ORCA region has a high diversity of plants (~3,800) and animals (~50,000) because of diverse habitats over a range of climatic and geologic conditions (NPS 2007). NPS has over 3,900 caves (NPS 2007), but Oregon Caves National Monument, Kings Canyon National Park, and Great Basin National Park are the only ones that have caves formed in marble. This makes Oregon Caves distinct among other caves.

The water that flows through Oregon Cave is fed by stream piracy (discrete water input) and by water dripping from speleothems (diffuse water input) (White 1988). A water-chemistry data set exists for ORCA, compiled from a ten-year sampling activity which began in 1991 and continued through 2001. The samples were collected from various drips in the cave and a few locations from the subsurface stream. A special feature of this data set is the inclusion of total organic carbon (TOC) concentrations. This data set provides an opportunity to compare the chemistries of marble and limestone karst waters, compare drip water chem-

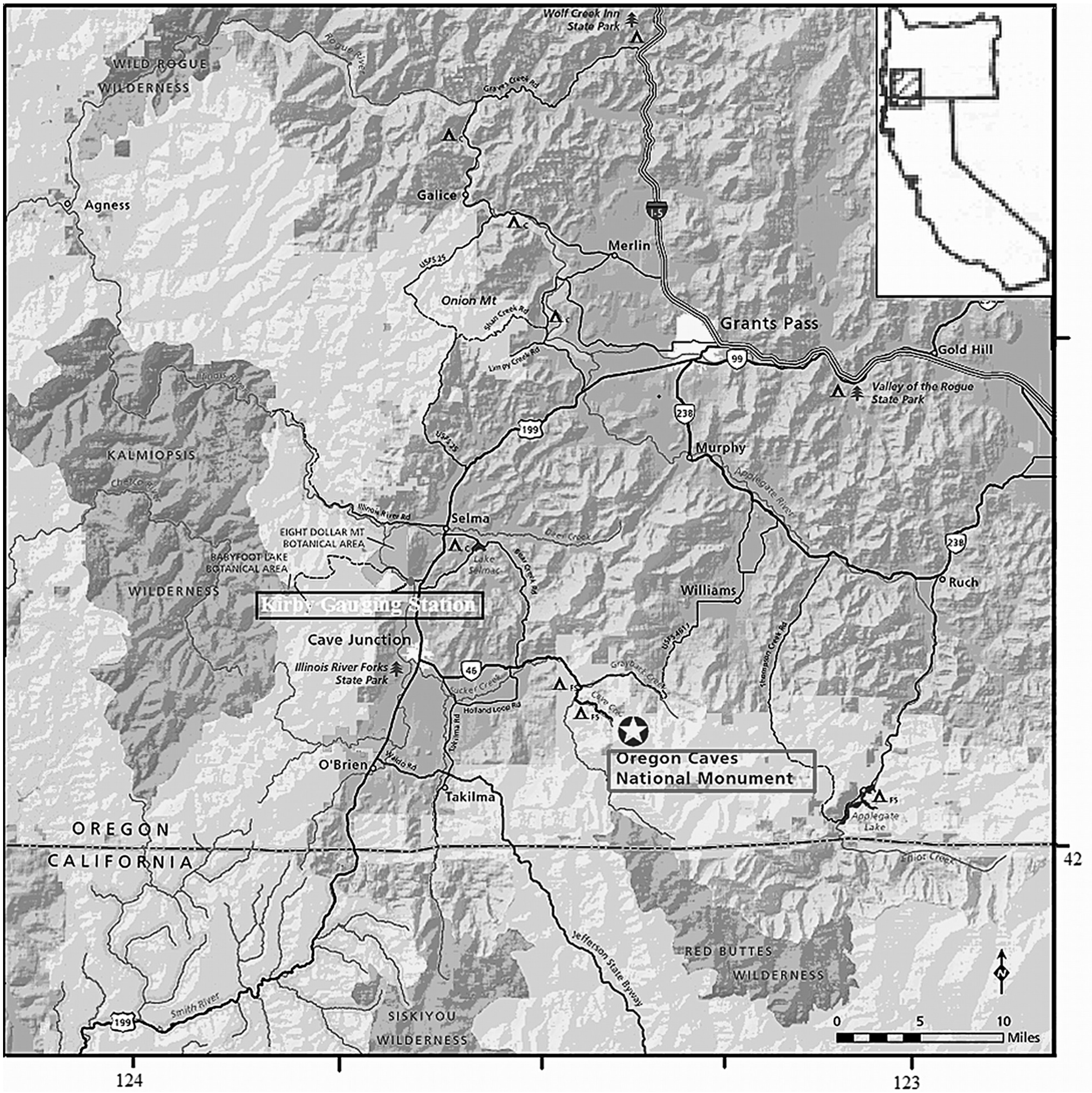

Figure 1 *Location of Oregon Caves National Monument and USGS Gauging station near Kirby in SW Oregon. After an ORCA informational brochure.*

istry to that of stream water, and to assess temporal variation in TOC in both drip and stream water.

Previous geochemical studies of cave-drip and stream water have mostly been done in limestone. A recent limestone drip-water study of a tour cave in Slovakia (Motyka et al. 2005) found that the composition of the host rock strongly influenced the water composition. For example, calcitic rock produces water concentrations high in calcium (Ca) and bicarbonate (HCO_3), while dolomitic rock with pyrite produces water concentrations high in Ca, HCO_3, magnesium (Mg), and sulfate (SO_4). Surface conditions in Slovakia, such as climate, plant cover and soil type, influenced total dissolved solid (TDS) content (332 to 520 mg/L) and calcite saturation indices (SI) (0.78 to 1.39). Drip-water testing in Lititz Spring, Pennsylvania (Toran and Roman 2006), found a reverse correlation between calcite SI and the partial pressure of carbon dioxide ($P\mathrm{co}_2$). Calcite SI ranged from 0.2 to 0.6 for log $P\mathrm{co}_2$ values from -1.9 to -2.4 atm respectively.

Seasonal variations in ionic concentrations were noted in drip water studies at several limestone caves (Doctor and Alexander 2004, Drever 1982, McDonald et al. 2002). Seasonal variations of soil carbon dioxide (CO_2) were determined to account for correlative concentrations of total dissolved ions (TDI) in drip-water chemistry at Pettyjohns Cave, Georgia (Mayer 1999) as higher levels of CO_2 increases carbonate dissolution (drip-water TDI ranged from 175 to 298 mg/L, log Pco_2 levels ranged from -3.19 to -2.1 atm. Work by Vesper and White (2006) indicate that as trace metal concentrations rise, carbonate concentrations decrease.

Study at Pettyjohns Cave (Mayer 1999) observed that stream-water ionic concentrations become dilute during periods of high flow (TDI from 34 to 40 mg/L at high flow, 124-153 mg/L during low flow) and tended to be lower than those in the drip water (stated above). Surface input streams at Pettyjohns had significantly lower calcium and bicarbonate concentrations (0.62 and 0.25 mg/L respectively) than the subsurface streams (10.51 and 29.5 mg/L) for the same date.

Few studies have been performed in marble caves. A study in Lilburn Cave, a marble cave in Sequoia and Kings Canyon National Park (Abu-Jaber et al. 2001) found Ca concentrations in the discharge spring ranged from 14 to 44 mg/L while input water concentrations ranged from 3.5 to 5.6 mg/L. The implication being that carbonate dissolution is occurring in the cave. Dissolution rate decrease during periods of high discharge was attributed to passage geometry. Water gushing through steep and wide passages has little residence time and limited rock-water interaction. Oregon Caves and Lilburn Cave are formed in a low-grade marble lenses. Metamorphism of limestone produces a hard and dense marble (Ford and Williams, 1989) with low porosity and (usually) low permeability, making the rock less penetrable than limestone. This may account for the development of cave passsages in marble, which are dominated by bedding planes and faults (Roth 2007).

Total organic carbon (TOC) is the sum of dissolved organic carbon (DOC) in solution with particulate organic carbon (POC). Some geochemical water studies discuss dissolved organic carbon (DOC) concentrations in water, but rarely report TOC. Because organic carbon is vital to support microbial life, an understanding of TOC in a system may help evaluate the health of the system. Howcroft and Hess (1997) performed a hydrology study of Redwood Canyon karst aquifer (Sequoia and Kings Canyon National Park) that measured TOC concentrations at several sites. However, the TOC levels that they measured were so low (< 0.1 to 1.0 mg/L), further analysis of TOC concentrations was abandoned.

Scientific research typically begins with a question and proceeds to data collection. However, I received the data first and then asked the questions. Here is this data set, the labor and costs have already been expended. This data set provides an opportunity to study marble karst water chemistry with the added distinction of having TOC information and allows the following questions to be addressed: 1) What differences, if any, are there between limestone and marble karst water chemistry? Although the composition of limestone and marble is the same, the expectation would be that the more stable configuration of the marble grains would inhibit rock-water interaction and limit the mineral contribution from the host rock. 2) What differences, if any, exist between drip water and stream water? The expectation would be for drip water to have higher concentrations of most chemical species given the longer contact time between the water and host rock. 3) What can be learned from the change in total organic carbon (TOC) over time and the relationship (if any) between the various sites? One would expect to see higher concentrations of TOC in the drip water given the organic content of soil.

Field Site Description

Oregon Caves National Monument (ORCA) is located on a north-facing slope of Mt. Elijah in the Siskiyou Mountains (Figure 2). These steep, densely-forested mountains consist of rocks from the Western Triassic-Paleozoic tectonostratigraphic terrane of the Klamath Mountains (Irwin, 1966) and are a “collage of oceanic and continental fragments juxtaposed against each other and the North American continent” (Charvet et al. 1990). The cave at ORCA lies within the Applegate group (Barnes et al. 1996) which consists of extrusive volcanics with lenses of slate, quartzite, chert, limestone and marble. The age of the marble has been estimated at 210 Ma (Irwin and Blome 2004). Adjacent rock includes meta-argillite, serpentinitized peridotite and quartz diorite.

Oregon Caves is only one cave at ORCA, but

Figure 2 View of the Siskiyou Mountains from a trail above the cave.

because of multiple openings it was once thought that there were multiple caves, and so the name Oregon Caves. It is a solution cave formed in a faulted and folded marble lens, carved by meteoric waters that have percolated through the soils. The cave has four natural openings and one additional manmade exit tunnel. There are 4.86 km of mapped passage. The marble is metamorphic limestone laced with bands of graphite and veins of chert. Soils of ORCA eroded from various parent materials. These are predominantly loamy and are ideal for the flora (Table 1) that shade the grounds and maintain the soil moisture content. The elevation at the exit spring is about 1220 m, 730 m below the summit of Mt. Elijah, where snowmelt waters supply the drainage basin.

A previous hydrological study (Roth 2005) indicates that most water enters the cave through vertical cracks and dome-pits and to a lesser degree by stream piracy. Precipitation entering the cave

Table 1. Some of the plant species found at Oregon Caves National Monument and the soil type parent rock material in which they grow. (Oregon State University, 2007)

Plant Species	Granitic	Serpentinite	Altered sediment and igneous
Oregon Grape	X		X
Douglas Fir	X	X	X
Pacific Ocean Spray	X		X
Deerfoot Vanillaleaf	X		X
Pacific Madrone	X	X	X
Poison Oak	X	X	X

takes hours to days to reach the upper part of the cave. Dye tracing at a stream above the cave took about 50 hours to reach the cave exit. Upper parts of the cave dry out by the end of summer but deeper parts remain wet year round. It is believed that some water takes months or years to work its way down cracks parallel to the orientation of the rock layers (Roth 2005).

The water samples used for this study were collected from two drip pools, three drip sites, two locations from the subsurface stream and one from a surface input stream (Figure 3). The sites are as follows: Bridge-Styx (Bridge River Styx), a lower cave stream, is 9 m above the spring and 18 m below the surface. Bridge-Styx is a mix of diffuse (drip) and discrete (surface stream infiltration) water. Imag (Imagination room) is 15 m above the spring and 17 m below the surface. It is a drip from a crack (diffuse). MI (Lake Michigan) is a drip pool 21 m above the spring and 47 m below the surface (diffuse). The Shower is a dome drip pool 30 m above the spring and 58 m beneath the surface (discrete). Ghost-Styx (Ghost River Styx) is an upper cave stream (discrete) 15 m above the spring and is 67 m beneath the surface. Wedding (Wedding Cake) is a drip from a bedding plane (diffuse) 40 m above the spring and is 52 m beneath the surface.

Materials and Methods

Geochemical data for this study were selected from a thirty-four-month collection period from November, 1991 through September, 1995. Samples were collected on a near-monthly basis at several surface and subsurface sites within ORCA. However, sampling was not always performed in the same locations, and not all tests were performed on all dates. Seven of the sites had fairly consistent sampling from May 1992 through October, 1993, these data were selected for this study. Hydrologically, the Shower drip pool is upstream of Ghost-Styx. MI drip pool, Wedding and Imag drips are at higher elevations than the subsurface streams. Bridge-Styx is downstream of all the sites

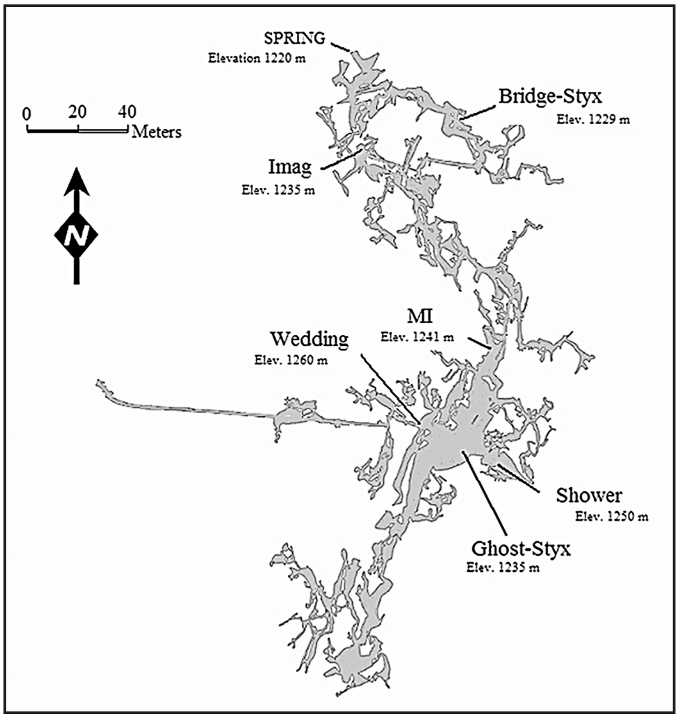

Figure 3 *Plan view of cave depicting locations of sampling sites used in this study. (After Roger Brandt, Oregon Caves National Monument Trail Brochure)*

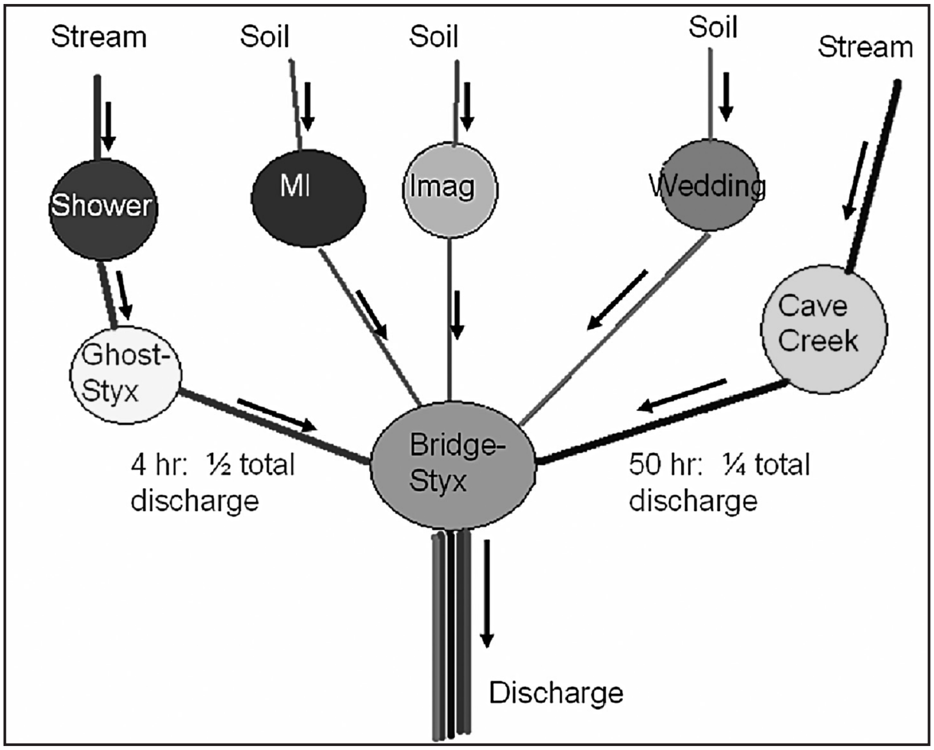

Figure 4 *A diagram of the flowpaths, including discharge results from previous dye tracing.*

sampled within the cave. Cave Creek is one of the cave's input streams. Dye injected at Cave Creek arrived downstream at Bridge-Styx but not at Ghost-Styx. Dye injected at Ghost-Styx also arrived downstream at Bridge-Styx. A diagram of the flowpath is in Figure 4. Included are the time delay and discharge contribution results from previous dye tracing.

At each site, the pH and temperature were recorded *in situ*. Water samples were collected and were sent to an analytical laboratory (Waterlab Corporation, certified lab #008) to be analyzed (using standard titration methods) for the following: total dissolved solids (TDS), carbon dioxide (CO_2), total organic carbon (TOC), total alkalinity ($CaCO_3$), calcium (Ca), magnesium (Mg), sulfate (SO_4), chloride (Cl), sodium (Na), iron (Fe), and zinc (Zn). Preliminary numerical analysis (median, maximum, minimum and standard deviation) was then performed. Graphs of water-chemistry variations over time were generated and analyzed. A Piper plot was constructed to show the ionic composition at the different sample sites. Both Piper and Stiff diagrams were constructed using RockWare® science applications software. The saturation index (SI) = -log (IAP/Kt) (ionic activity of reaction/ equilibrium constant) of the water with respect to calcite and the partial pressure of CO_2 ($P\text{co}_2$) were calculated using PHREEQC1, speciation water resource application software (Parkhurst, 2007). The charge balance error was offset by adding potassium (K^+), which was not measured, although expected considering the granitic diorite in the area. For three sites on only three dates, the charge balance error could not be rectified even with the addition of 1000 mg/L K^+, an excessive amount. In close examination of those samples, the pHs were found to be particularly low (5.11, 5.38, and 5.60) and likely incorrect, however these were the reported values. Instead of adjusting the pH to correct for charge balance, an option in PHREEQC1, the samples were removed from further consideration.

Results

Two distinct source waters are present in the cave—diffuse water and discrete water. Diffuse water is meteoric water that percolates through the soil, drips into the cave through cracks (Imag) and

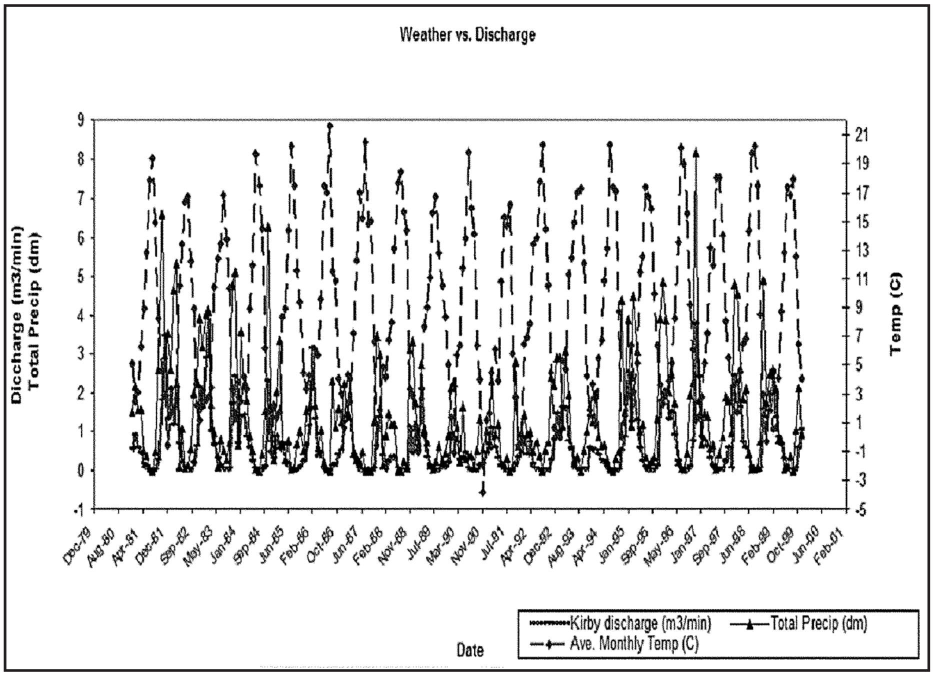

Figure 5 *Graph showing average monthly temperatures, total monthly precipitation levels and downstream discharge rates for August, 1980, through December, 1999, at Oregon Caves National Monument.*

bedding planes (Wedding) and forms drip pools (MI). Discrete water is surface input stream (Cave Creek), dome water (Shower) and upper cave stream (Ghost-Styx). Eventually, the two source waters converge downstream at Bridge-Styx (Figure 4).

The stream spring is 1220 m above sea level. Average air temperature in the cave is 7°C (Roth 2005). Low temperatures tend to increase the solubility of calcite. Average precipitation at ORCA is approximately 132 cm/year (Hale 2007). The average monthly temperatures rarely fall below 0°C (Figure 5), therefore little time delay between snowfall and snowmelt was assumed. Discharge data obtained from Kirby station (USGS Hydrologic Unit, Figure 1), which is downstream from the spring and along the Illinois River, seemed to support this assumption.

Numerical analysis, diffuse water. Mean values for water chemistry of diffuse sites are shown in Table 2. Drip and pool water pH ranged between 5.38 and 11.82. Temperature ranged between 5.8 and 11.8°C. Total dissolved solids ranged from 0.02 to 1.3 mg/L. Carbon dioxide levels were between 200 and 2050 ppm. Total alkalinity for diffuse sites ranged between 96.0 and 182.0 mg/L. Total organic carbon concentration ranged from 0.1 to 24.1 mg/L. Calcium concentrations spanned from 21.5 to 60.8 mg/L. Magnesium concentrations ranged between 0.32 and 9.12 mg/L. Sulfate concentrations ranged from 0.1 to 10.8 mg/L. Chloride concentrations spanned from 0.1 to 55.5 mg/L. Sodium concentrations for diffuse flow ranged from 0.1 mg/L to 47.7 mg/L. Iron concentrations were consistently less than 0.01 mg/L at both Wedding and MI, but reached concentrations as high as 8.64 mg/L at Imag. Zinc concentrations were consistently less than 0.001 mg/L at both Wedding and MI, but reached concentrations as high as 0.29 mg/ at Imag.

Numerical analysis, discrete water. Mean values for water chemistry of discrete sites are shown in Table 2. Discrete water pH ranged between 4.27 and 11.78. Temperatures ranged from 5.80 to 11.5°C. Total dissolved solids ranged from 0.07 to 2.0 mg/L. Carbon dioxide concentrations were between 200 and 2,325 ppm. Total alkalinity for discrete sites ranged between 100 and 300 mg/L. Total organic carbon ranged from 0.1 to 47.1 mg/L. Calcium concentrations were between 6.10 and 57.6 mg/L. Magnesium concentrations ranged between 0.44 and 47.2 mg/L. Sulfate concentrations ranged from 0.1 to 4.5 mg/L. Chloride concentrations ranged from 0.1 to 16.5 mg/L. Sodium concentrations were from 0.1 mg/L to 19.8 mg/L. Iron concentrations were less than 0.2 mg/L, but Bridge-Styx (downstream) had a one-time, high iron concentration of 11.1 mg/L. Zinc concentrations were less than 0.001 mg/L for all discrete sites.

Table 2. Mean values for diffuse, discrete, and surface stream water

Water sampling sites	Ca (mg/L)	pH	Temp. (C)	TDS (mg/L)	Alkal. (mg/L $CaCO_3$)	TOC (mg/L)	SI (Calcite)	P_{CO_2} (atm.)
Diffuse								
Imag	45	8.14	8.82	0.17	134	7.25	0.63	$10^{-2.3}$
Wedding	46	8.42	8.62	0.20	138	6.91	0.81	$10^{-2.2}$
MI	43	8.42	8.13	0.16	126	8.99	0.83	$10^{-2.2}$
Discrete								
Shower	42	8.51	7.88	0.22	119	6.36	0.93	$10^{-2.2}$
Ghost-Styx	43	8.22	8.09	0.18	123	11.04	0.84	$10^{-2.2}$
Bridge-Styx	39	8.01	7.51	0.15	140	15.84	0.31	$10^{-2.0}$
Surface								
Cave Creek	25	8.22	9.09	0.12	84	6.85	0.13	$10^{-2.6}$

Mean values for water chemistry of the surface stream are in Table 2. Cave Creek water pH ranged between 7.35 and 9.48. Temperatures ranged from 5.70 to 13.3°C. Total dissolved solids ranged from 0.05 to 0.80 mg/L. Carbon dioxide concentrations were between 150 and 600 ppm. Total alkalinity for Cave Creek ranged between 18 and 142 mg/L. Total organic carbon ranged from 0.4 to 27.9 mg/L. Calcium concentrations were between 6.13 and 49.6 mg/L. Magnesium concentrations ranged between 1.44 and 12.00 mg/L. Sulfate concentrations ranged from 1.07 to 3.8 mg/L. Chloride concentrations ranged from 0.11 to 4.7 mg/L. Sodium concentrations were from 1.64 mg/L to 12.7 mg/L. Iron concentrations were less than 0.01 mg/L. Zinc concentrations were less than 0.001 mg/L.

Temporal analysis, diffuse water. Graphs of diffuse, water-chemistry variability over time indicate the sites were very similar in overall composition and fluctuation patterns. Diffuse water temperatures fluctuated greatly during the study period. Except for winter 1993-1994, the diffuse data had similar variation patterns in temperature, but with different amplitudes. Seasonal pH variations at the diffuse sites were seen. During dry summer months, pH tended to increase. During wet winter months pH level and during spring pH declined. Except for two samples, one collected in spring 1993 and one in summer 1994, TDS concentrations remained low and unchanging. Calcium concentrations increased slightly during the summer of 1992 and except for a slight decline spring 1993 remained relatively constant for the rest of the study period. Diffuse sites had relatively little variation in total alkalinity during the study period. Saturation indices for calcite (Figure 6) indicate that, except for late winter 1993, diffuse sites were oversaturated with respect to calcite. Partial pressure of carbon dioxide ($P\mathrm{co}_2$) (Figure 7) ranged from $10^{-3.5}$ to $10^{-1.29}$ atm. For the study period, these sites had $P\mathrm{co}_2$ levels 1 to 200 times the atmospheric standard of about $10^{-3.5}$ atm. A plot of SI for calcite verses log $P\mathrm{co}_2$ values (Figure 8) indicates a strong reverse correlation between $P\mathrm{co}_2$ and calcite SI. Total organic carbon concentrations at all three sites increased slightly during summer 1992. Concentrations of TOC then diminished at Wedding and Imag as concentrations at MI continued to increase through early fall. Fluctuations in TOC concentrations at all three sites were moderate for most of 1993. Seasonal variations in CO_2 concentrations were evident, with higher concentrations during dry summers and lower concentrations during wet winters. Magnesium (Mg) and SO_4 concentrations were low with relatively little variation during the study period. Chloride and Na concentrations were likewise, except at Wedding, which had high concentrations in May and August, 1992.

Temporal analysis, discrete and surface water. Discrete water chemistry variability over time indicates the sites were very similar in overall composition as well as fluctuation patterns. The surface stream, Cave Creek, had generally lower ionic concentration than discrete water. Discrete water temperatures fluctuated widely between sites as well as seasonally during the study period. Cave Creek and Bridge-Styx showed greater response to surface temperature changes than did Shower or Ghost-Styx. Seasonal pH variations at the discrete sites were seen. During late, dry summer months, pH tended to peak but during wet winter months pH would decrease. A drop in pH occurred at Ghost-Styx in July, 1993. Except for two events, spring 1993 and summer 1994, TDS concentrations remained low and unchanging. Calcium concentrations increased slightly during the summer of 1992 and (except for a slight decline in spring 1992 and a drop at Bridgen in fall 1993) remained relatively constant for the rest of the study period. Cave Creek had notably lower Ca concentrations. Discrete sites had relatively little variation in total alkalinity during the study period except for a peak at Bridge-Styx fall 1993. Cave Creek had notably lower alkalinity concentrations. Calcite SI (Figure 6) indicate that for most of the study period, discrete sites in the cave were oversaturated with respect to calcite. Cave Creek was oversaturated with respect to calcite 60% of the times sampled. Partial pressure of carbon dioxide (Figure 7) ranged from $10^{-3.3}$ to $10^{-1.1}$ atm. For the study period, these sites had $P\mathrm{co}_2$ levels 1.5 to 250 times the atmospheric standard of about $10^{-3.5}$ atm. A plot of SI for calcite verses log $P\mathrm{co}_2$ values (Figure 8) indicates a strong, reverse correlation between $P\mathrm{co}_2$ and calcite SI. Total organic carbon concentrations fluctuated greatly during the second half of 1992. Concentrations decreased slightly in spring 1993, increased early June, and held fairly constant for the remainder of the study period. Seasonal variations in CO_2 concentrations (except in Cave Creek) were evident, with higher concentrations during dry summers and lower concentrations during wet winters. Magnesium (Mg) and SO_4 concentrations were low with relatively little variation during the study period, except at Bridge-Styx, which had a peak in Mg concentrations during spring and fall of 1993. Chloride concentrations were low and showed little variation during the study period except for two dates at Ghost-Styx and one at Shower. Sodium concentrations displayed an increasing trend until May1993 then decreased. Ghost-Styx displayed greater Na concentration fluctuations than the other discrete sites.

Piper/Stiff analysis, diffuse water. The Piper diagram in Figure 9 shows the ionic composition of the water samples. The open circles represent samples from diffuse sites and plot in the carbonate-bicarbonate. The samples plot in the high

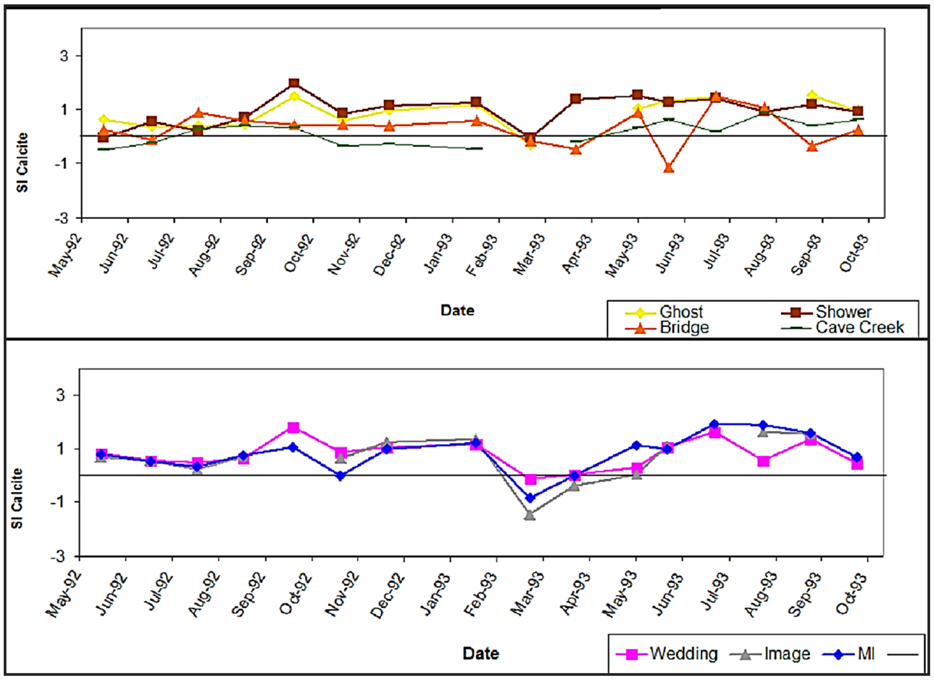

Figure 6 *Graphs showing saturation index (SI) for calcite. The top graph shows discrete water sites. The lower graph shows diffuse water sites.*

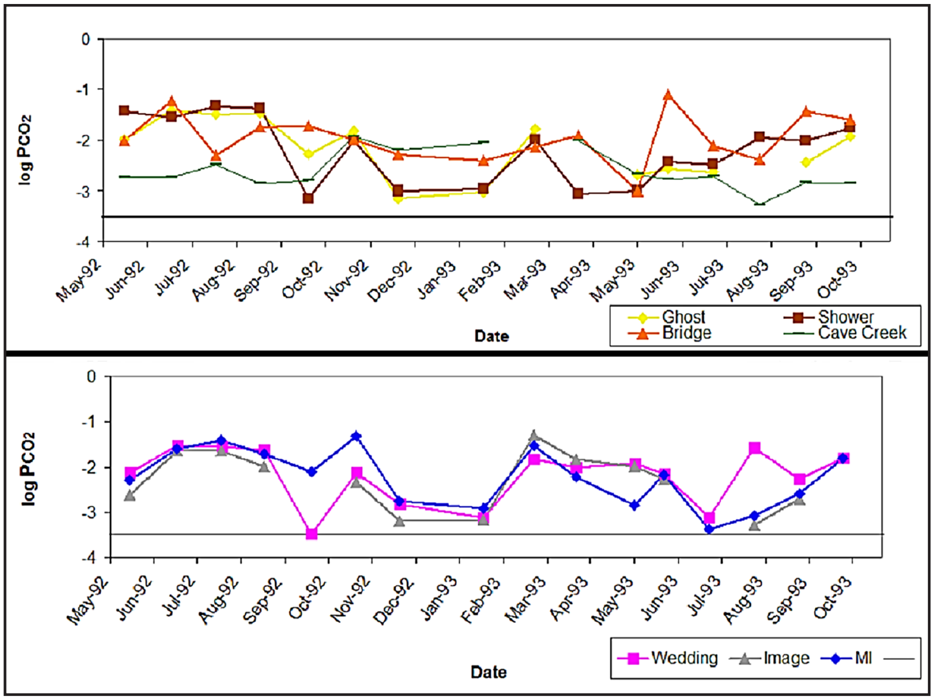

Figure 7 *Graphs showing partial pressure for CO_2. The top graph shows discrete water sites. The lower graph shows diffuse water sites. Pco_2 levels were 1 to 250 times atmospheric pressure.*

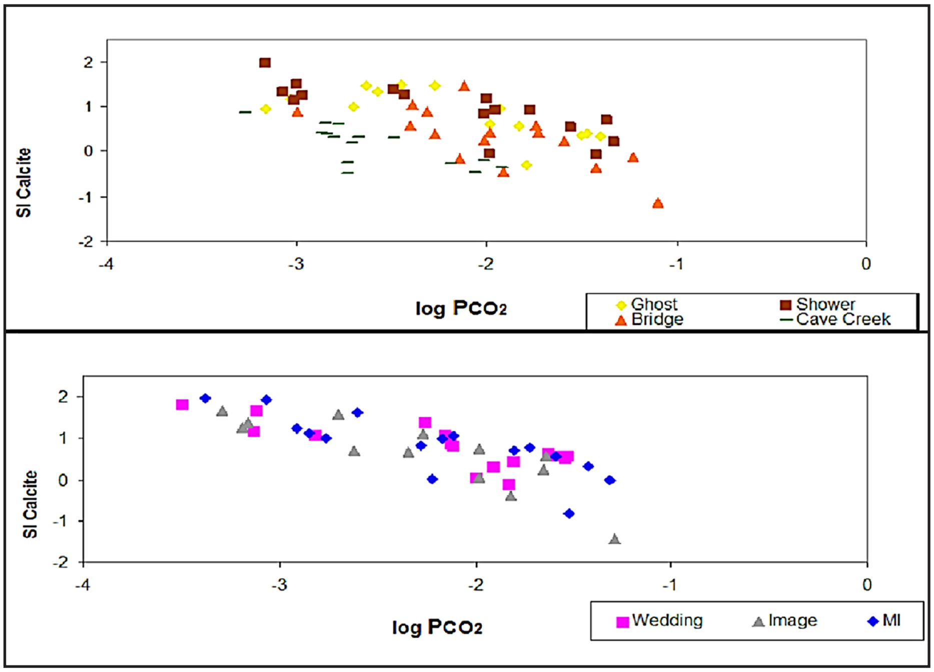

Figure 8 *Plots showing a reverse correlation between calcite SI and Pco_2.*

carbonate range with low magnesium content. The outlying open circle in the cation triangle represents the high concentrations of Na detected in the samples at Wedding, and the outlying open circle in the anion triangle represents the high concentrations of Cl detected in the samples at Wedding. The samples plot in the high carbonate range, as would be expected from a highly calcitic marble. The Stiff (shape) diagram in Figure 10 shows the relative abundance of major ion concentrations of

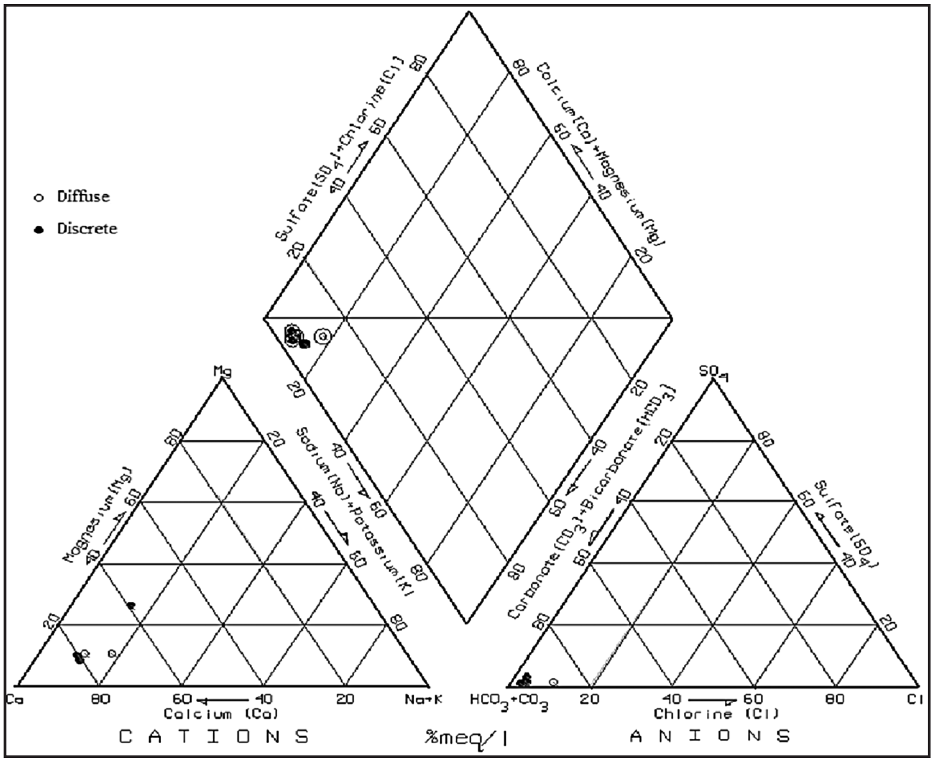

Figure 9 *Piper diagram showing ionic composition of the samples. Open circles are from diffuse water sites, closed circles are from discrete water sites.*

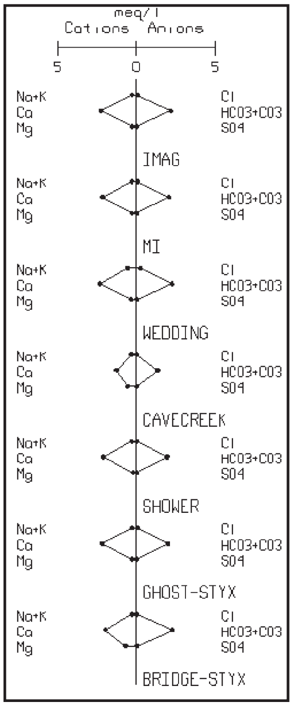

Figure 10 *STIFF (shape) diagram of mean cation/anion of the sites showing relative abundance of ion concentrations of the different sample sites.*

the different sample sites. Mean ionic concentrations for diffuse sites are plotted at the top of the diagram. A glance at the diagram shows that the ionic composition for the three diffuse sites were very similar, though Wedding has higher concentrations of Cl and Na.

Piper/Stiff analysis, discrete and surface water. The closed circles on the Piper diagram in Figure 9 represent samples from discrete and surface sites. The outlying closed circle in the cation triangle represents higher concentrations of Mg found in the samples from Cave Creek and Bridge-Styx. The discrete samples plot in the high carbonate range as would be expected from a highly calcitic marble. The Stiff diagram in Figure 10 shows the relative abundance of major ion concentrations of the different sample sites. Mean ionic concentrations for discrete sites are plotted on the lower part of the diagram. A glance at the diagram shows the ionic composition for Shower and Ghost-Styx were very similar. Bridge-Styx reflects the higher concentrations of Mg found in Cave Creek but not seen at Shower or Ghost-Styx.

Discussion and Conclusions

The goal of this study was to compare the chemistries of marble and limestone karst waters, compare drip-water chemistry to that of stream water, and to assess temporal variation in TOC in both drip and stream water. As to the question of would there be differences between limestone and marble water chemistry, the expectation was that the more stable configuration of the marble would inhibit rock-water interaction and limit the mineral contribution from the host rock. The ionic composition in this cave was highly carbonate with little Mg, which is a reflection of the composition of the marble, and indicates extensive rock-water interaction. As in the Slovakian cave (Motyka et al. 2005), composition of the host rock strongly influenced the water composition. Because the water in Oregon Caves was usually supersaturated with respect to calcite, further dissolution of Ca could not take place. This explains the relative flat line of the Ca graph. The high Ca concentrations may account for this cave's relatively low concentrations of TDS, Fe, Zn, and Mg (Vesper and White 2006). A reverse correlation between calcite SI and $P\text{co}_2$, similar to that observed by Toran and Roman (2006), is seen in Figure 8. When samples became undersaturated in calcite during February, 1993 (Figure 6), there was an increase in TDS concentrations as well as $P\text{co}_2$. This coincided with a heavy snowmelt event. Similar correlation between high flow, TDS, $P\text{co}_2$, and calcite SI were noted in several limestone caves (Mayer 1999, McDonald et al. 2002, Doctor and Alexander 2004, Motyka et al. 2005). These observations suggest that differences in the rock's crystal structure had little influence on differences in resultant water chemistry.

As to the question of what differences exist between drip (diffuse) water and stream (discrete) water, the expectation was that drip water would have higher concentrations of most species. As expected, drips were higher in Ca. The cold temperatures of the cave and the acidic pH of the soil would promote dissolution of Ca. The composition of the samples from MI and Image were very similar, which indicates similar source water with similar travel histories. The notable difference in the samples at Wedding was the occasional presence of Na and Cl. Part of the cave is overlain by paved trails. It may be that ice melt (salt) used for the trails is finding its way into the source water for Wedding. Cave Creek, the surface stream had concentrations of Mg that were seen downstream at Bridge but not seen in the samples from the drips, or other discrete sites. This indicates that Cave Creek is not the source water for Shower, Ghost-Styx, or the drips but joins the subsurface stream before the Bridge. This is supported by previous dye tracing. What was unexpected was that water of Cave Creek was often saturated with respect to calcite. This would indicate that surface water flows over marble outcrops prior to entering the cave.

Total organic carbon (TOC) was surprisingly similar in drips (diffuse), streams (discrete) and in Cave Creek. The expected result was that TOC would be higher in the drips, attributed to high organic material in the soil. The inference, therefore, is that the surface stream passes over high amounts of organic material prior to entry into the cave. There were insufficient data to understand the reason for the TOC fluctuations seen across the site over the study period.

Now that we have this information, we could learn more with subsequent work. Therefore, a future study should have a consistent set of collection sites with consistent collection criteria. Optimally, those criteria should include site discharge information, when possible, and collection order. It would be beneficial to collect specific soil information, such as depth. One area for further investigation would be to identify the source water for Shower and Ghost-Styx. It is known that there are other surface creeks that could be possible source water. Future study could be expanded to include these streams in the sampling.

Acknowledgments

I would like to extend a special thanks to Dr Carol Wicks, at University of Missouri, Columbia, for pushing me beyond my comfort zone. Thanks go to John Roth, Resource Management Specialist at ORCA, for providing the data for this research and for his continued informational support throughout this project. Thanks go to Elizabeth Hale, Physical Science Technician at ORCA, for her untiring answers to my endless questions and to Derek Marohn, staff at ORCA, for his support to this project. Thanks go to the Geological Society of America (GSA), GeoCorps America program, for providing the opportunity to intern at ORCA. Thanks go to the USGS and specifically David Parkhurst for development and distribution of PHREEQC1 software. Recognition goes to Waterlab Corporation (certified lab #008) for the geochemical analysis of the water samples used for this project.

Literature Cited

Abu-Jaber, N., J.W. Hess, and W. Howcroft. 2001. Chemical erosion of the Lilburn Cave system, Kings Canyon National Park, California. *Groundwater*, 39:223–229.

Barnes, C.G., M.M. Donato, and S.L. Tomlinson. 1996. The enigmatic Applegate group of southwestern Oregon: Age correlation and tectonic affiliation. *Oregon Geology*, 58:79–91.

Charvet, J., C. Compos, C. Coulon, H. LaPierre, C. Lecuyer, P. Martin, and O. Rover. 1990. Tecno-magmatic evolution of Paleozoic and early Mesozoic rocks in the Eastern Klamath Mountains, California and Blue Mountains, eastern Oregon-western Idaho. *Geological Society of America Special Papers*, 255:255–276.

Doctor, D.H. and E.C. Alexander. 1998. Results of monitoring the isotopic composition and hydrology of infiltrating drip waters in Mystery Cave, Minnesota. American Geophysical Union Poster, Spring Meeting.

Drever, J.I. 1982. *The Geochemistry of Natural waters*. Prentice-Hall, Inc., Englewood Cliffs New Jersey. 1982. 388 p.

Ford, D., and P. Williams. 1989. *Karst Geomorphology and Hydrology*. Unwin and Hyman, London. 601 pp.

Hale, E. 2007. Oregon Caves Weather Statistics, 1961–2006, Oregon Caves National Monument. Unpublished report, ORCA.

Howcraft, W. and J. Hess. 1998. Summary of 1997 hydrologic investigation at the Redwood Creek Karst Kings Canyon National Park, California. Cave Research Foundation, California Newsletter, Lilburn Projects Report.

Ingebritsen, S., W. Sanford, and C. Neuzil. 2006. *Groundwater in Geologic Processes*, 2nd ed. Cambridge. New York: Cambridge University Press. 562 pp.

Irwin, W.P. 1966. Geologic reconnaissance of the Northern Coast Ranges and Klamath Mountains, California with a summary of mineral resources. *California division of Mines and Geology Bulletin,* 80 pp.

Irwin, W.P., and C.D. Blome. 2004. Map showing fossil localities of the Rattlesnake Creek, Western and Eastern Hayfork and North Fork terranes of the Klamath Mountains. *U.S. Geological Survey, Open File Report*, 01–1094.

Mayer, J. 1999 Spatial and temporal variation of groundwater chemistry at Pettyjohns Cave, northwest Georgia: *Journal of Cave and Karst Studies*, 61:131–138.

McDonald, J., R. Drysdale, and D. Hill. 2004. SE Australia El Niño recorded in Australian cave drip waters: Implications for reconstructing rainfall histories using stalagmites. *Geophysical Research Letters*, 31:L22202, doi:10.1029/2004GL020859.

Motyka, J., M. Gradziński, P. Bella, P. and P. Holúbek. 2005. Chemistry of waters from selected caves in Slovakia—a reconnaissance study: *Environmental Geology*, 48:682–692.

National Park Service, U.S. Department of the Interior, Oregon Caves National Monument. (March 2007, *www.nps.gov/orca/*).

National Park Service, U.S. Department of the Interior, Geologic Resources Division, Cave and Karst Program. (March 2007, *http://www2.nature.nps.gov/geology/caves/program.htm*).

Oregon State University. 2007. The ecological provinces of Oregon, Siskiyou ecological province, (March 2007, *http://oregonstate.edu/dept/range/projects/EcologicalProvincesOfOregon/siskiyou.htm*).

Parkhurst, D.L. 2007. U.S. Geological Survey. (Feb 2007, *http://wwwbrr.cr.usgs.gov/projects/GWC_coupled/phreeqci/index.html*).

Roth, J.E. 2005. Oregon Caves National Monument—Subsurface Management plan— Environmental Assessment. U.S. Department of the Interior, National Park Service.

Toran, L. and Roman, E. 2006. CO_2 outgassing in a combined fracture conduit karst aquifer near Lititz Spring, Pennsylvania, pp 267–274 *in*

Harmon, R.S. and C.M. Wicks, eds., Perspectives on karst geomorphology, hydrology, and geochemistry—A tribute volume to Derek C. Ford and William B. White. *Geological Society of America Special Paper* 404, United States Department of Agriculture, Natural Resource Conservation Service. (March 2006, *http://soils.usda.gov/technical/classification*).

United States Geological Survey: Hydrologic Unit 17100311 (March 2007, *http://waterdata.usgs.gov/nwis/monthly?referred_module=sw&search_site_no=14377100&format=sites_selection_links*).

Vesper, D.J. 2005. Contamination of cave waters by heavy metals. pp 127-131 *in* Culver, D.C., and W.B. White, eds., *Encyclopedia of Caves*. 680 pp.

Vesper, D.J. and W.B. White. 2006. Comparative storm response of contaminants in a carbonate aquifer, Fort Campbell, Kentucky-Tennessee. pp 267–274 *in* Harmon, R.S., and C.M. Wicks, eds., Perspectives on karst geomorphology, hydrology, and geochemistry—A tribute volume to Derek C. Ford and William B. White. *Geological Society of America Special Paper*, 404.

White, W.B. 1988. *Geomorphology and Hydrology of Karst Terrains*. New York: Oxford Univer-