Using Chemical Data to Define Flow Systems in Cuatro Cienegas, Coahuila, Mexico

by

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Abstract

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The Cuatro Cienegas basin in Coahuila, Mexico was declared a National Protected Area in 1994 by the Mexican government. Its principle uniqueness is in its aquatic fauna, which are dependent on the abundant springs in this desert valley. However, the basin's hydrogeology is not very well understood. The springs in the basin have extreme variability in temperature, salinity, water chemistry, and discharge over small spatial scales. By gathering physical and chemical data in the field and using standard computer methods, the extremely complex flow systems in this critically sensitive desert wetland have been delineated. Five distinct flow systems are defined in the basin by the chemical data. These include the Churince system in the southwest, the Garabatal-Becerra-Rio Mesquites system flowing from the southwest to northeast portion of the basin, the Tio Candido-Hundidos system in the center of the eastern side of the basin, the Santa Tecla system in the southeast, and the Anteojo system in the north. The physical characteristics of the basin, including spring and canal locations, have been examined and show variable mixing within each system and complex physical flow systems. The Churince, Rio Mesquites, and Tio Candidio systems have separate source springs and terminal playa lakes. The Tio Candido and Rio Mesquites systems are related through canal and possible karst flow.

Chemical processes involved in the evolution of Cuatro Cienegas waters have been evaluated from the analyses of 35 samples collected in April 2004, June 2004, and January 2005. Calcium and sulfate dominate the water chemistry. However, high alkalinities are encountered in pools located closest to the mountains, especially in the Anteojo system. The Anteojo and Santa Tecla systems have lower conductivity/TDS than other systems. The water chemistry for the basin has been integrated into a Geographic Information System (GIS) to examine the spatial variations in chemistry and temperature throughout the basin. Highly saline waters (31.4 mg/L Na to 810.7 mg/L Na) are encountered throughout the basin, but the highest salinities occur toward the end of the flow systems. Furthermore, the temperature of the water at various pozas in the basin may reflect the source of the water via regional and/or karst flow. The Cuatro Cienegas water chemistry is mainly evaporation controlled, but there are other important processes involved, including the dissolution and precipitation of various mineral phases. In order to understand the variability within each flow system, a reaction pathway and mixing geochemical model has been developed for each system using PHREEQC. These baseline data provide a framework for necessary future hydrologic studies in the basin.

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CHAPTER 1: INTRODUCTION

Purpose and Scope of Project

The Cuatro Cienegas basin, Coahuila, Mexico, is a national preserve that was set aside by the Mexican government in 1994 to protect the basin's endemic and endangered fauna that depend on consistent spring-water flows. This ecosystem is one of the few remaining desert wetlands in North America and has been compared to the Galapagos Islands in Ecuador in terms of biologic diversity (National Public Radio, 2001). Over the past few years these wetlands have been slowly diminishing in water level and area, raising concerns over the sustainability of groundwater use. The groundwater levels have dropped approximately 30 to 60 cm in the last five years. This is disrupting the protected ecosystem that serves as a habitat for a large group of diverse and endemic organisms (Lesser, 2001). A large number of these organisms are on the threatened or endangered list set up by the Mexican government, and more than 70 organisms are endemic to the region (Desert Fishes Council Web, 2003). Among the endemic fauna are species of fishes, isopods, hydrobiid snails, scorpions, snakes, and turtles (Meyer, 1973). Though water levels have been steadily declining for years, a comprehensive hydrogeologic characterization of the basin has never been conducted.

Before an extensive characterization can be completed, the overall flow systems and general hydrogeologic patterns in the basin must be understood. By gathering geochemical data from surface-water and groundwater samples collected in the basin, using a Geographic Information System (GIS), standard analytical techniques, and developing a geochemical model for each flow system, complex groundwater flow paths in this critically sensitive desert wetland have been delineated. Analytical results indicate that the Cuatro Cienegas water chemistry is mainly evaporation controlled, but there are other possible processes involved, including regional interbasin groundwater flow and mixing with deeper groundwater. Results from this study can serve as a baseline for future groundwater studies in the basin.

Physiographic Setting

LOCATION

Cuatro Cienegas is located in the state of Coahuila, Mexico, approximately four hours into Mexico from the border at Eagle Pass, Texas/Piedras Negras, Mexico (Figure 1). It is in the Chihuahuan Desert on the eastern edge of the Basin and Range Province at 26° 59' N latitude and 102° 04' W longitude. The valley floor is approximately 40 kilometers from east to west and 30 kilometers from north to south, at approximately 740 m above mean sea level (Minckley, 1969).

POPULATION

The Cuatro Cienegas basin has approximately 15,000 inhabitants and the municipality of Cuatro Cienegas depends entirely on groundwater supply (Martinez, 2000). Several small towns lie within the vicinity of the protected borders of the Cuatro Cienegas reserve. These include Lodosos, San Lorenzo, San Vicente, La Vega, La Reforma, El Venado, and Antiguos Mineros (Figure 2). The economy of

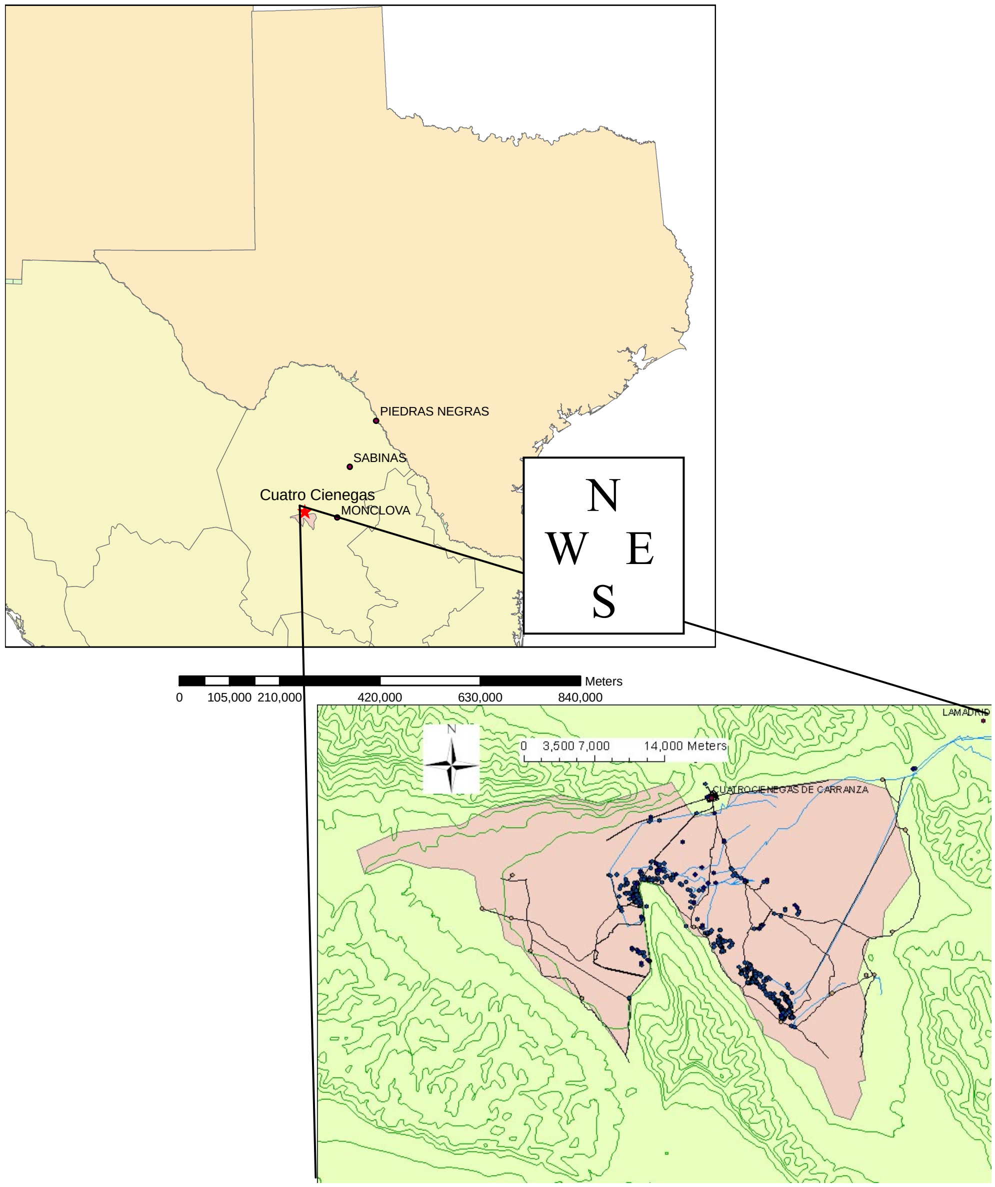

Figure 1: Location of Cuatro Cienegas, Coahuila, Mexico. The blue points on the basin map indicate spring locations, blue lines are canals, and black lines are roads.

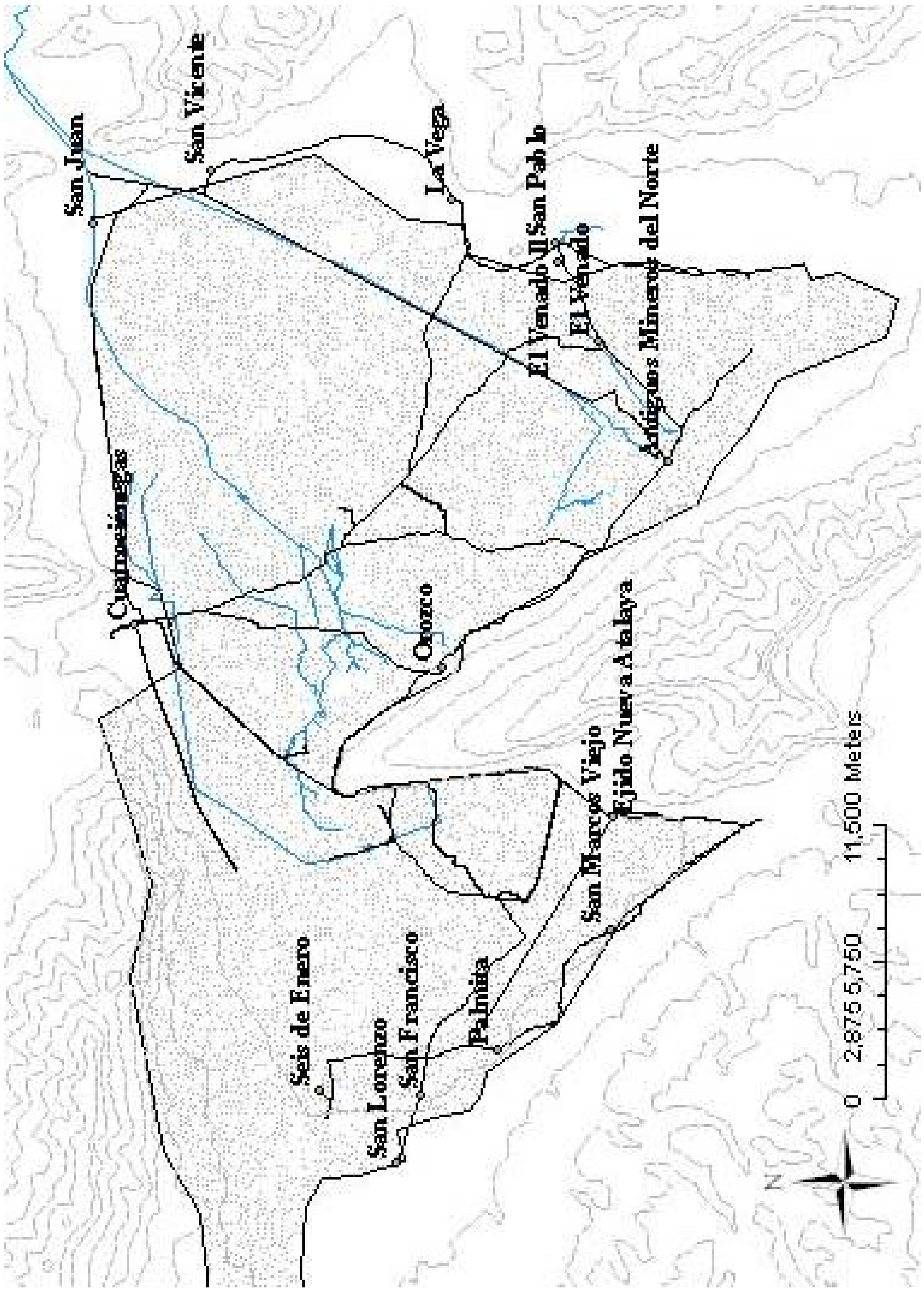

Figure 2: Map of the towns in the Cuatro Cienegas Basin. Blue lines are canals, black lines are roads in the basin.

the communities within the basin, including Cuatro Cienegas, is based primarily on agriculture. The main crop grown is alfalfa.

CLIMATE AND VEGETATION

The climate of Cuatro Cienegas is arid, with less than 200 mm of annual rainfall and up to 2,000 mm annual evaporation potential (SEMARNAT, 2003). Flash flooding can occur with high intensity rainfall events of up to 30 mm/day (Minckley, 1969). The rainy season is typically between May and October, with the majority of annual precipitation during the month of June. During the sampling period for this project, anecdotal evidence suggested that the basin received an unusually large amount of precipitation. The historically dry months of December and January received some precipitation in 2004/2005.

Temperatures in Cuatro Cienegas drop to below freezing (0°C) in the winter with snow often falling on the mountain tops. Summer temperatures rise above 44°C (111.2°F) and typically fall to 24°C (75.2°F) during the night (Minckley, 1969). A comparable climate has existed in the basin for 30,000 years, with similar vegetation covering the valley floor as inferred from pollen chronology and radiocarbon dating (Meyer, 1973).

Vegetation in the basin is diverse. Pine forests exist above 2000 meters in elevation on the mountain tops. Vegetation at lower elevation in the mountains consists of scrub oak, prickly pear, agave, acacia, and barrel cactus. The lowest elevations of the mountains have creosote bush, several types of cacti, yucca trees, and mesquite trees (Meyer, 1973). The valley floor contains vegetation resistant to drought and saline waters. Grasses, mesquite trees, prickly pear cactus, yucca, and other succulents are common in the open basin away from springs, streams, and pools (Meyer 1973). Sedges, cattails, ash, willow trees, and saline-tolerant grasses exist where water is readily available in pools, springs, and streams (Meyer, 1973). Salt cedar has also been introduced into the basin.

Geologic Setting

Several features define the basin geometry and control water flow in the basin, which is surrounded by mountain ranges on every side, some peaking at 2,500 meters high. Sierra de la Madera, locally known as Sierra de Anteojo, together with the Sierra Menchaca, forms the northern boundary for the basin. The anticline of Sierra de San Marcos plunges to the north at the center of the southern end of the basin, splitting the basin into eastern and western sub-valleys. Sierra la Fragura forms the western boundary for the basin, and Sierra de la Purísma and Sierra San Vicente comprise the eastern and northeastern boundaries (Figure 3).

Other noteworthy features include the Puerto de Jora, Puerto San Marcos, and Puerto Salado. These are the valleys between mountains serving as entrances/exits to the basin in the northwest corner, southwest corner, and northeast corner of the basin, respectively. The Puerto Salado serves as the outlet to the basin and is part of the Rio Grande system (Minckley, 1969). Though these low points allow easy passage for residents in the area, the basin is naturally hydrologically closed due to alluvial deposit buildup that has isolated the basin (Minckley, 1969).

The mountains in the basin are anticlinal in structure, produced by uplift and two episodes of faulting starting in the Jurassic and continuing into the Cretaceous.

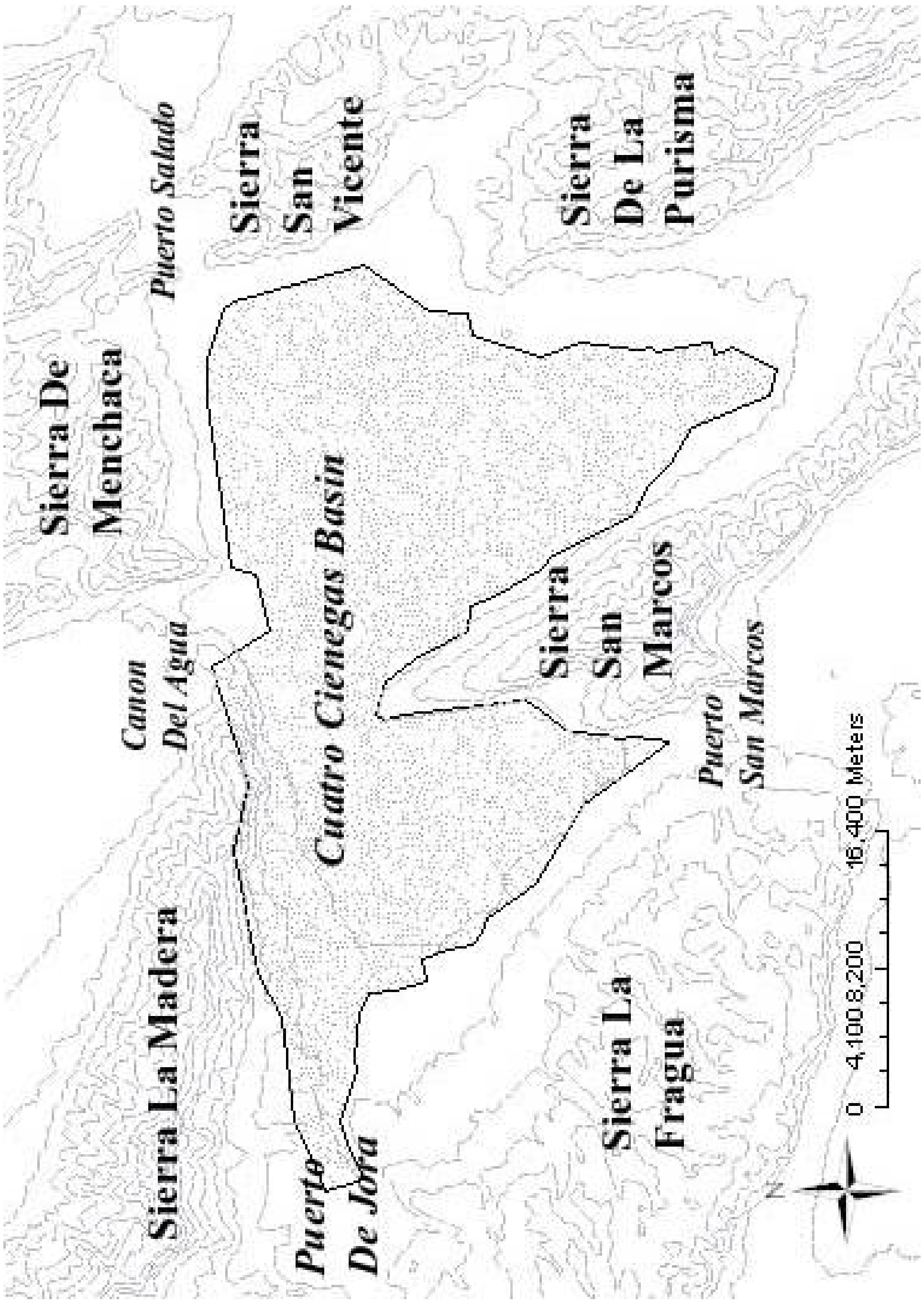

Figure 3: Detail map of Cuatro Cienegas, showing major features (Modified from Minckley, 1969). Blue lines are canals, and black lines are roads.

Other episodes of faulting began and ended in the Tertiary. The San Marcos Fault is the most dominating fault in the area, located to the southwest of the basin at Sierra La Fragua, striking at N62°W (McKee, et. al., 1990) (Figure 4).

STRATIGRAPHY

Geologic units within the Cuatro Cienegas basin are primarily composed of calcite, evaporite, and sandstone on an igneous basement (Table 1). The Permian basement is of granitic composition and contains intrusions and prominent xenoliths (McKee et al., 1990, and Minckley, 1969). The San Marcos Formation lies above the basement. Deposited in the early Cretaceous, it is an immature sandstone with hematite cement, interbedded with conglomerate containing quartz, volcanic clasts, and mudstones. Igneous clasts in the unit may be boulder-sized (McKee et al., 1990). The Padilla Formation, located above the San Marcos Formation or basement, was deposited in the early Cretaceous. It is a massive dolomite unit with interbedded shale, sandstone, and evaporites in some areas (Jones, et al., 1984).

La Mula, Neocomian in age, is located above the Padilla Formation. It is a red shale subdivided into three units. The lower unit is a red hematite cemented sandstone and shale unit, with some intermittent limestone beds transitioning from the Padilla Formation. It was formed at a prograding marine margin in shallow water. The middle unit is a cross-bedded quartz sandstone and conglomerate containing fault-generated debris, feldspar, and quartz. The upper unit, a fine-grained shale, corresponds to a rise in sea level (Jones et al., 1984).

The fossiliferous La Virgen Formation, above La Mula, contains gypsum evaporite beds, thin dolomite beds, fine-grained limestone, shale, and clay. The

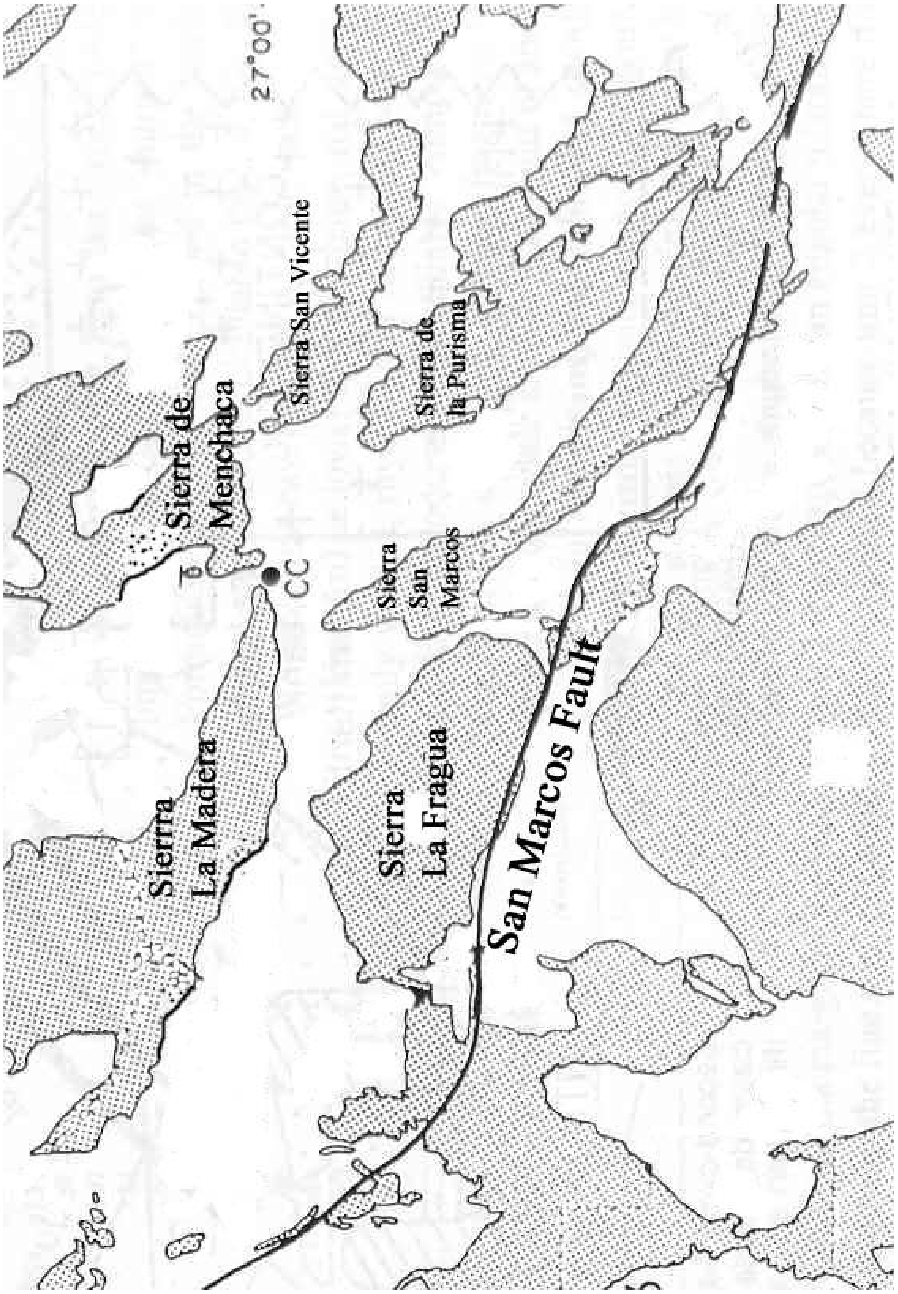

Figure 4: Map showing the San Marcos Fault (modified from McKee, et. al., 1990). The bold line is the mapped fault. CC is the town of Cuatro Cienegas.

Formation Name	Description	Age	Aquifer Permeability
Alluvium	Sand, gravel, lake deposits, evaporite deposits, travertine	Quaternary	Permeable
Eagle Ford	Clay, lutite, calcite	Cretaceous	Low Permeability
Buda	Calcite, stratified, interbedded sand and gravel	Cretaceous	Low Permeability
Del Rio	Sandy limestone, lutite	Cretaceous	Low Permeability
Georgetown	Grey limestone, stratified	Cretaceous	Permeable
Washita Group	Limestone	Cretaceous	Permeable
Kiamichi	Lutite, limestone	Cretaceous	Low permeability
Aurora	Limestone, gypsum	Cretaceous	Very Permeable
La Peña	Dark laminated shale, hematitic	Cretaceous	Low Permeability
Cupido	Oolite grainstone, gypsum	Cretaceous	Very Permeable
La Virgen	Gypsum, dolomite, limestone, shale and clay	J/K	Low Permeability
La Mula	Hematitic shale, sandstone, limestone, conglomerate with feldspar and quartz rich detritus	J/K	Low Permeability
La Padilla	Massive dolomite, interbedded shale, sandstone and evaporites	J/K	Low Permeability
San Marcos	Sandstone, hematite cement, interbedded conglomerate	J/K	Low Permeability
Basement	Igneous- primarily granite and diorite	Permian	Low Permeability

Table 1: Stratigraphic column for the Cuatro Cienegas basin (modified from Martinez, 2000, Mckee, et. al., 1990, and Lesser, 2001).

overlying Cupido Formation is similar in composition to the La Virgen Formation. It typically forms cliffs in the area and is composed of marine shelf oolite limestone. This formation has a sharp contact with the overlying La Peña Formation, a dark colored laminated shale with a pinkish tint on weathered surfaces (Jones et al., 1984). Overlying the La Peña Formation, the Aurora Formation is composed of limestone beds with high permeability due to fractures and dissolved calcite and gypsum. The Aurora serves as an aquifer in the basin, and is closely related to the Edwards Limestone found in the Central Texas Region (Smith, 1970).

The overlying Kiamichi Formation is a thin unit of calcite, which is overlain by the Washita group in the Cuatro Cienegas basin. The Washita Group is a limestone that tops the mountains surrounding the basin, and has high secondary porosity from faulting and dissolution of calcite. The Georgetown Formation overlies the Washita Group. The Georgetown, Del Rio, Buda, and Eagle Ford Formations crop out in the Austin, Texas area and continue south through the Cuatro Cienegas basin. In Mexico, the Georgetown Formation is a permeable, stratified limestone, grey in color. Dolomite is also present in this unit (Martinez, 2000). The Del Rio Formation is a sandy limestone containing lutite. The Buda consists of stratified calcite beds, inter-bedded with sand and gravel (Martinez, 2000). Finally, the interior of the basin is composed of Quaternary alluvium, travertine, and evaporite minerals.

Different sources, including Lehman et. al., 1998; Martinez, 2000; McKee et al., 1990; Lesser, 2001; and Jones et al., 1984, detail the stratigraphy. It is clear that the Washita Group tops most of the mountains, the Aurora lies underneath, overlying the La Peña, Cupido, and San Marcos Formations (Figure 5). Below the alluvium in the valley floor is the Eagle Ford Formation, followed by the Washita group and

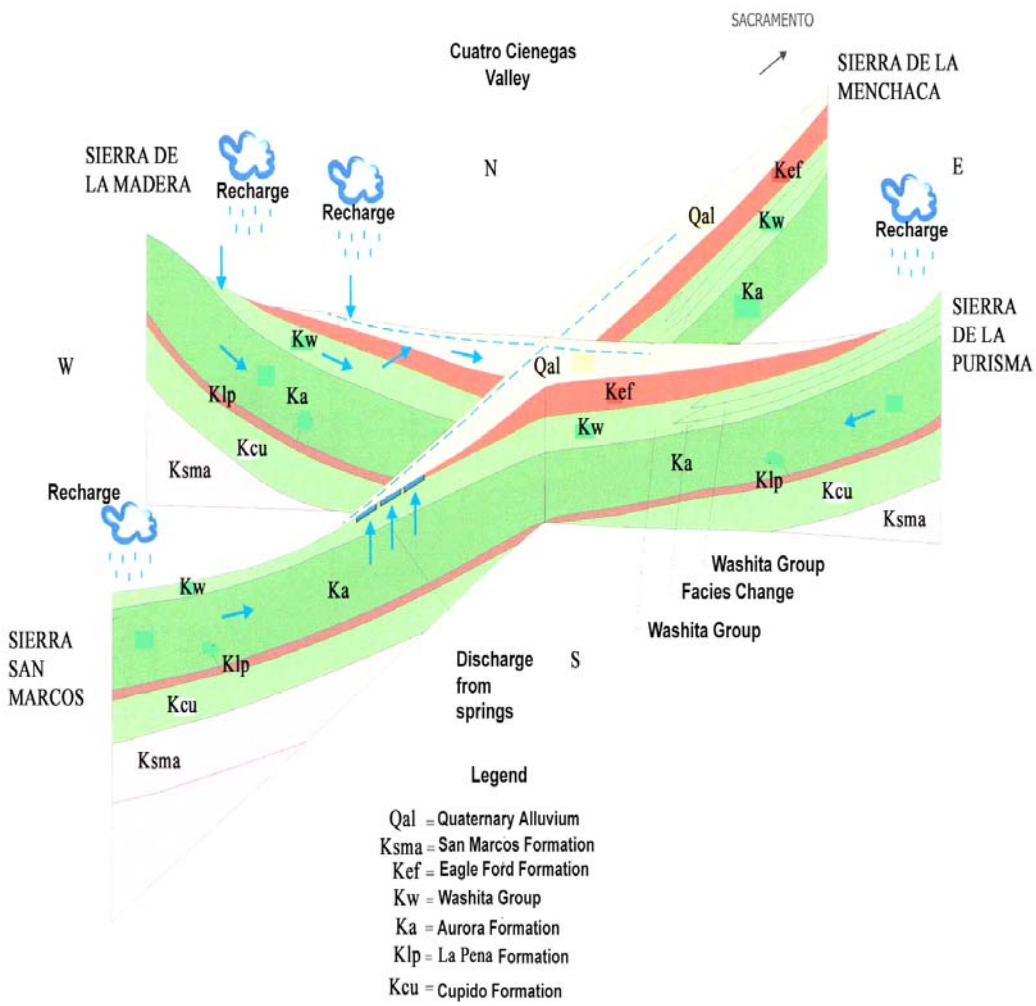

Figure 5: Map showing stratigraphy (modified from Lesser, 2001). This is a cross-sectional view of the valley, looking north from the southeast tip of the eastern lobe of the basin.

lower units (Lesser, 2001). However, much is still unknown about the stratigraphy of the units underlying the basin due to the basin fill, complex faulting, and karst features of the basin.

STRUCTURE

Local and regional faults are widespread in the Cuatro Cienegas Basin and surrounding mountains (Martinez, 2000). At the end of the Paleozoic Era, sedimentary rocks were deposited in the Las Delicias Basin and intruded by granitic rocks (McKee et al., 1990). During the Jurassic, the Cuatro Cienegas Basin was located in the Sabinas Basin, which was north of the Coahuila Platform (Lehmann et al., 1998) (Figure 6). Faulting in the Jurassic by the San Marcos fault uplifted the area, producing the anticlinal mountains of Cuatro Cienegas. High rates of erosion, a result of the faulting, resulted in large quantities of sediment deposited in the Jurassic Sea (McKee et al., 1990). Faulting continued into the late Jurassic and early Cretaceous. The San Marcos Formation was deposited at this time. Cretaceous sediments were deposited within the Cupido-Sligo shelf margin at the peak of greenhouse climatic conditions (Lehmann et. al., 1998) (Figure 6). Another faulting episode began in the early Tertiary, which resulted in the deposition of the Cupido Formation. Late Tertiary faulting, associated with the Laramide Orogeny, later reversed the displacement of rock units (McKee et al., 1988, 1990).

In Cuatro Cienegas, the Sierra San Marcos is the main feature from which springs issue. The San Marcos fault lies at the south end of the mountain, and may serve as a conduit for interbasin flow. A westward dipping normal fault runs along the entire west side of the Sierra San Marcos from north to south (Martinez, 2000). A

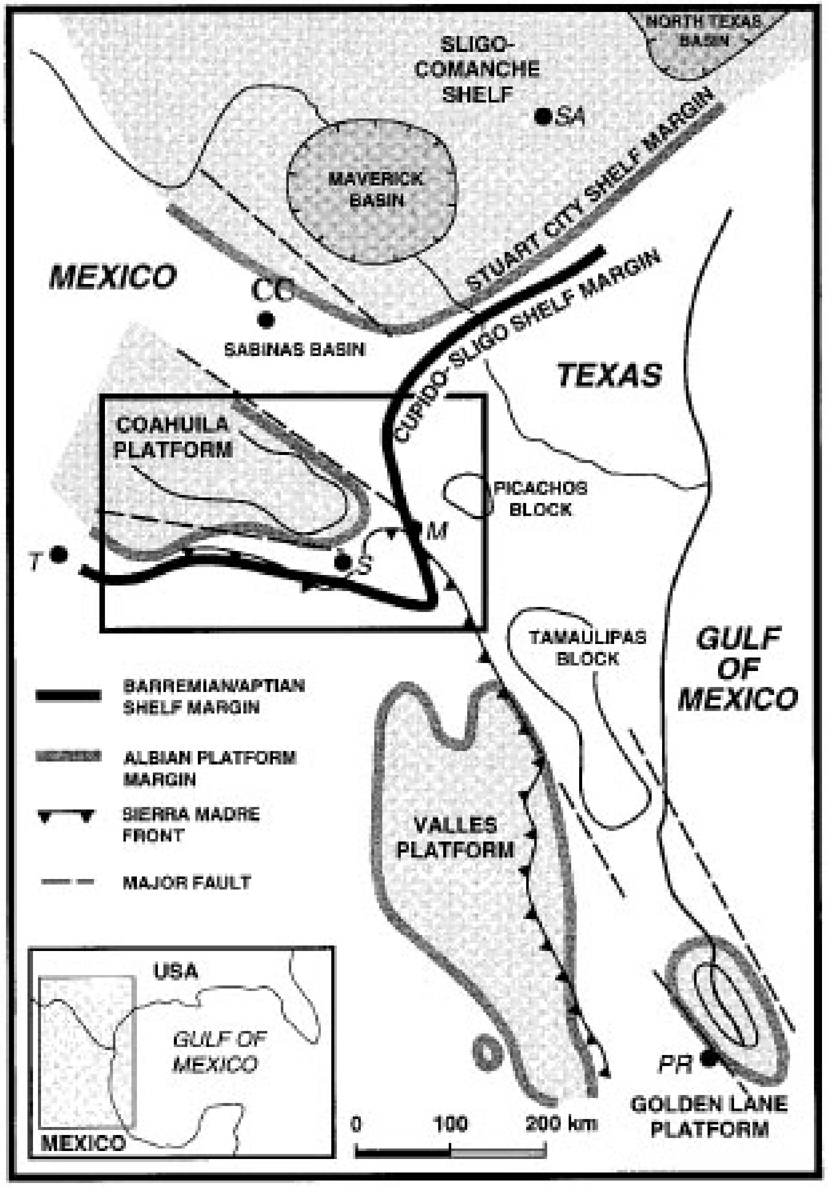

Figure 6: Regional geology map (modified from Lehmann et. al., 1998). Cities are marked by initials: CC is Cuatro Cienegas, SA is San Antonio, M is Monterrey, S is Saltillo, T is Torreon, PR is Poza Rica.

fault has also been mapped along the southeast side of the mountain (Figure 7). This may affect spring density adjacent to the mountain. Though no surface evidence exists, other faults may exist, facilitating spring development along the Sierra San Marcos.

HYDROGEOLOGY

Cuatro Cienegas' endemic fauna is dependent on continuous spring-flow. The basin has a spring density of 12 to 15 pozas (springs) per square kilometer, and are especially dense near the Sierra de San Marcos, which separates the basin into its east and west lobes (Figure 3) (Winsborough, 1990). Approximately 300 springs/pools have been quantified by Mexican Environmental and Natural Resources Secretary (SEMARNAT), but hundreds more springs are presumed to exist (Lesser, 2001). The springs in the basin exhibit extreme variability in temperature, salinity, water chemistry, and discharge over small spatial scales. Temperature in the springs varies from 18^{o} Celsius to 35^{o} Celsius, and is highly dependent on the time of year it is sampled (Figure 8) (Minckley, 1969).

Minckley described seven flow systems in the basin (1969). These were the Churince, Becerra/Garabatal, Rio Mesquites, Rio Puente Chiquito, Tio Candido/Escobeda, Santa Tecla, and Rio Salado de los Nadadores (Rio Grande). This project combines the Becerra/Garabatal, Rio Mesquites, and Rio Puente Chiquito systems under the assumption that they are inter-related and have the same terminal point evidenced by their proximity and mixing from canals. Therefore, five flow systems are hypothesized for the Cuatro Cienegas basin. These include the

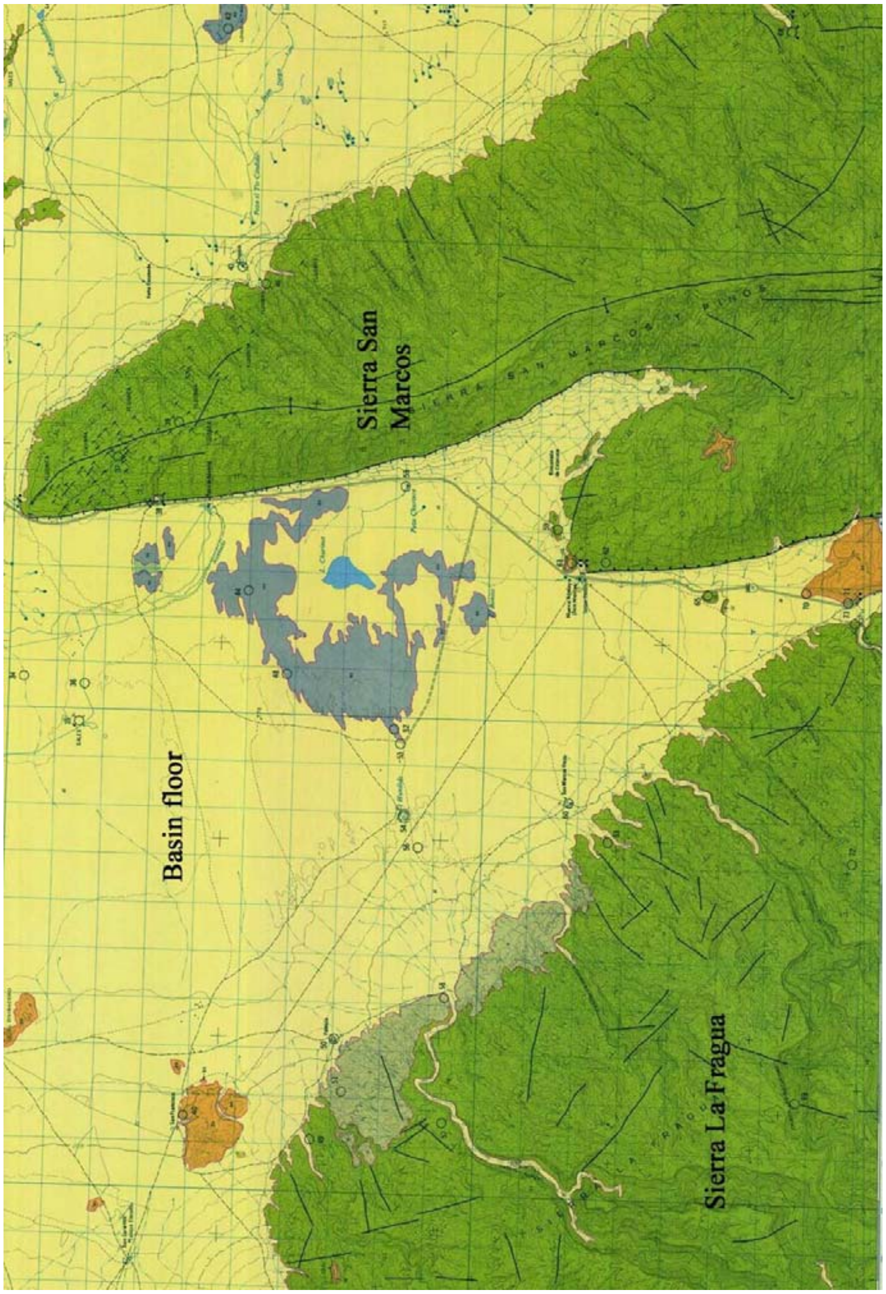

Figure 7: Map showing faults along the Sierra San Marcos and Sierra La Fragua (modified from CETN, 1973). Dark black lines on the map indicate faults.

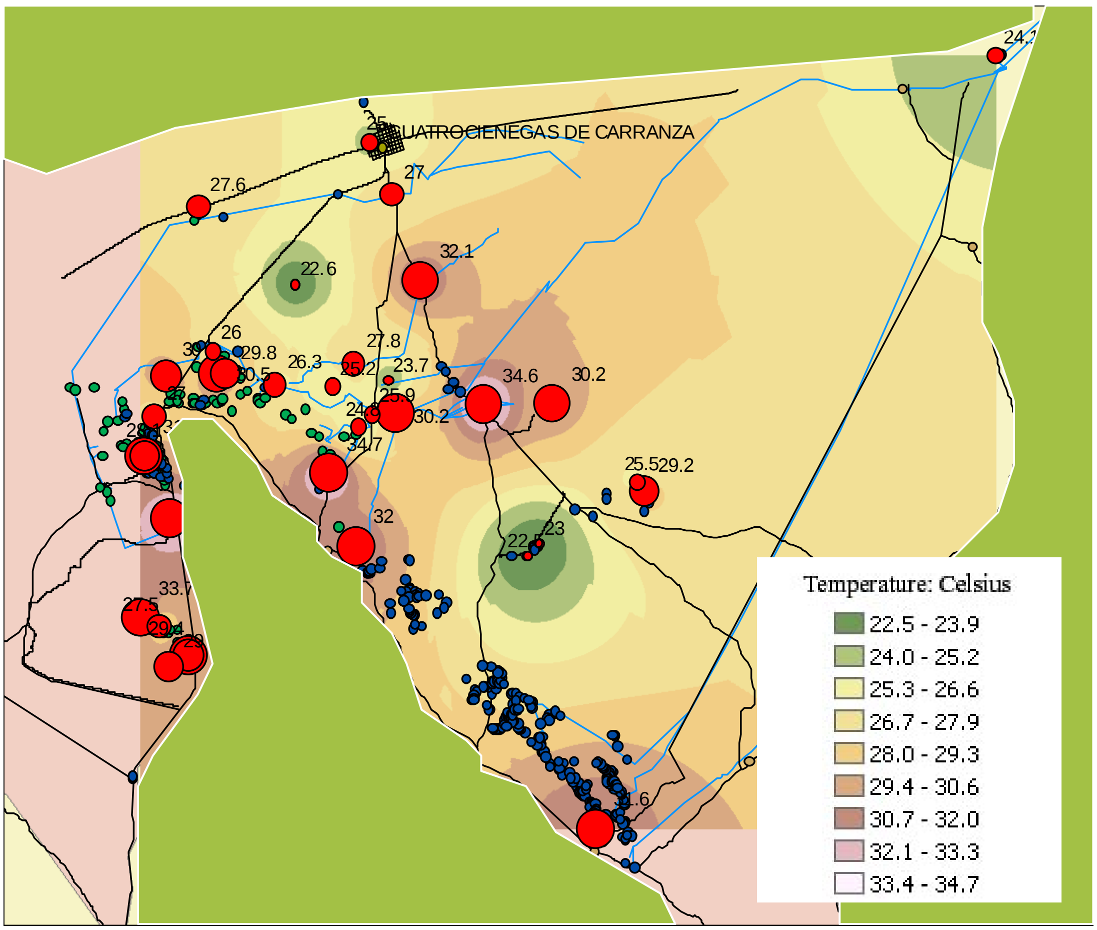

Figure 8: Temperature map for springs in the basin. The size of the red points is proportional to the temperature of the surface water at the sample site. The blue and green points on the map are springs in the basin where no temperature data was collected. Note that no data exists for the most western edge of the basin. The raster calculated a probably value that may not correspond to actual temperatures in the western portion of the basin.

Churince system in the southwest, the Garabatal-Becerra-Rio Mesquites system flowing from the southwest to northeast part of the basin, the Tio Candido-Hundidos system in the center of the eastern side of the basin, the Santa Tecla system in the southeast, and the Anteojo system in the north portion of the basin (Figure 9). As a result of channelization, the canal leading out of the basin is most likely a mixture of four systems: the Garabatal-Becerra-Rio Mesquites, Tio Candido-Hundidos, Santa Tecla, and Anteojo. The outlet of the basin (cumulative Cuatro Cienegas systems) drains to the Rio Grande system.

Four main types of water bodies exist in the basin. They include source springs (commonly called “pozas”), pools fed by surface flows (also often locally termed "pozas"), stream channels, and playa lakes. Source springs, such as Poza Becerra, Poza Churince, and Poza Tierra Blanca surface from sinkhole formations and are the beginning springs in a flow system (Figure 10). Other springs, such as Poza Escobedo and Poza Mojarral Oeste (Poza Azul), are also a result of karstification, but occur away from the source. Channels, as part of the Rio Mesquites, are formed from the erosion from the headwaters of the springs. Playa lakes are generally found at the termination of a flow system. Due to tectonic uplift in the Pleistocene, many of the terminal playa lakes in the region were drained (Minckley, et al., 1968). Only Laguna Grande (Churince system), Las Playitas (Rio Mesquites system), and Los Gatos (Hundidos system) now exist in the basin.

Flow systems in the Cuatro Cienegas basin exhibit a high level of variability in physical properties and flow pathways. Most water bodies in the systems have low turbidity with visibility up to 5 meters or more. In bodies where a large amount of evaporation has occurred, the water is more opaque and may have a white to red tint

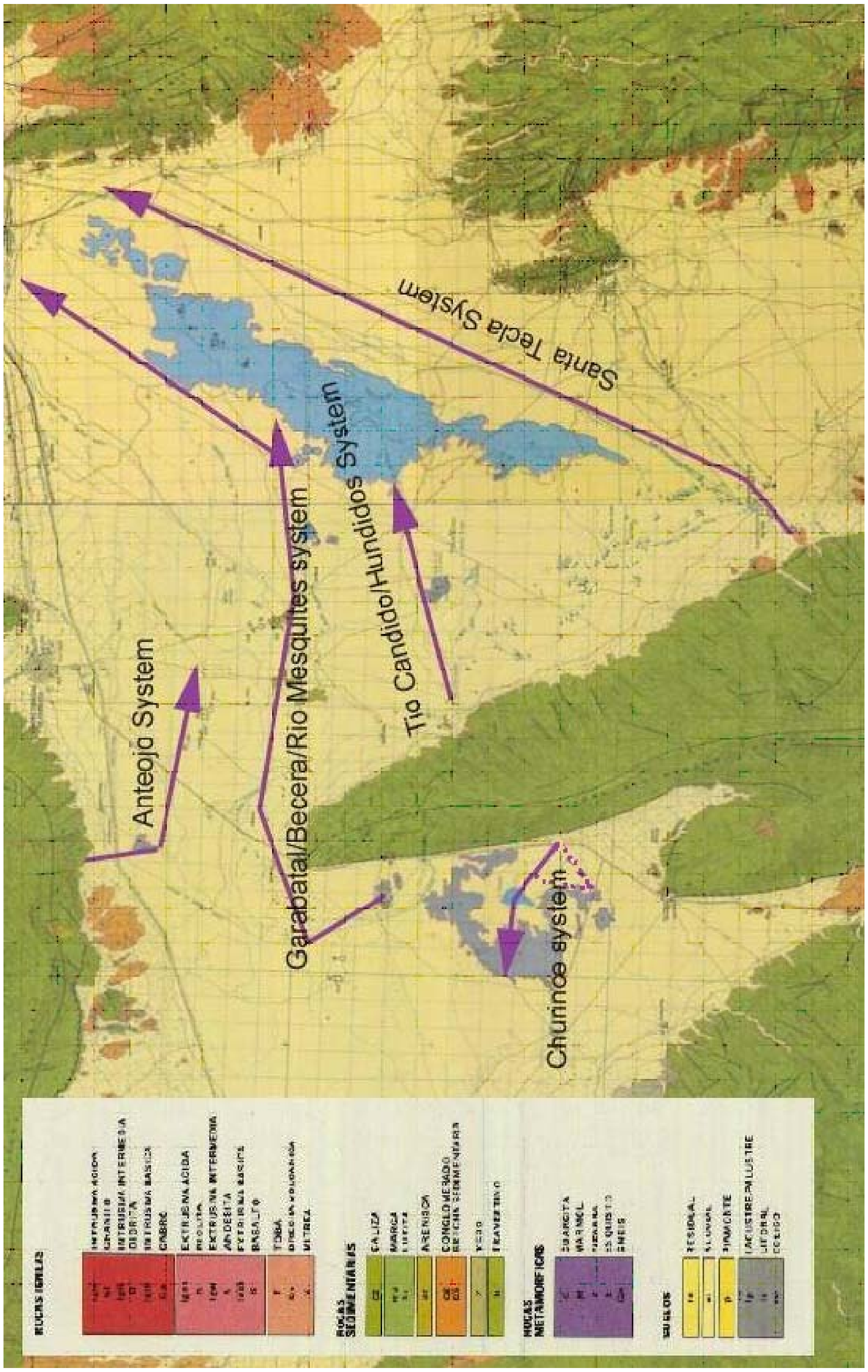

Figure 9: Five flow systems in Cuatro Cienegas (modified from CETN, 1973). The dotted purple line is an inferred groundwater flow path. The solid lines indicate probable groundwater flow paths.

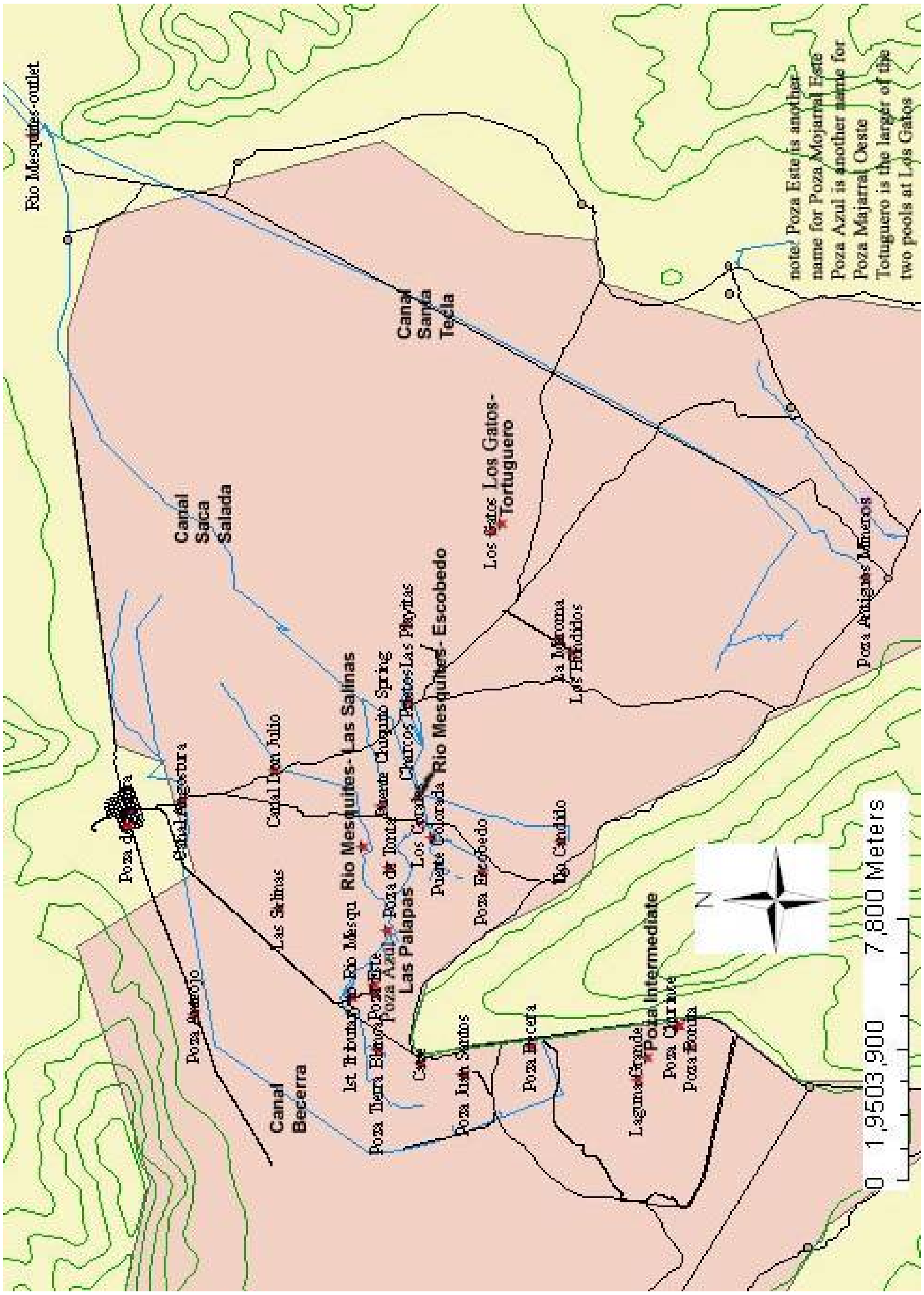

Figure 10: Map showing the sample locations and names of water bodies in the basin. Blue lines are canals, and black lines are roads.

due to the presence of cyanobacteria (Minckley et. al., 1968). Due to mineralization along the flow path, channels and pozas (springs) have often precipitated salts and travertine, closing them off from the surface (Minckley, 1969). The flow systems have created an underground network of conduits through which the water flows.

There has been limited research on the hydrogeology of the Cuatrocienegas basin. Knowledge about the basin's remarkable uniqueness was established in 1939 through E.G. Marsh, and biologists have studied the fauna within the basin since 1958 (Meyer, 1973). Minckley and Cole (1968) conducted a preliminary limnologic study of the springs in the basin, creating a baseline for the average chemistry of the springs. Their work demonstrated the similarity of the springs to one another. For her research on the stromatolites in the springs, Barbara Winsoborough (1990), analyzed springs for their major ion chemistry. Her results were similar to those of Minckley. Neither source elaborated on the possible evolution of the chemistry. The most elaborative work conducted on the chemistry in the basin was conducted by Johannesson, et. al. (2004). The study was conducted to analyze the water chemistry and isotopic signatures of the springs in the basin to determine the source of water to the basin. The study found that the Cuatro Cienegas waters were closely related to the Cupido-Aurora aquifer. This connection requires more study.

Canals

The Cuatro Cienegas Basin was naturally closed until 1898 when it was artificially opened via canals leading out of the basin in the northwest and into the Rio Grande system (Minckley, 1969) (Figure 11). The first canal, Saca Salada canal,

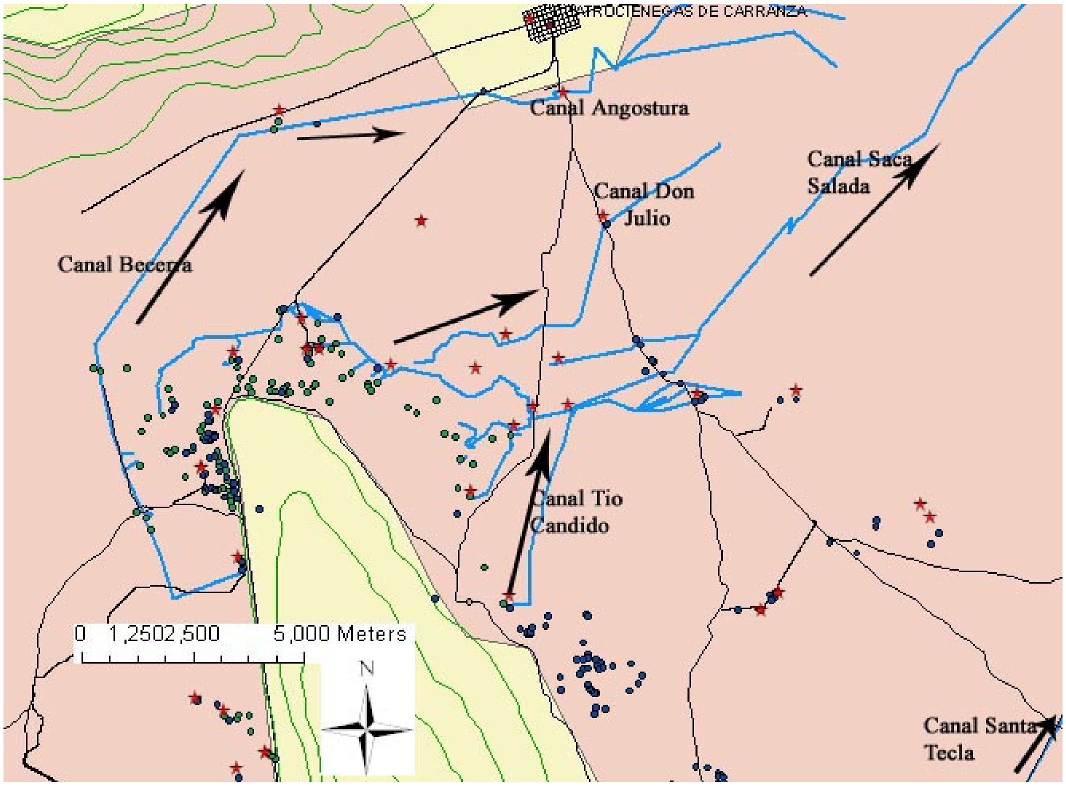

Figure 11: Map of canal locations and names. Arrows indicate flow direction, red stars indicate sampled sites, blue and green points are springs in the basin that were not sampled.

was built to open the naturally closed basin to transport water north, into the Rio Grande system (Minckley, 1969). This canal routes water from the following locations: Tierra Blanca, Rio Mesquites, Canal de la Puerto Colorada, Canal de Escobedo, Canal de Tío Cándido, Puentes Cuatas, Canal de las Puentes Cuatas, Canal de la Puente Chiquita, Canalón, and Saca Salada (PROFAUNA and WWF, 1999). The Santa Tecla canal was constructed in 1966 (PROFAUNA and WWF, 1999). It joins the Saca Salada canal in the northeast corner of the basin to divert water out of the basin. Several canals were built to provide water for irrigation within the basin. These include the Becerra, Antiguos Mineros del Norte, El Venado, El Agua Grande, La Vega, San Vicente, and Julio Arredondo (PROFAUNA and WWF, 1999). The Becerra canal was built from Poza Becerra to re-route water in 1964. This resulted in drying out several surrounding marsh areas (Minckley, 1969). Another canal was built in 1898 to route water from Poza Escobeda into Puente Chiquita (Minckley, 1969).

CHAPTER 2: METHODS

Several techniques were utilized to obtain a clear conceptual model of the processes occurring in the Cuatrocienegas basin. Previous studies in and around the basin were considered in order to define a conceptual model of the basin hydrogeology. Groundwater samples were collected and analyzed for major cation and anion chemistry, and the chemical data was evaluated graphically using Aqua Chem and geochemically modeled using PHREEQC (Calmbach/Waterloo Hydrogeologic, Inc., 1998 and Parkhurst, et. al., 1999). GIS was utilized to view the physical locations, topography, layout of the basin, and chemical spatial variability within the basin.

Names of water bodies in the basin are not consistently used among researchers, making it difficult to place geographic locations with the poza name. Therefore, in this project, I have tried to consistently use the terminology that Minckley used in his research. Several new sites were sampled, including a cave at the foot of the Sierra San Marcos, a well in the town of Cuatro Cienegas (Pozo de Sandra), a sinkhole that was discovered during the June 2004 research trip (Poza de Tonta), and the larger of the two pools at Los Gatos (Los Gatos- Tortuguerra). A table showing the latitude and longitude for each site with the poza name I am using in this project is located in the appendix.

Water Sample Collection Procedures

In April of 2004, I collected nine water samples from springs and pools throughout the Cuatrocienegas basin. An additional 26 samples were collected in June 2004, and four were collected in January 2005. All samples were collected using the same procedures. However, alkalinities were analyzed solely in the lab for the April and January samples because of time constraints and restrictions for carrying materials across the Mexican border.

Samples that varied from the protocol due to weather constraints include SBE-21 (Canal Angostura), SBE-22 (Pozo in Cuatrocienegas), SBE-23 (Poza Anteojo), and SBE-25 (Rio Mesquites outlet). These samples were collected in one large bottle 250 mL bottle, rinsed thoroughly with distilled water, due to a rain storm. They were filtered and acidified according to the protocol in the lab immediately after collection.

SAMPLE COLLECTION

In order to minimize collection contamination, water was collected in grab samples taken approximately 1-1.5 ft from the bank of each sample site at a depth of about 10 inches. Water for the alkalinity and anion bottles was filtered and un-acidified, while water for the cation bottles was filtered and acidified. The cation bottles washed in a 25 percent hydrochloric acid bath for 24 hours prior to use. For all samples, water was hand-filtered with a syringe through 0.2 micron filter paper into the bottles. Each bottle was rinsed three times with the filtered water prior to filling the bottle. Each bottle was filled to the top, making every effort to prohibit air from entering. Samples collected for cation analysis were acidified in the field using

0.1 molar nitric acid. The samples were labeled upon collection with the date, sample number, and specified use.

FIELD PARAMETERS

Field parameters were measured at each site except samples SBE-35 (the water from a cave at the foot of the Sierra San Marcos) and SBE-21 (Canal Angostura). The cave water was collected in April 2004 during a quick stop without time to collect field data. The water from Canal Angostura was collected upon the onset of a rain storm with little time to collect the sample.

Measured field parameters included dissolved oxygen (DO), oxidation reduction potential (ORP), temperature, conductivity, and pH. These measurements were taken using the Myron L Company 6P-CE Ultrameter, Oakton DO 100 series DO meter, and Acumet pH meter. The sensors in the meter were rinsed three times with the sample water prior to obtaining readings. Measurements were not taken until each instrument stabilized. After the results were written down, each instrument was rinsed three times with distilled water and dried. Each instrument was calibrated with standard solutions prior to use.

Alkalinity was also measured in the field by titrating to the bicarbonate endpoint. Samples collected in April and January were not analyzed in the field for alkalinity. Because of heavy rainfall, samples SBE-21, SBE-22, SBE-23, and SBE-25 were not immediately analyzed, but were within an hour of collection. All other samples were analyzed at the site.

Chemical Analysis

Upon return from the field, the samples were shipped to the University of Minnesota for anion analysis on a Dionex ICS-2000 ion chromatography system. Samples were also analyzed at The University of Texas for cation concentrations using the GUI Platform ICP-MS. In order to accurately analyze the water, the samples were diluted proportional to their specific conductance prior to analysis. Dilution for source springs was 1:10, for intermediate springs was 1:40 to 1:100, and for terminal lakes was 1:200 to 1:500.

Annual precipitation chemistry was downloaded from the National Atmospheric Deposition Program/ National Trends Network (NADP/NTN) rain station TX04, located in Big Bend National Park, Texas. This is the precipitation collection station closest to Cuatro Cienegas. The rainwater chemistry was downloaded as precipitation-weighted means for the calendar year for a 10 year time period (1993-2003).

All analytical results were entered into a chemical spreadsheet and imported to AquaChem 3.7, created by Waterloo Hydrologic, Inc. Charge balances were calculated using AquaChem. It was also utilized to graph the Piper plot, Schoeller plots, and the cross plots for the basin's spring chemistry. Waters within each hypothesized flow-path were placed into separate Schoeller plots to view the patterns within specific regions. Cross plots were created for Na^{+} vs. Cl^{-}, Mg^{2+} vs. Cl^{-}, SO_4^{2-} vs. Cl^{-}, gypsum SI (saturation index) vs. SO_4^{2-}, Cl^{-} vs. Br^{-}, Ca^{2+} + Mg^{2+} vs. HCO_3^{-}, Ca^{2+} vs. Mg^{2+}, dolomite SI vs. Cl^{-}, and calcite SI vs. Cl^{-}.

PHREEQC Geochemical Modeling

Geochemical modeling was conducted using PHREEQC (Parkhurst et. al., 1999). The program was utilized to calculate saturation indices and moles of species in the waters, and to determine the chemical reactions that occur for the source spring waters to evolve from rainwater. The rainwater was reacted with several different mineral phases and evaporated in order to compare with the source waters. Reactions taking place from the source springs to the terminal lakes were also modeled.

Geographic Information System

Geographic Information Systems (GIS) are useful tools in viewing hydrochemical information on a spatial scale. This was important in the Cuatro Cienegas Basin to assess where the source springs were located in relation to the terminal lakes and surrounding flow systems. It was utilized to spatially analyze trends in measured parameters and chemical species. ArcGIS version 9.0, developed by ESRI, was utilized in this project.

All base files for the Cuatro Cienegas basin and Mexico were obtained from Jennifer Howeth from the Biology Department at The University of Texas at Austin and Angela Moline from the Biology Department at Colorado State. The data were in both geographic coordinates (North American Datum-1927) and projected coordinates (Universal Transverse Mercator- UTM, Zone 13). All of the data were ultimately gathered into the UTM Zone 13 projection for the ease of study.

The chemical data, field data, and Global Positioning System (GPS) data were entered into a Microsoft Excel database upon return from the field. Each sample location was recorded using a handheld GPS device. The GPS was not utilized for samples taken in April. GPS locations for samples from the Angostura Canal and Pozo de Sandra (Figure 10) were not obtained due to weather conditions at the site. However, they have been manually added to the final map.

Using the Spatial Analyst toolbar in GIS, the chemical data in the sample location layer was interpolated to a raster using the inverse distance weighted, spline, and kriging methods. All three methods were utilized to determine which had the most realistic results. They also created temperature and alkalinity rasters for the basin. The inverse distance weighted method provided the most realistic map in all cases.

CHAPTER 3: RESULTS

General Water Chemistry

Temperature and conductivity in the springs varies dramatically within the basin. Temperature in the pozas varied in the suite of samples between 23.7 degrees Celsius and 34.7 degrees Celsius (74.7- 94.5 degrees Fahrenheit) (Tables 2, 3, 4, 5, 6, 7, and 8). Conductivity in the source spring samples was between 1,390 microSiemans (µS) and 1,670 µS in the Santa Tecla and Anteojo systems to 2,300-2,500 µS in the Churince, Garabatal- Becerra- Rio Mesquites, and Tio Candido-Hundidos systems. Conductivities ranged between 2,700 µS and 4,100 µS for the sites in the centers of the systems, while the termination pozas/lakes ranged between 5,600 µS to greater than 11,000 µS.

Charge balances for the samples were calculated following analysis. Most of the samples had a charge balance of less than 5 percent. However, the some samples collected in April 2004, including Poza Mojarral Oeste (Poza Azul), Poza Mojarral Este, Poza Churince, Poza La Maroma, Poza Los Hundidos, and the first tributary to the Rio Mesquites had large charge balance errors of 12.1 percent, -25.2 percent, -33.5 percent, 13.6 percent, 18.6 percent , and -6.4 percent respectively. Laguna Grande, collected in June, had a charge balance error of -17.9 percent. Such large charge balances indicate that something with the analytical work may have been recorded in error. All of the samples were diluted, some to a greater degree than others. If the dilution order was misinterpreted, this could cause error. For three of these samples, the anion value is twice the expected value. These samples were not considered in the next sections, unless specified to locate a trend or general

CHURINCE SYSTEM (concentrations in ppm)

ID	Site	Temp- C	pH	Cond (uS)	CBE%	Na	Si	Mg	K
SBE-4	Poza Churince	31.10	7.22	2550	1.90	145.94	7.76	106.80	7.98
SBE-20	Poza Bonita	29.00	7.43	2604	3.70	153.89	8.71	113.96	9.03
SBE-2	Laguna Intermediate	27.50	7.81	2803	-1.10	158.25	8.37	108.22	7.98
SBE-3	Laguna Grande	33.70	8.01	11180	-17.90	810.70	14.28	505.91	39.04
SBE-30-4/SBE-4A	Poza Churince-April	29.40	7.59	10730	-33.50	140.90	6.62	92.69	6.57

Site	Ca	Sr	F	Cl	Br	NO3 - N	SO4	Alk (HCO3)	Li	B	Al
Poza Churince	340.030	13.287	2.657	104.8	0.491	1.183	1221	176.66	0.0758	0.2569	BDL
Poza Bonita	370.534	13.961	2.749	106.4	0.494	1.284	1278	177.14	0.0819	0.2677	BDL
Laguna Intermed.	348.244	13.443	2.873	117	0.545	0.35	1412	100.04	0.0845	0.2480	BDL
Laguna Grande	477.055	25.089	12.19	800.3	3.477	0.017	5858	140.79	0.3946	1.3791	BDL
Poza Churince-April	298.693	13.598	5.081	198	0.904	0.062	2390	183.2440	0.0754	0.2588	BDL

Site	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	As	Se	Rb
Poza Churince	0.0050	BDL	BDL	0.0076	0.0037	BDL	BDL	0.0200	0.0121	0.0064	0.0092
Poza Bonita	0.0050	BDL	BDL	0.0044	0.0039	BDL	BDL	BDL	0.0130	0.0062	0.0107
Laguna Intermed.	0.0032	BDL	BDL	BDL	BDL	BDL	BDL	BDL	0.0103	BDL	0.0084
Laguna Grande	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	0.0326	BDL	0.0483
Poza Churince-April	0.0052	0.0002	0.0007	0.0040	0.0067	0.0013	0.0033	0.0274	0.0107	0.0052	0.0090

Site	Mo	Cd	Sn	Sb	Cs	Ba	La	Hg	Pb	Bi	Th	U
Poza Churince	0.0691	BDL	BDL	BDL	0.0040	0.0155	BDL	BDL	BDL	.0001	0.0001	0.0089
Poza Bonita	0.0637	BDL	BDL	BDL	0.0044	0.0103	BDL	BDL	BDL	.0001	0.0001	0.0093
Laguna Intermed.	0.0507	BDL	BDL	BDL	0.0039	0.0118	BDL	BDL	BDL	BDL	BDL	0.0078
Laguna Grande	0.1148	BDL	BDL	BDL	0.0171	BDL	BDL	BDL	BDL	BDL	BDL	0.0134
Poza Churince-April	0.0595	0.0003	0.0002	0.0002	0.0040	0.0153	0.0001	N/R	0.0005	0.0002	0.0001	0.0083

Table 2: Churince System Chemistry

CHURINCE SYSTEM (concentrations in ppm)- Data from January 2005

	Date	pH	Temp	Cond (uS)	TDS (ppm)	CBE %	mL acid	Alkalinity
Poza Churince	1/30/2005	7.26	25.5	2447	1760	0.2	0.675	164.7
Laguna Intermediate	1/30/2005	8.28	13.6	4724	3712	-0.8	0.453	110.532
Laguna Grande	1/30/2005	8	15.3	2721	2009	-2.5	0.734	179.096

Site	Na	Mg	Si	K	Ca	F	C2H3O2	Formate	Cl	Br
Poza Churince	151.43	97.39	8.15	7.20	319.60	2.592	0.0375	<0.010	103.55	0.46
Laguna Intermediate	163.79	106.32	8.34	7.48	369.31	2.7565	0.087	0.016	112.25	0.481
Laguna Grande	391.62	239.96	14.66	19.49	506.98	5.58	0.185	<0.050	273.45	0.94

Site	SO4	NO3	HCO3	Thiosulfate	Li	B	Al	V	Cr	U
Poza Churince	1210	1.249	164.7	0.018	0.0907	0.3308	0.0306	0.0135	0.0010	0.0082
Laguna Intermediate	1402	0.596	179.096	0.026	0.0833	0.2894	BDL	0.0211	0.0017	0.0086
Laguna Grande	2725.5	0.02	110.532	0.08	0.2886	1.0632	0.0600	0.0229	0.0025	0.0258

Site	Mn	Fe	Co	Cu	As	Se	Rb	Sr	Mo	Cs	Ba
Poza Churince	BDL	0.0038	0.0020	0.0850	0.0108	BDL	0.0081	13.0449	0.0475	0.0033	0.0162
Laguna Intermediate	BDL	BDL	BDL	0.1595	0.0114	BDL	0.0091	14.0587	0.0502	0.0033	0.0135
Laguna Grande	0.0013	0.0036	0.0030	0.1390	0.0269	BDL	0.0237	19.1981	0.1088	0.0077	0.0082

Table 3: Churince System Chemistry from Jan. 2005.

GARABATAL- BECERRA- RIO MESQUITES SYSTEM (concentrations in ppm)											
ID	**Site**	**Temp ©**	**pH**	**Cond (uS)**	**CBE%**	**Na**	**Si**	**Mg**	**K**	**Ca**	**Sr**
SBE-1	Poza Becerra	33.400	7.140	2360	2.500	146.165	7.702	108.775	8.981	357.795	13.025
SBE-5 (R)	Poza Juan Santos	31.000	7.160	2791	-1.200	149.990	7.449	105.812	8.895	343.994	12.893
SBE-35-9	Cave				-4.000	246.279	6.240	110.869	19.498	359.500	13.575
SBE-26	Poza Tierra Blanca	30.000	7.390	2865	0.100	161.845	7.268	113.052	9.439	385.613	13.906
SBE-24	Rio Mesquites- Las Palapas	26.300	7.950	2893	-0.300	166.353	7.670	114.838	9.641	386.956	13.885
SBE-12	Rio Mesquites- Las Salinas	27.800	7.910	3192	1.300	198.189	9.910	139.824	11.927	429.447	14.265
SBE-18	Canal Don Julio	32.100	7.860	3280	-2.400	189.688	8.703	126.833	10.998	424.501	14.599
SBE-25 (R)	Rio Mesquites-outlet	24.100	8.190	3516	0.800	225.236	11.698	161.638	13.254	483.222	14.664
SBE-19	Poza de Tonta	25.200	7.800	2991	-2.900	165.044	7.794	113.469	9.784	381.640	13.824
SBE-15-R	Puente Chiquito Spring	23.700	7.260	4154	-1.800	314.294	10.677	183.370	16.808	493.053	15.385
SBE-25 (R)	Rio Mesquites-outlet	24.100	8.190	3516	0.800	225.236	11.698	161.638	13.254	483.222	14.664
SBE-14	Los Corales	25.900	7.810	3120	0.400	181.015	9.452	127.692	10.869	431.289	14.231
SBE-11	Rio Mesquites- Escobedo	30.200	7.760	3137	-0.200	185.194	10.072	129.751	10.840	422.179	14.324
SBE-17	Charcos Prietos	34.600	8.070	3530	-2.200	212.722	12.477	140.182	11.108	483.646	15.669
SBE-16	Las Playitas	30.200	8.330	5795	-1.200	455.159	21.616	304.875	24.249	713.573	24.970
SBE-10	Poza Escobedo	34.700	7.120	2646	4.500	143.759	8.064	115.424	9.397	393.018	12.923
SBE-13	Puente Colorada	24.800	7.890	3074	0.300	172.932	9.499	125.179	10.531	430.439	13.872
SBE-31-5/SBE-5A	Poza Juan Santos- April	28.100	7.590	11180	-0.700	154.858	7.048	102.853	8.015	326.402	13.798
SBE-32-6	Las Salinas- April	22.600	8.240	18000	-5.600	14969.868	0.000	15633.487	1694.835	461.264	27.126
Site	**F**	**Cl**	**Br**	**NO3 – N**	**SO4**	**Alk (HCO3)**	**Li**	**B**	**Al**	**V**	**Cr**
Poza Becerra	2.683	101.200	0.531	1.534	1266.000	167.384	0.086	0.268	BDL	0.005	BDL
Poza Juan Santos	2.844	105.300	0.588	1.024	1317.000	197.396	0.089	0.243	BDL	0.004	BDL
Cave	2.652	232.200	0.878	2.689	1533.000	199.592	0.092	0.281	BDL	0.005	0.000
Poza Tierra Blanca	2.986	114.700	0.567	1.246	1414.000	205.204	0.131	0.378	0.044	0.004	BDL
Rio Mesquites- Las Palapas	3.009	119.400	0.587	0.830	1445.000	200.568	0.149	0.385	0.040	0.004	BDL
Rio Mesquites- Las Salinas	3.252	136.900	0.657	0.549	1637.000	188.856	0.117	0.300	0.033	0.004	BDL
Canal Don Julio	3.301	142.100	0.716	0.355	1721.000	160.796	0.147	0.411	0.040	0.005	BDL
Rio Mesquites-outlet	3.565	162.300	0.759	0.451	1899.000	178.120	0.121	0.376	BDL	0.004	BDL
Poza de Tonta	3.093	123.500	0.650	0.685	1521.000	189.344	0.135	0.381	0.030	0.004	BDL
Puente Chiquito Spring	3.805	228.700	0.986	0.153	2205.000	224.236	0.171	0.291	0.033	0.004	BDL
Rio Mesquites-outlet	3.565	162.300	0.759	0.451	1899.000	178.120	0.121	0.376	BDL	0.004	BDL
Los Corales	3.302	129.400	0.636	0.489	1603.000	190.320	0.116	0.311	BDL	0.004	BDL
Rio Mesquites- Escobedo	3.406	130.000	0.631	0.446	1621.000	186.904	0.108	0.284	BDL	0.004	BDL
Charcos Prietos	3.931	146.500	0.710	0.084	1970.000	145.668	0.152	BDL	BDL	BDL	BDL
Las Playitas	6.803	314.100	1.460	0.042	3519.000	91.256	0.296	0.767	BDL	BDL	BDL
Poza Escobedo	2.713	102.400	0.514	1.373	1278.000	197.396	0.083	0.250	BDL	0.004	BDL
Puente Colorada	3.265	125.200	0.619	0.609	1560.000	215.696	0.112	0.330	BDL	0.003	BDL
Poza Juan Santos- April	2.546	92.370	0.465	0.985	1271.000	204.472	0.090	0.282	BDL	0.005	0.000
Las Salinas- April	10.020	21615.000	76.260	1.680	78420.000	0.000	2.704	9.311	BDL	0.129	0.016

Table 4: Becerra- Garabatal- Rio Mesquites System Chemistry.

GARABATAL- BECERRA- RIO MESQUITES SYSTEM (cont.)- concentrations in ppm											
Site	**Mn**	**Fe**	**Co**	**Ni**	**Cu**	**Zn**	**As**	**Se**	**Rb**	**Mo**	**Ag**
Poza Becerra	BDL	0.0114	0.0040	0.0067	BDL	0.0139	0.0124	0.0062	0.0134	0.0586	0.0010
Poza Juan Santos	BDL	BDL	BDL	BDL	BDL	0.0444	0.0117	BDL	0.0129	0.0439	BDL
Cave	0.0045	0.0016	0.0067	BDL	0.0112	0.0047	0.0131	0.0092	0.0273	0.0695	BDL
Poza Tierra Blanca	BDL	BDL	0.0046	BDL	BDL	BDL	0.0129	BDL	0.0151	0.0555	BDL
Rio Mesquites- Las Palapas	BDL	0.0159	0.0047	BDL	BDL	BDL	0.0128	BDL	0.0156	0.0549	BDL
Rio Mesquites- Las Salinas	BDL	BDL	BDL	BDL	BDL	BDL	0.0121	BDL	0.0163	0.0558	BDL
Canal Don Julio	BDL	BDL	BDL	BDL	BDL	BDL	0.0132	BDL	0.0173	0.0600	BDL
Rio Mesquites-outlet	BDL	0.0100	BDL	BDL	BDL	BDL	0.0129	BDL	0.0178	0.0585	BDL
Poza de Tonta	BDL	0.0131	BDL	BDL	BDL	0.0441	0.0118	BDL	0.0155	0.0563	BDL
Puente Chiquito Spring	BDL	BDL	0.0060	BDL	BDL	BDL	0.0145	BDL	0.0227	0.0699	BDL
Rio Mesquites-outlet	BDL	0.0100	BDL	BDL	BDL	BDL	0.0129	BDL	0.0178	0.0585	BDL
Los Corales	BDL	BDL	BDL	BDL	BDL	BDL	0.0124	BDL	0.0163	0.0556	BDL
Rio Mesquites- Escobedo	BDL	BDL	BDL	BDL	BDL	BDL	0.0124	BDL	0.0158	0.0537	BDL
Charcos Prietos	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	0.0180	0.0486	BDL
Las Playitas	BDL	BDL	BDL	BDL	BDL	BDL	0.0550	BDL	0.0364	0.0823	BDL
Poza Escobedo	BDL	0.0033	0.0040	BDL	BDL	0.0097	0.0116	0.0063	0.0131	0.0581	BDL
Puente Colorada	BDL	BDL	BDL	BDL	BDL	BDL	0.0112	BDL	0.0150	0.0487	BDL
Poza Juan Santos- April	0.0004	0.0010	0.0077	0.0020	0.0031	0.0075	0.0125	0.0047	0.0151	0.0482	BDL
Las Salinas- April	0.1141	BDL	0.0229	BDL	0.3420	BDL	0.0494	0.3346	1.5860	0.0176	BDL
Site	**Cd**	**Sn**	**Sb**	**Cs**	**Ba**	**La**	**Hg**	**Pb**	**Bi**	**Th**	**U**
Poza Becerra	BDL	BDL	BDL	0.0046	0.0185	BDL	BDL	BDL	0.0001	BDL	0.0106
Poza Juan Santos	BDL	BDL	BDL	0.0048	0.0175	BDL	BDL	0.0016	BDL	BDL	0.0091
Cave	0.0004	0.0004	0.0005	0.0029	0.0171	0.0003	N/R	0.0005	0.0001	0.0001	0.0119
Poza Tierra Blanca	BDL	BDL	BDL	0.0052	0.0153	BDL	BDL	BDL	BDL	BDL	0.0112
Rio Mesquites- Las Palapas	BDL	BDL	BDL	0.0053	0.0150	BDL	BDL	BDL	BDL	BDL	0.0112
Rio Mesquites- Las Salinas	BDL	BDL	BDL	0.0056	0.0134	BDL	BDL	BDL	BDL	BDL	0.0102
Canal Don Julio	BDL	BDL	BDL	0.0062	0.0139	BDL	BDL	BDL	BDL	BDL	0.0107
Rio Mesquites-outlet	BDL	BDL	BDL	0.0058	0.0111	BDL	BDL	BDL	BDL	BDL	0.0110
Poza de Tonta	BDL	BDL	BDL	0.0054	0.0147	BDL	BDL	BDL	BDL	BDL	0.0104
Puente Chiquito Spring	BDL	BDL	BDL	0.0063	0.0065	BDL	BDL	BDL	BDL	BDL	0.0123
Rio Mesquites-outlet	BDL	BDL	BDL	0.0058	0.0111	BDL	BDL	BDL	BDL	BDL	0.0110
Los Corales	BDL	BDL	BDL	0.0058	0.0132	BDL	BDL	BDL	BDL	BDL	0.0104
Rio Mesquites- Escobedo	BDL	BDL	BDL	0.0057	0.0126	BDL	BDL	BDL	BDL	BDL	0.0105
Charcos Prietos	BDL	BDL	BDL	0.0065	0.0094	BDL	BDL	BDL	BDL	BDL	0.0079
Las Playitas	BDL	BDL	BDL	0.0112	BDL	BDL	BDL	BDL	BDL	BDL	0.0128
Poza Escobedo	BDL	BDL	BDL	0.0045	0.0184	BDL	BDL	BDL	0.0001	0.0001	0.0102
Puente Colorada	BDL	BDL	BDL	0.0055	0.0132	BDL	BDL	BDL	BDL	BDL	0.0097
Poza Juan Santos- April	0.000	0.000	0.000	0.005	0.018	0.000	N/R	0.000	0.000	0.000	0.010
Las Salinas- April	0.011	0.012	0.018	0.062	0.014	0.007	N/R	0.007	0.004	0.003	0.033

Table 5: Becerra- Garabatal- Rio Mesquites System Chemistry (Continued).

TIO CANDIDO- HUNDIDOS SYSTEM (concentrations in ppm)

ID	Site	Temp- C	pH	Cond (uS)	CBE%	Na	Si	Mg	K	Ca	Sr
SBE-9	Tio Candido	32.00	7.16	2540	1.10	137.043	7.666	102.404	8.250	320.608	11.791
SBE-10	Poza Escobedo	34.70	7.12	2646	4.50	143.759	8.0641	115.424	9.396	393.018	12.923
SBE-34-8	Los Hundidos	22.50	7.69	13570	18.60	541.172	26.469	339.579	24.007	935.433	26.858
SBE-33-7	La Maroma	23.00	7.30	13820	13.60	543.039	28.429	349.104	25.149	885.284	25.175
SBE-6-MD	Los Gatos	25.50	7.77	5605	-2.50	480.635	23.647	302.647	25.316	551.460	15.798
SBE-7	Tortuguera- Los Gatos	29.20	7.92	5742	-5.20	423.116	21.796	289.150	24.908	577.799	15.066

Site	F	Cl	Br	NO3 - N	SO4	Alk (HCO3)	Li	B	Al	V	Cr
Tio Candido	2.511	95.91	0.496	1.223	1168	186.66	0.0754	0.2435	BDL	0.0049	BDL
Poza Escobedo	2.713	102.4	0.514	1.373	1278	197.40	0.082	0.2499	BDL	0.0044	BDL
Los Hundidos	5.255	249.6	1.2	0.203	2598	424.3160	0.267	0.6555	BDL	0.0083	0.0007
La Maroma	4.045	332.5	1.546	0.118	2830	363.5600	0.266	0.6355	BDL	0.0074	0.0010
Los Gatos	5.497	338.2	1.533	0.036	3163	161.53	0.252	0.5696	BDL	BDL	BDL
Tortuguera- Los Gatos	5.617	346.5	1.532	0.027	3247	153.96	0.258	0.6457	BDL	BDL	BDL

Site	Mn	Fe	Co	Ni	Cu	Zn	As	Se	Rb	Mo
Tio Candido	BDL	0.0040	0.0036	BDL	BDL	0.0126	0.0099	BDL	0.0108	0.0524
Poza Escobedo	BDL	0.0033	0.0040	BDL	BDL	0.0097	0.0116	0.0063	0.0131	0.0581
Los Hundidos	0.0077	0.0503	0.0189	BDL	0.0270	0.0749	0.0198	0.0192	0.0444	0.0918
La Maroma	0.0053	0.0106	0.0172	BDL	0.0310	0.0702	0.0220	BDL	0.0455	0.1046
Los Gatos	BDL	0.0172	BDL	BDL	BDL	BDL	BDL	BDL	0.0356	0.0695
Tortuguera- Los Gatos	BDL	BDL	BDL	BDL	BDL	BDL	0.0147	BDL	0.0348	0.0700

Site	Cd	Sn	Sb	Cs	Ba	La	Pb	Bi	Th	U
Tio Candido	BDL	BDL	BDL	0.0040	0.0166	BDL	0.0011	.0001	BDL	0.0091
Poza Escobedo	BDL	BDL	BDL	0.0045	0.0184	BDL	BDL	.0001	0.0001	0.0102
Los Hundidos	0.0015	0.0024	0.0019	0.0129	0.0159	0.0013	0.0015	0.0003	0.0003	0.0167
La Maroma	0.0016	0.0020	0.0021	0.0122	0.0136	0.0013	0.0013	0.0003	0.0003	0.0164
Los Gatos	BDL	BDL	BDL	0.0090	BDL	BDL	BDL	BDL	BDL	0.0082
Tortuguera- Los Gatos	BDL	BDL	BDL	0.0091	BDL	BDL	BDL	BDL	BDL	0.0090

SBE-34-8 and SBE-33-7 were collected in April, 2004

Table 6: Tio Candido- Hundidos System Chemistry.

ANTEOJO SYSTEM (concentrations in ppm)											
ID	**Site**	**Temp- C**	**pH**	**Cond (uS)**	**CBE%**	**Na**	**Si**	**Mg**	**K**	**Ca**	**Sr**
SBE-21	Canal Angostura	27.00	8.14	1698	2.50	32.221	7.468	72.788	3.107	302.313	6.474
SBE-22	Poza de Sandra	24.80	7.21	1670	2.60	38.476	9.836	81.925	2.864	224.094	4.641
SBE-23	Poza Anteojo	27.60	7.21	1786	4.00	31.458	7.330	71.194	3.208	320.832	6.401
Site	**F**	**Cl**	**Br**	**NO3 – N**	**SO4**	**Alk (HCO3)**	**Li**	**B**	**Al**	**V**	**Cr**
Canal Angostura	1.455	22.07	0.147	0.224	911.1	118.10	0.0245	0.0941	BDL	0.0016	BDL
Poza de Sandra	0.627	83.97	0.566	3.827	558.2	290.12	0.0208	0.1178	BDL	0.0035	0.0031
Poza Anteojo	1.501	21.23	0.156	0.593	863.6	183.49	0.0249	0.0994	0.0164	0.0013	BDL
Site	**Mn**	**Fe**	**Co**	**Ni**	**Cu**	**Zn**	**As**	**Se**	**Rb**	**Mo**	**Ag**
Canal Angostura	BDL	0.0039	0.0032	BDL	BDL	0.0225	BDL	BDL	0.0019	0.0057	BDL
Poza de Sandra	0.0038	0.3774	0.0028	0.0057	0.0032	1.0209	0.0008	0.0042	0.0012	0.0077	BDL
Poza Anteojo	BDL	0.0386	0.0031	BDL	BDL	0.0471	BDL	BDL	0.0017	0.0060	BDL
Site	**Cd**	**Sn**	**Sb**	**Cs**	**Ba**	**La**	**Hg**	**Pb**	**Bi**	**Th**	**U**
Canal Angostura	BDL	BDL	BDL	0.0002	0.0054	BDL	BDL	BDL	0.0001	BDL	0.0024
Poza de Sandra	0.0002	BDL	BDL	.0001	0.0187	BDL	BDL	0.0002	0.00002	0.00003	0.0040
Poza Anteojo	BDL	BDL	BDL	0.0001	0.0175	BDL	BDL	0.0015	0.0001	BDL	0.0023

Table 7: Anteojo System Chemistry.

SANTA TECLA SYSTEM (concentrations in ppm)											
ID	Site	Temp –C	pH	Cond (uS)	CBE%	Na	Si	Mg	K	Ca	Sr
SBE-8-Reprep	Poza Antiguos Mineros	31.60	7.57	1390	4.10	57.06	5.70	51.483	3.900	179.500	4.520
Site	F	Cl	Br	NO3 – N	SO4	Alk (HCO3)	Li	B	Al	V	Cr
Poza Antiguos Mineros	0.951	45.63	0.219	0.992	527.4	141.76	0.0364	0.1218	0.0353	0.0030	BDL
Site	Mn	Fe	Co	Ni	Cu	Zn	As	Se	Rb	Mo	Ag
Poza Antiguos Mineros	0.0080	0.0184	0.0018	BDL	BDL	0.0178	BDL	BDL	0.0041	0.0112	BDL
Site	Cd	Sn	Sb	Cs	Ba	La	Hg	Pb	Bi	Th	U
Poza Antiguos Mineros	BDL	BDL	BDL	0.0009	0.0431	BDL	BDL	BDL	BDL	BDL	0.0032

Table 8: Santa Tecla System Chemistry.

magnitude of concentration for a water sample.

Due to the magnitude of error, the samples with large charge balance errors were re-analyzed for anion concentrations in August, 2005 (Appendix B). A white mineral had precipitated in the bottles for samples SBE-30, SBE-33, and SBE-34. Dr. Rick Knurr, Senior Scientist at the University of Minnesota, indicated that the charge balances may be off due to the high sulfur concentrations. The chloride concentrations reproduced well, but sulfur did not. The precipitate in the anion sample bottles may have caused error in the analysis. Samples SBE-3, SBE-27, and SBE-28 reproduced well. Dilution errors in June may be at fault in these analyses. Correcting the sulfate concentrations in the samples would most likely accommodate charge balance inconsistencies. This was not carried out due to time constraints, but provides a reliable explanation for the large errors.

In concentrated hard waters, as found in Cuatro Cienegas, Minckley et. al. (1968) found that perfect charge balances were rarely encountered. This is likely due to the amount of dilution required to analyze the samples. The June 2004 sample for Laguna Grande, the terminal lake for the Churince system, had a charge balance of -17.9 percent. However, the analysis for Laguna Grande in January 2005 had a charge balance of -2.5 percent and was utilized in place of the sample collected in June. Los Gatos- Tortuguera, and Las Salinas had charge balances of -5.2 percent and -5.6 percent. These are two of the most concentrated lakes in the basin. The most highly evaporated lakes had a higher conductivity and were diluted much more than the samples close to the sources. Since these samples were very close to the cut-off for acceptable balance (5 percent) and were terminal lake samples, they were not discarded (Freeze, et. al., 1979).

The rainwater samples downloaded from the NADP site had a large amount of charge balance error. This is most likely due to the absence of HCO_3^- analysis. The error in most samples ranged from 7 percent to 25 percent. Only one sample was deemed useful from the downloaded data. The rainwater from 2003 had a charge balance error of 1.1 percent. It was an ammonium, calcium- sulfate, nitrate type water, with a pH of 5.19.

Nearly all of the samples in the Cuatro Cienegas basin are Ca-SO_4 facies waters (Figure 12). The Las Salinas and Laguna Grande samples, the two most concentrated lakes, are the only exceptions. Las Salinas is a Mg-Na-SO_4 water, and Laguna Grande is a mixed cation-sulfate water.

CROSS PLOTS

All cross plots were graphed in units of mmol/L on a log-log scale. The purple line on the Na^+ vs. Cl^- plot is the 1:1 evaporation line (Figure 13). Most of the Cuatro Cienegas waters plot slightly above the line. The rainwater samples plotted lie directly on the 1:1 line, and the Cuatro Cienegas waters are proportionately more concentrated than the rain water. The 0.86 line represents the seawater signature. The Mg^{2+} vs. Cl^- plot is similar to the previous plot with a general trend of 1:1, but the samples show slightly more scatter (Figure 14). The Cl^- vs. Br^- plot has a linear trend of y= x + 2.85 (Figure 15). The mass ratio between the two is slightly less than 288 (the seawater signature) for the source springs, but approaches 288 in the terminal lakes.

Though the line for the SO_4^{2-} vs. Cl^- plot does not bisect the origin, the samples lie on the 1:1 line at a y intercept of 6.0 mmol/L (Figure 16). The gypsum SI

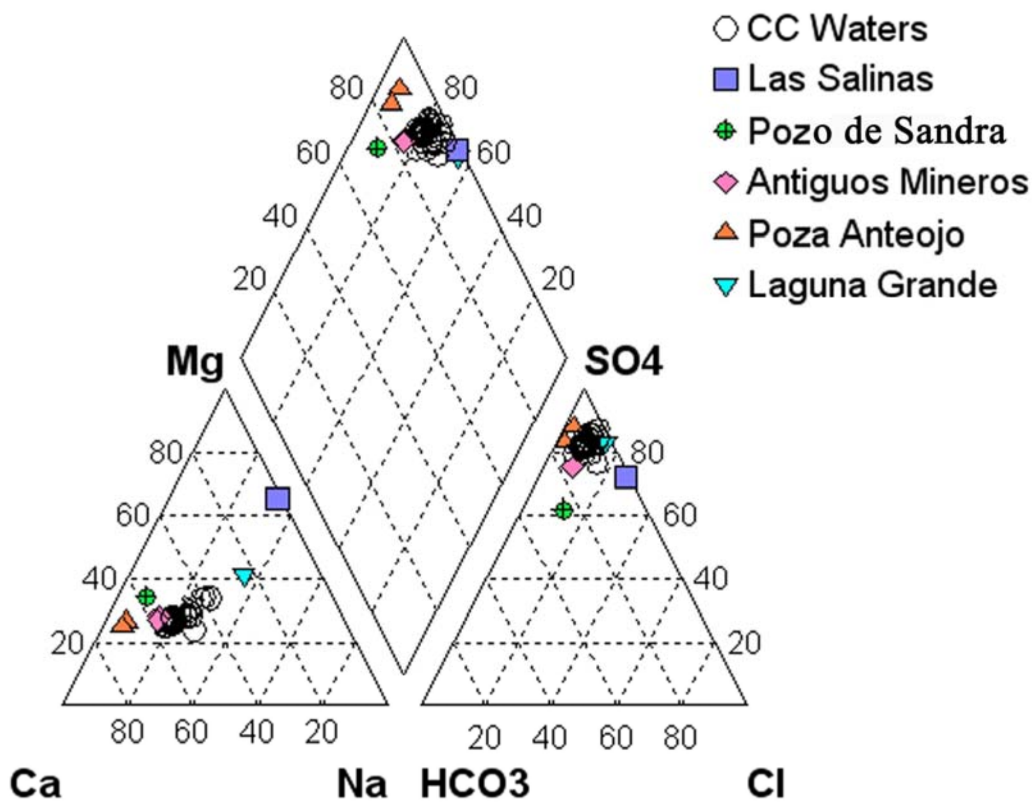

Figure 12: Piper plot of the Cuatro Cienegas waters. Most of the sites were calcium-sulfate type waters. Only the outliers on the plot have been identified.

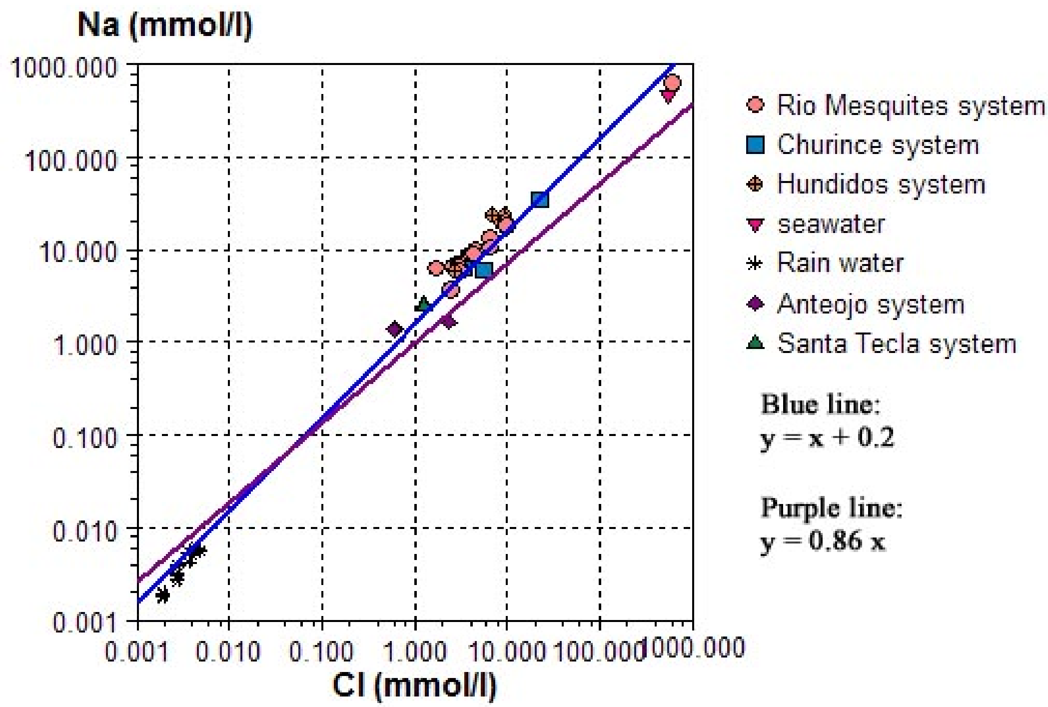

Figure 13: Na-Cl cross plot. The Purple line represents the seawater signature. The blue line represents the 1:1 evaporation line.

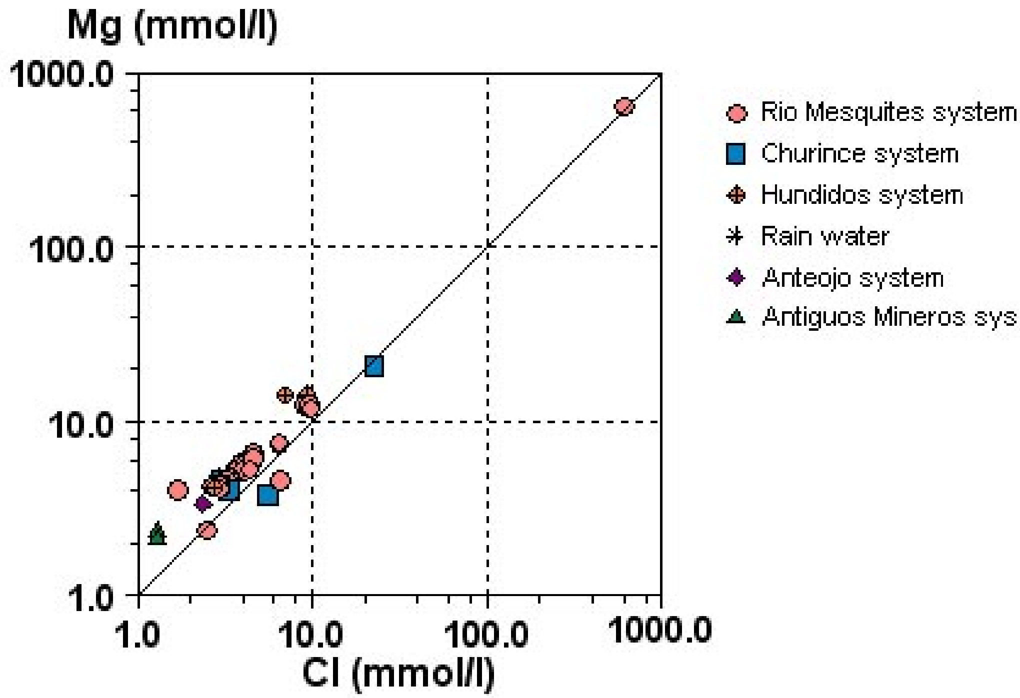

Figure 14: Mg-Cl cross plot. The black line represents the 1:1 evaporation line.

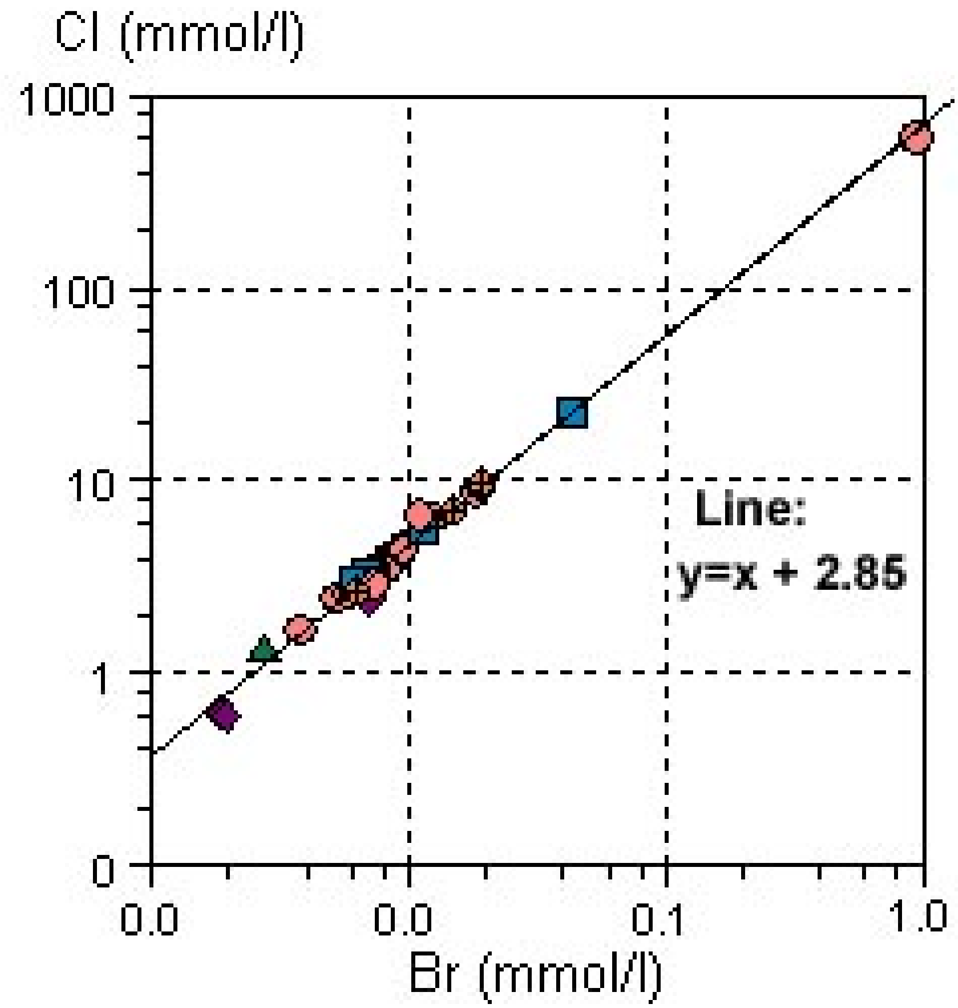

FIGURE 15: CL- VS. BR- CROSS-PLOT. The black line represents the 1:1 evaporation line.

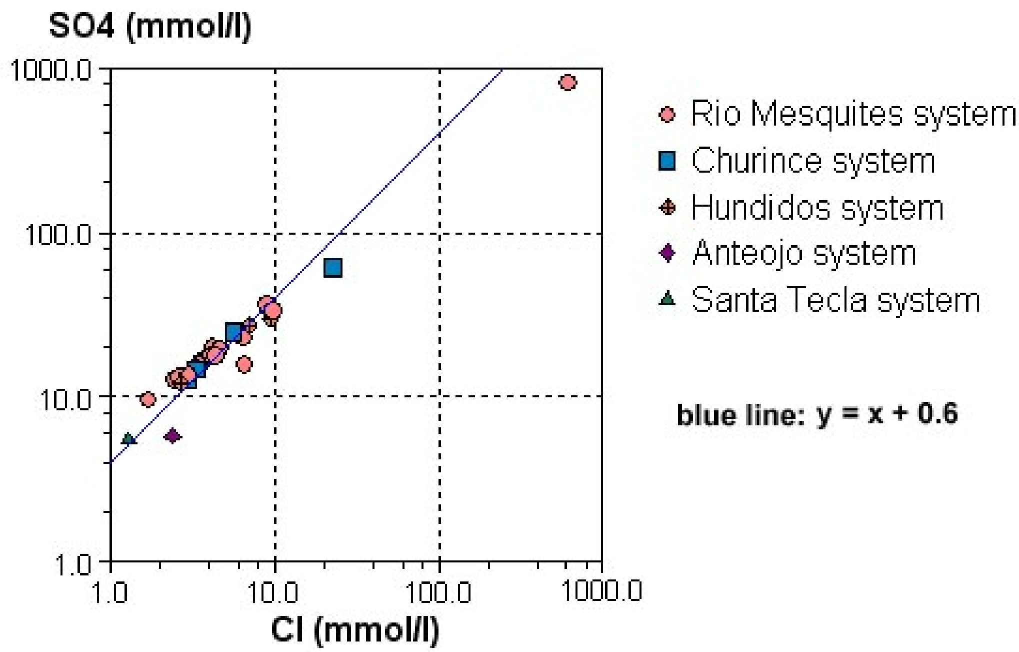

Figure 16: SO_4-Cl cross-plot. The blue 1:1 line represents the evaporation signature.

vs SO_4^{2-} plot is shown in Figure 17. The SI is the Saturation Index for gypsum in the water samples. An SI of zero indicates that the sample is at equilibrium with respect to that mineral. Anything below zero is undersaturated with respect to gypsum, and an SI above zero is supersaturated with respect to gypsum. Samples that were supersaturated with respect to gypsum include Laguna Grande (Churince system), Las Salinas, Playitas, and Los Gatos (Rio Mesquites system). These samples are all located at or near the terminal lakes of the flow system.

The Ca^{2+} vs. Mg^{2+} plot has a 1:2 trend-line. Ca^{2+} concentrations are almost twice the Mg^{2+} concentration (Figure 18). Exceptions occur in the samples with higher specific conductance. The sizes of the points in the figure are proportional to the chloride value of the sample. The $Ca^{2+} + Mg^{2+}$ vs. HCO_3^- plot has sample points proportional to the chloride concentration (Figure 19). Its trend-line on the plot is 1:2. The plots for calcite SI vs. Cl^- and dolomite SI vs. Cl^- show that the SI increases as the Cl^- concentrations increase (Figures 20 and 21).

GIS ANALYSIS

Using the Interpolate to Raster tool in Spatial Analyst, a rasters were created to demonstrate spatial patterns for conductivity within the basin. Las Salinas and the Cave samples did not have conductivity measurements associated with them. Las Salinas was estimated to be 11 mS and the Cave, 1.7 mS. These numbers were chosen based on the total dissolved solids in the sample. The Cuatro Cienegas roads served as barrier polylines for the raster, which was set with a 50 meter grid size. The inverse distance weighted (IDW), spline, and kriging methods were all used in order

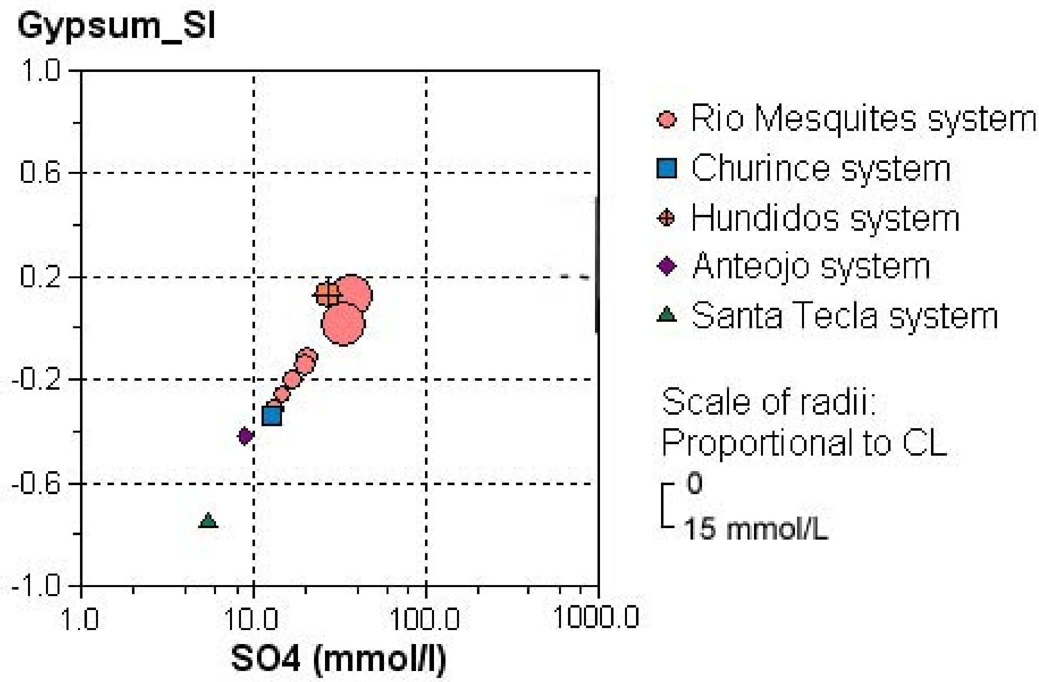

Figure 17: Gypsum SI- SO_4 cross plot. The size of the symbol for each site is proportional to its chloride concentration. An SI of more than 0 is supersaturated with respect to gypsum.

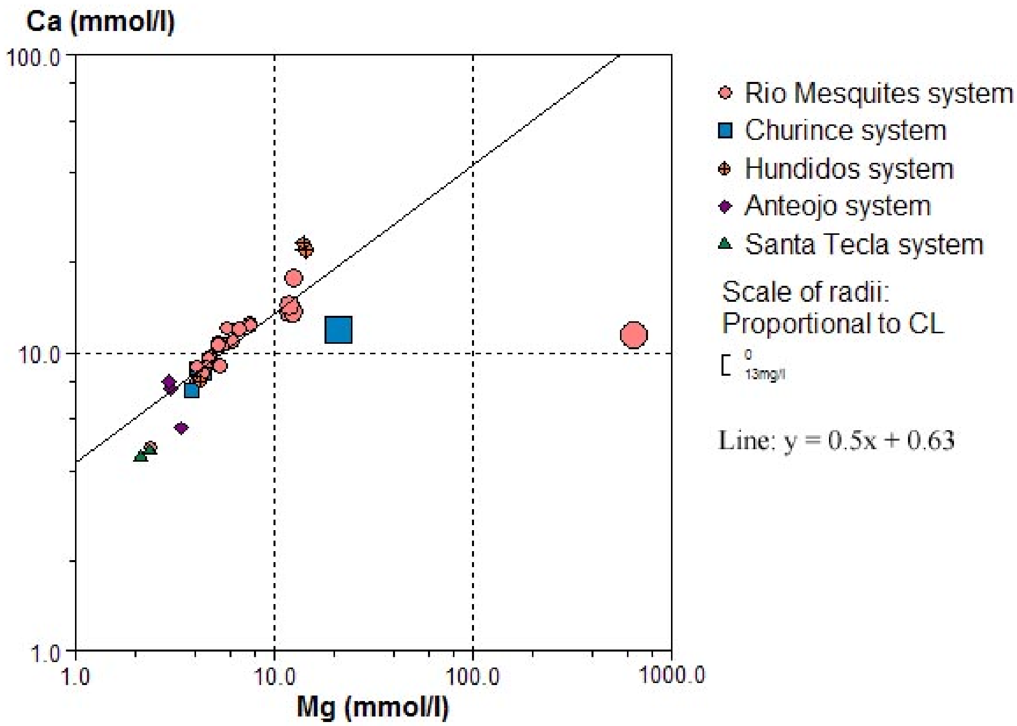

Figure 18: Ca^{2+} vs. Mg^{2+} cross plot. The trend-line is y = 0.5x + 0.63. Symbol size is proportional to the Cl- concentration.

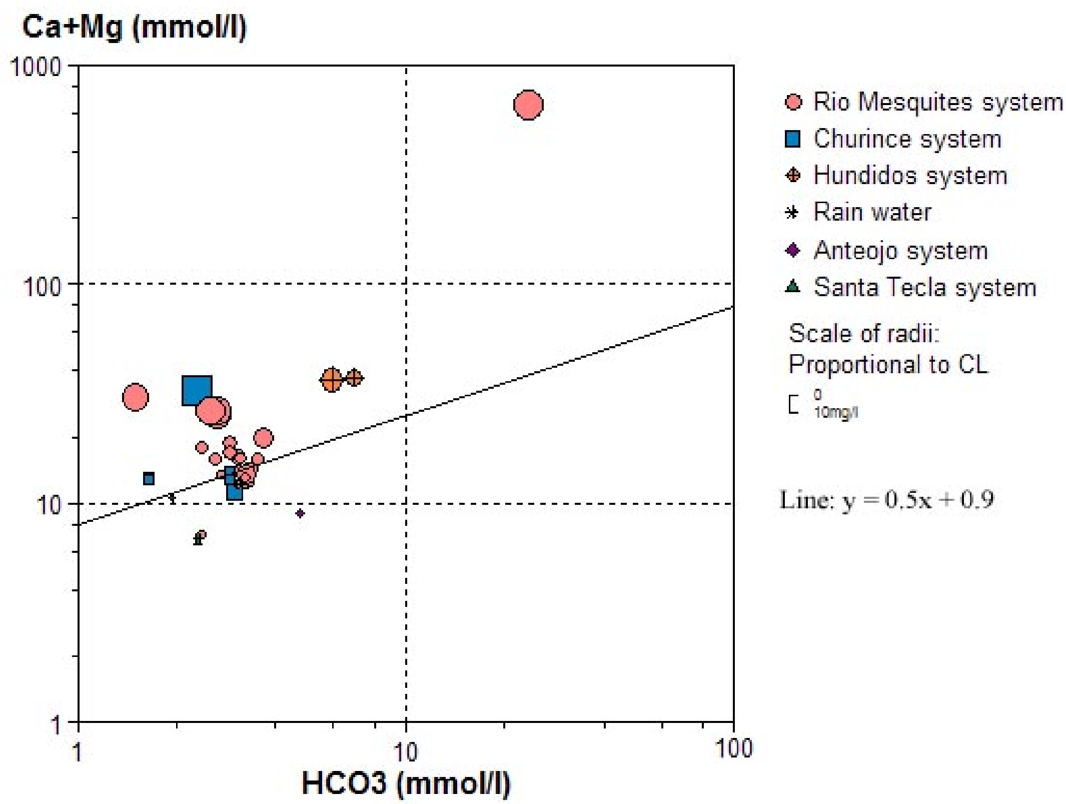

Figure 19: $Ca^{2+} + Mg^{2+}$ vs. HCO_3^- cross- plot. The trend-line is y = 0.5x + 0.9. Symbol size is proportional to the Cl- concentration.

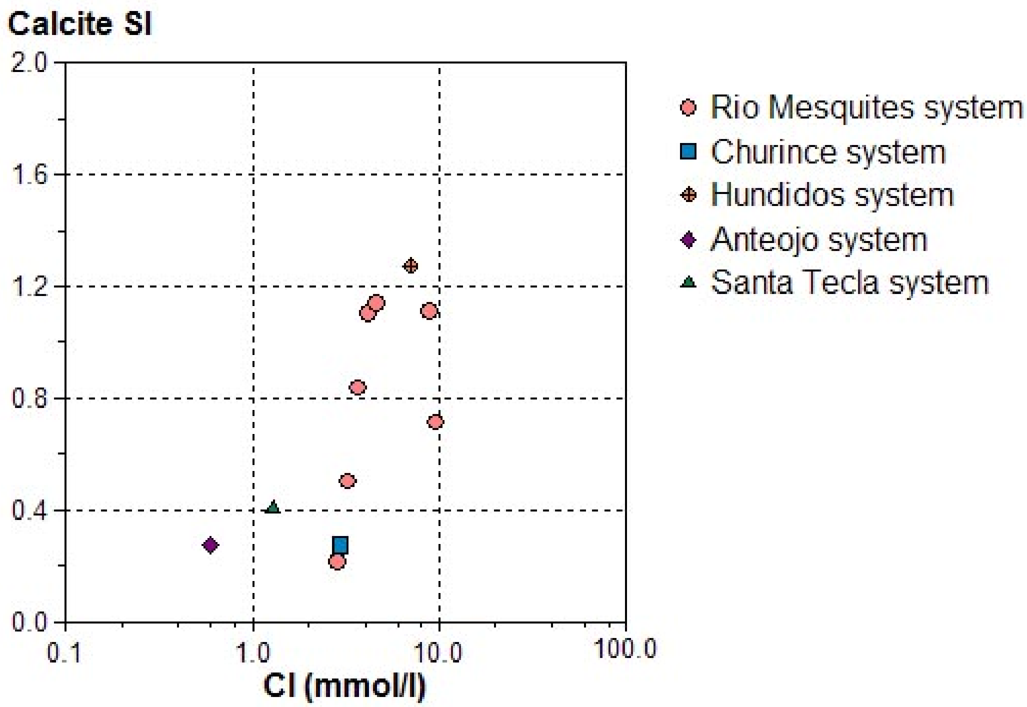

Figure 20: Calcite SI vs. Cl$^-$ cross-plot.

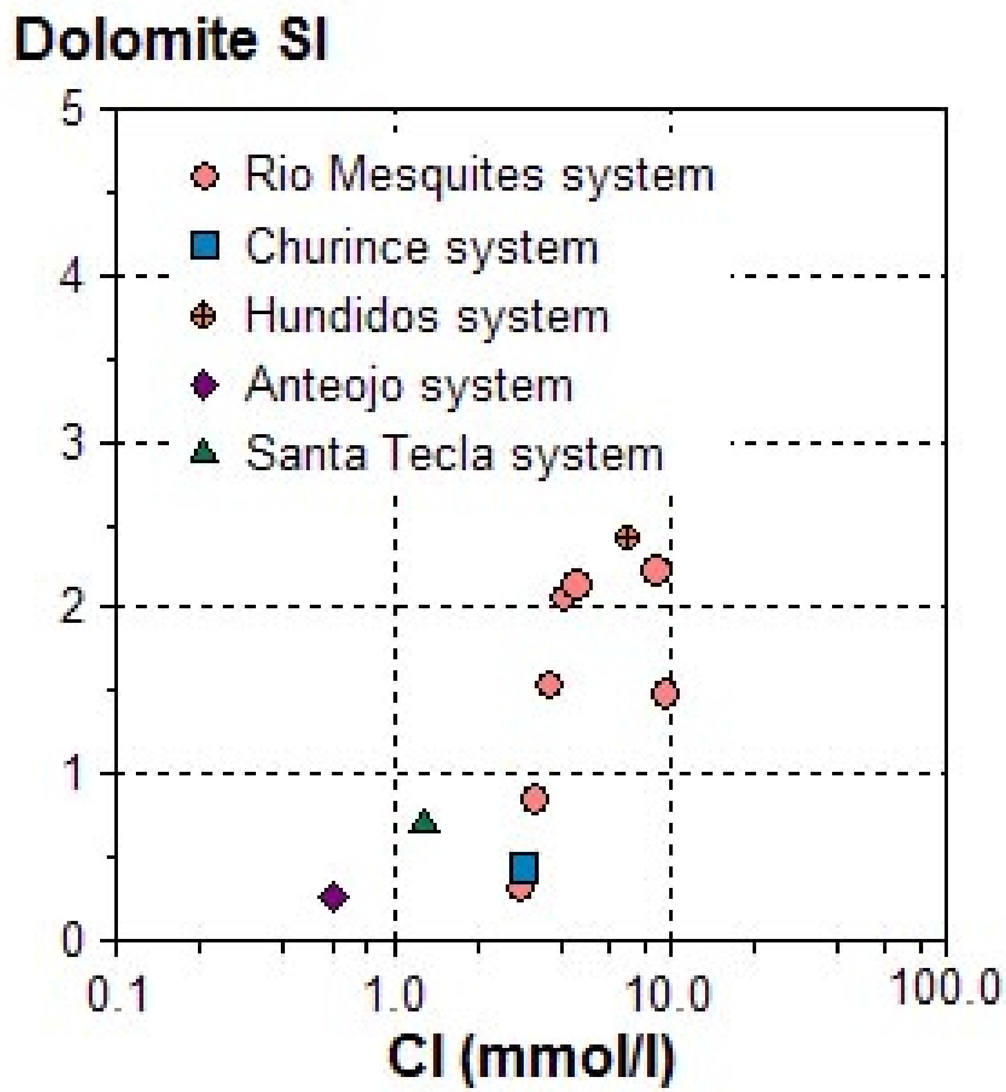

Figure 21: Dolomite SI vs. Cl^- cross-plot.

to determine which method best fit the field results. The kriging and spline methods produced unrealistic results, while IDW best represented conductivity patterns in the basin. The IDW conductivity map is shown in Figure 22.

A raster was also created to demonstrate spatial patterns for temperature within the basin. Canal Angostura and the Cave were input as 27 degrees, which was an average temperature, because they had no temperature data associated with them. This was necessary so that the sample would not have to be deleted from the other analyses of the sample site. The Cuatro Cienegas roads served as barrier polylines for the raster, which was set with a 50 meter grid size. The inverse distance weighted (IDW), spline, and kriging methods were all used. The IDW method was the most accurate, according to the field data, and a map is shown in Figure 8.

Flow System Chemistry

Schoeller plots are useful in visualizing water chemistry trends for related waters within each system. Each water system has a unique chemical signature, shown by the Schoeller plots. Most of the systems in the basin are similar in chemical composition to the Rio Mesquites system, which is the most diverse in terms of number and type of spring issuing from the system (Figures 23 and 24). Of the five systems, the Santa Tecla and Anteojo systems have the lowest TDS. This is demonstrated by comparing the source springs for the systems (Figure 25). The Anteojo system can be distinguished from the Santa Tecla system because the Anteojo system has lower chloride concentrations than the Santa Tecla system.

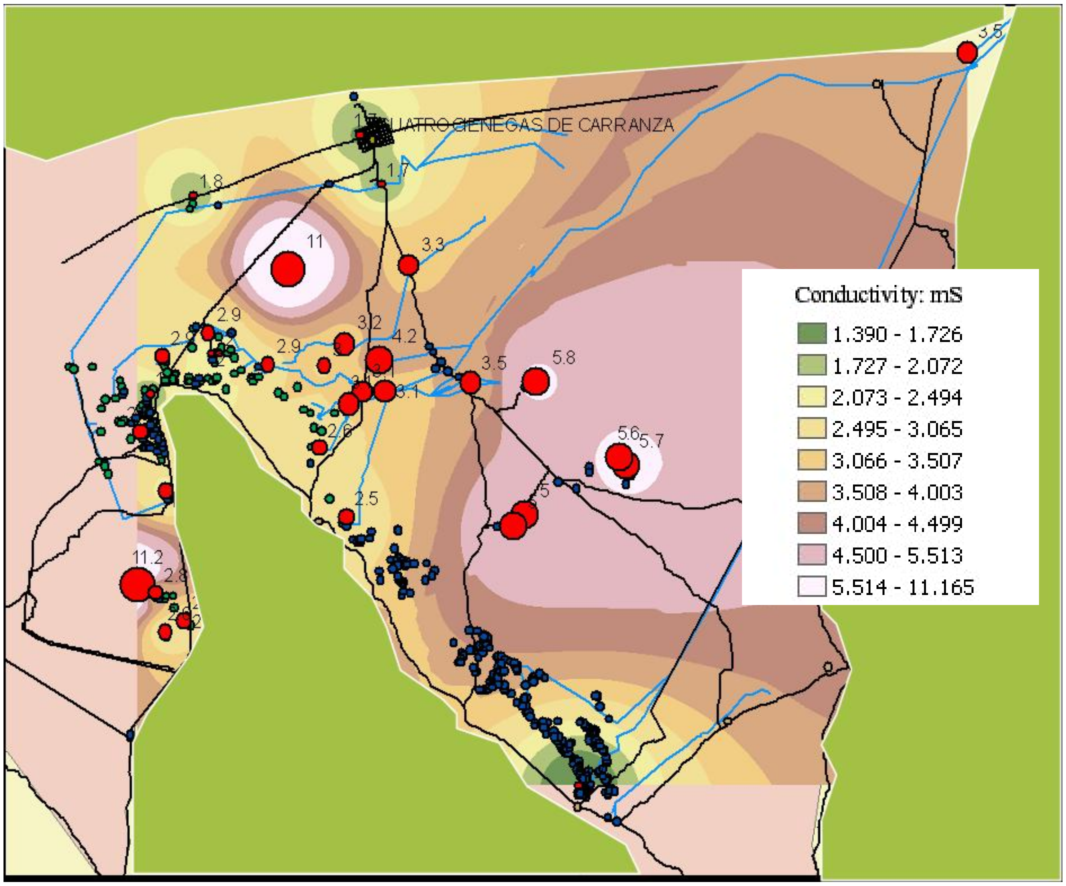

Figure 22: GIS raster from spatial analyst: Conductivity map. The size of the red points is proportional to the conductivity. The blue and green points on the map are springs in the basin where no conductivity data was collected.

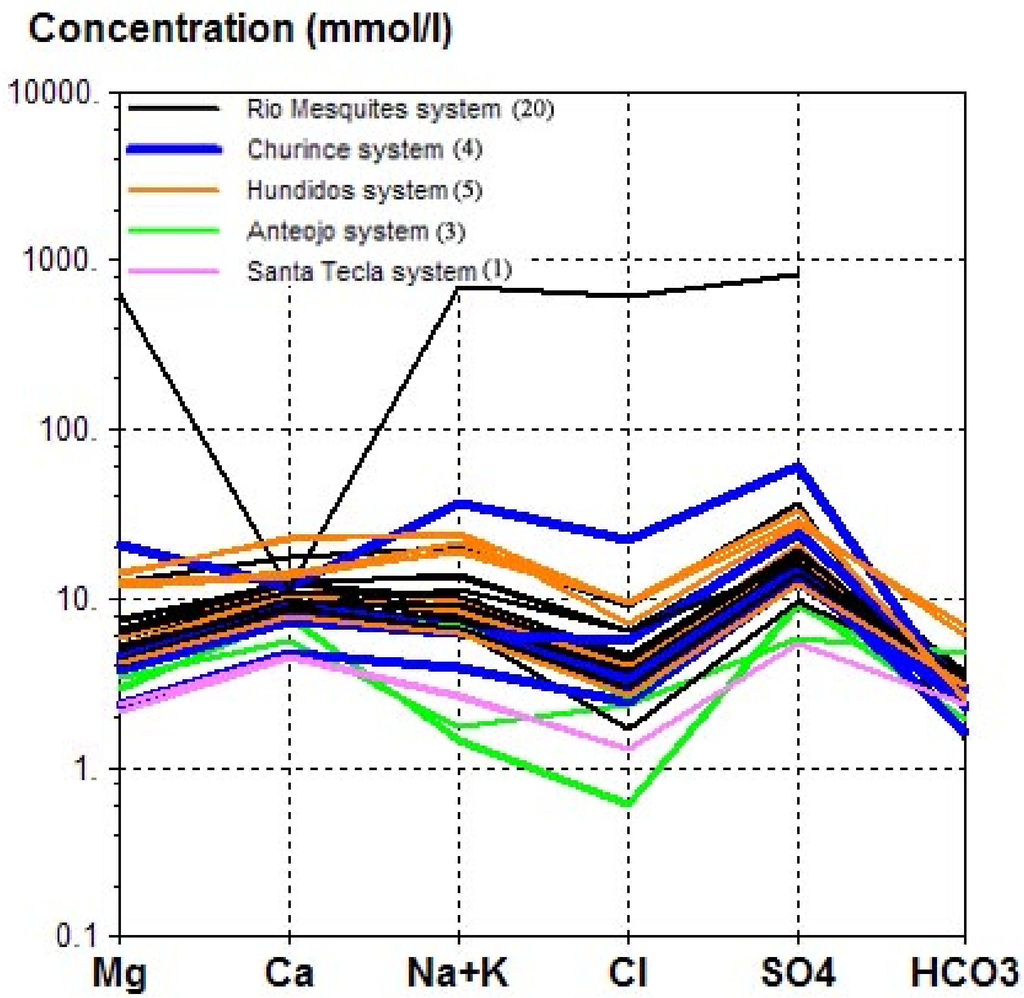

Figure 23: Scholler plot of all systems in the Cuatro Cienegas basin.

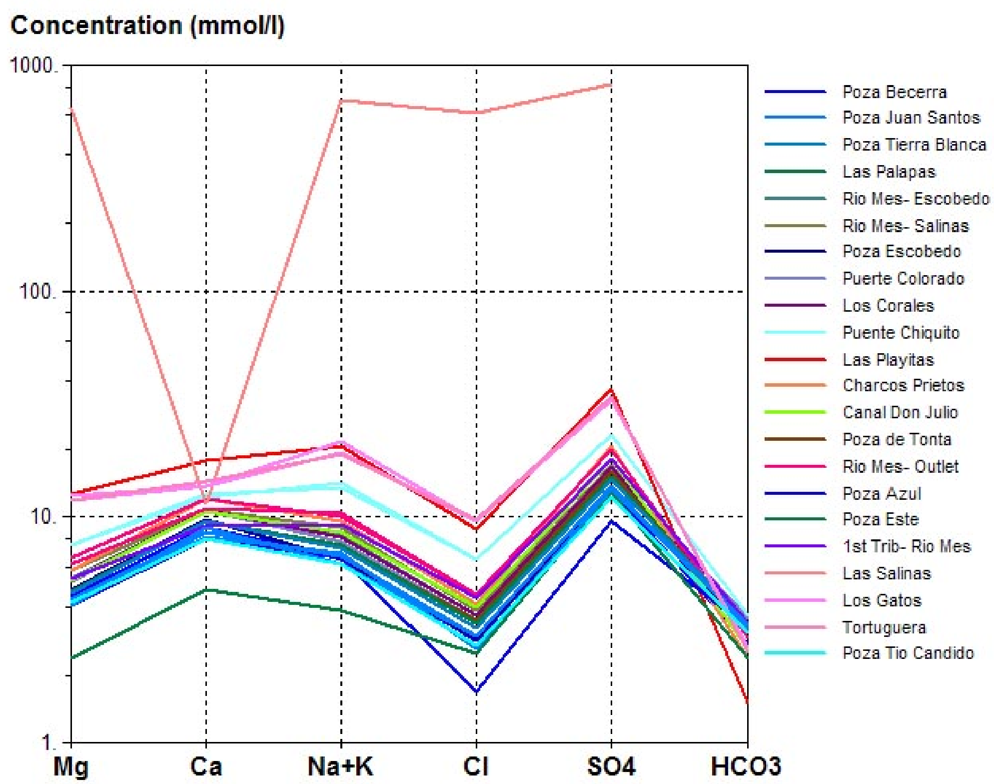

Figure 24: Scholler plot of the Becerra-Garabatal-Rio Mesquites system.

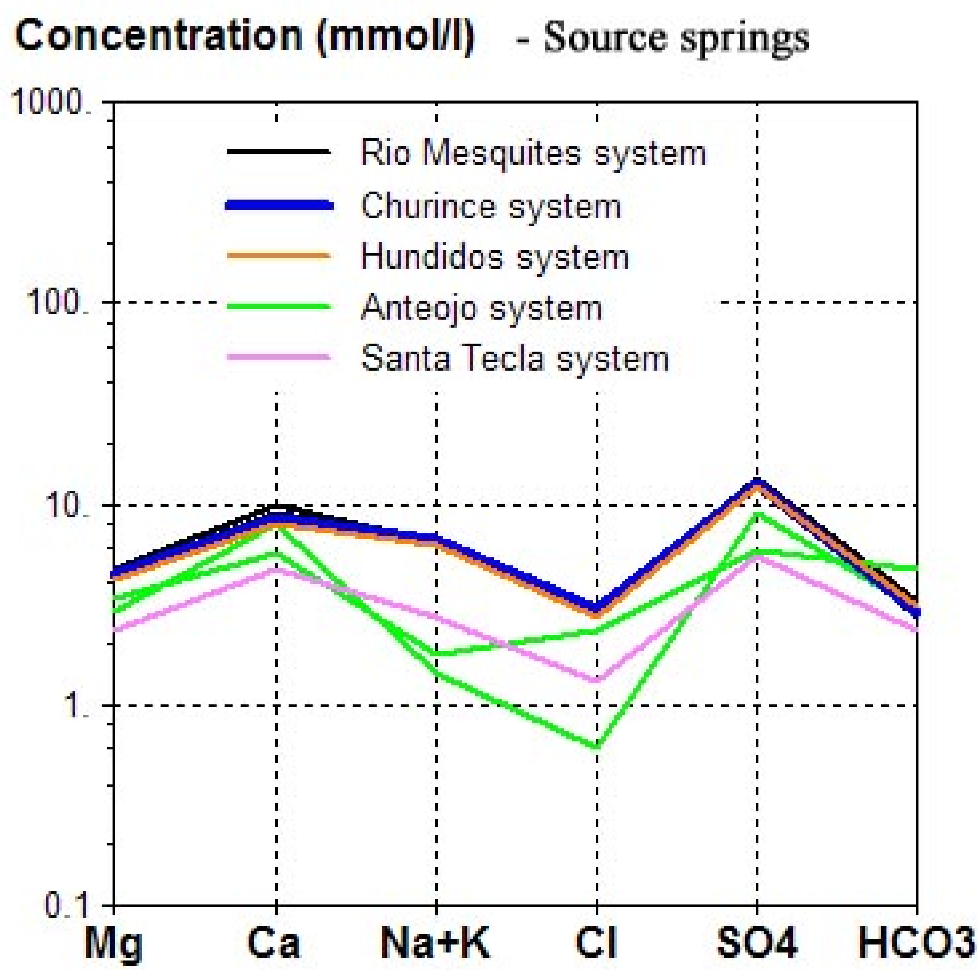

Figure 25: Schoeller plot of the source springs for each system.

The Churince system has slightly lower TDS than the average Rio Mesquites system, but is more highly concentrated than the Santa Tecla or Anteojo systems. In this system, Laguna Intermediate is very similar in chemistry to Poza Churince and Poza Bonita, but has higher chloride and lower bicarbonate concentrations (Figure 26). Laguna Grande stands out from the other pozas in the system, mainly due to the high rate of evaporation and distance from the source water.

The Tio Candido/Hudidos system and the Rio Mesquites systems are very similar in their water chemistry (Figure 23). All samples taken in the Tio Candido/Hundidos system are in the same range as the Rio Mesquites system and increase in TDS as the distance from the mountains increases from Poza Tio Candido to Poza Escobedo, Rio Mesquites, Poza Los Hundidos, and Poza La Maroma.

The Rio Mesquites system is the most complex of the systems. TDS increases downstream, as distance from the source increases (Figure 24). Poza Mojarral Oeste (Poza Azul) and Poza Mojarral Este have the lowest concentrations of the Rio Mesquites system. Las Salinas is by far the most concentrated pool. Las Playitas had the second highest TDS, followed by Poza Tortuguera and Los Gatos, then Puente Chiquito.

CHURINCE SYSTEM

The Churince system is composed of four pozas/lakes (Figure 27). They include Poza Churince and Poza Bonita as the source springs, Laguna Intermediate as the middle lake, and Laguna Grande as the terminal lake. This system is similar to the Rio Mesquites system because its source springs originate very close to and on the western edge of the Sierra San Marcos. However, it is an isolated system. There is a

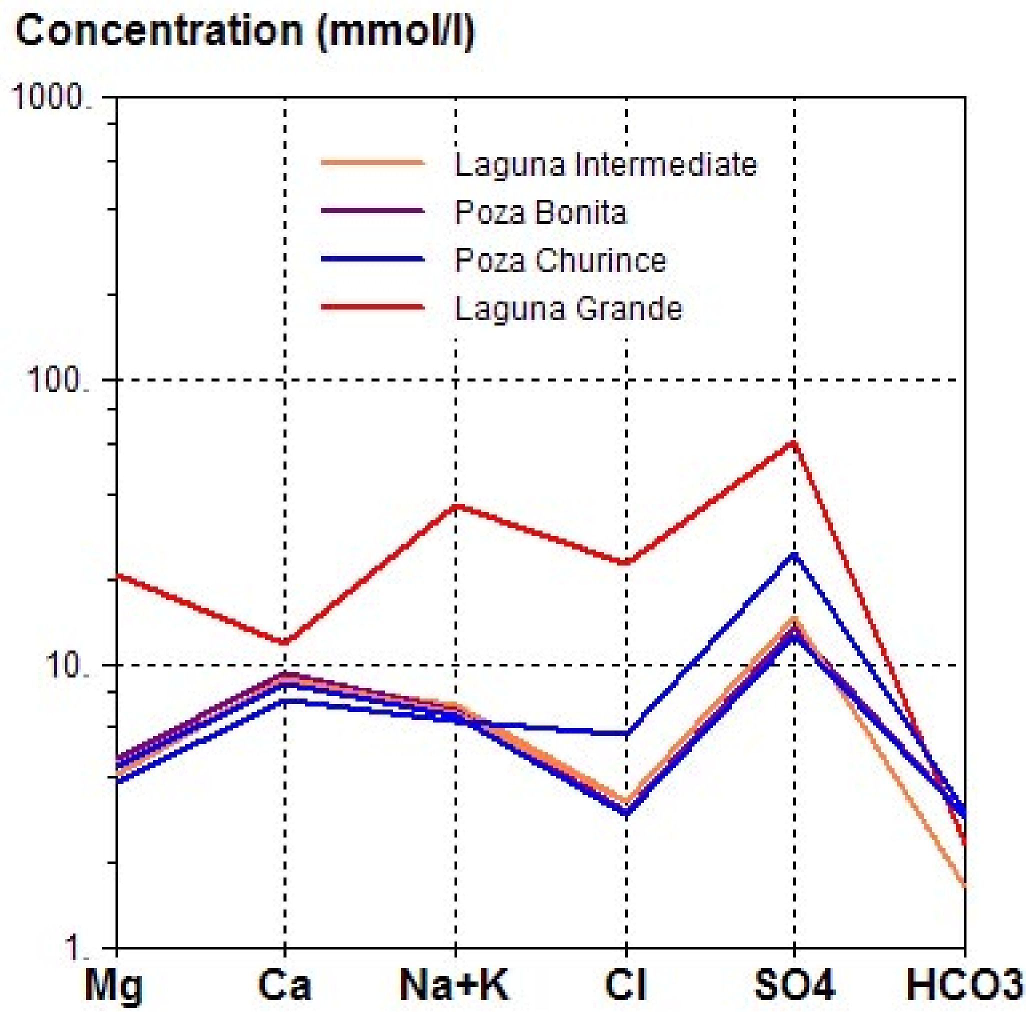

Figure 26: Scholler plot of the Churince system.

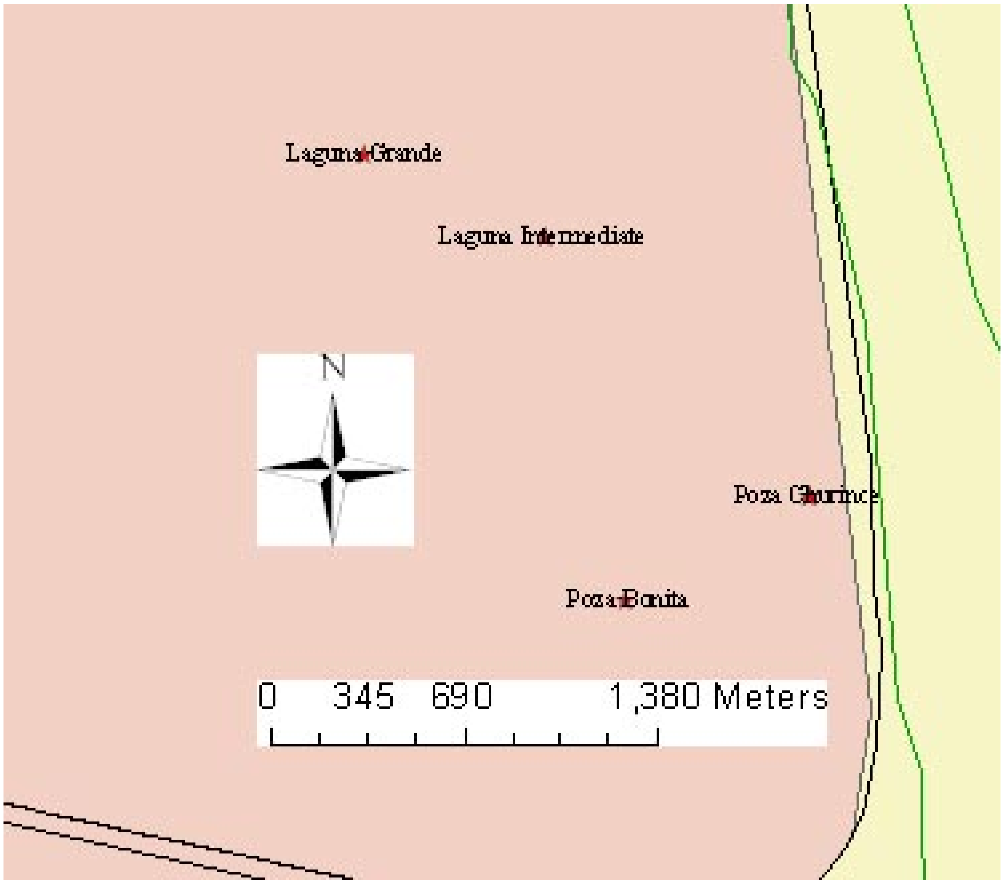

Figure 27: Map of the Churince System.

possibility that through underground conduits, the source springs may be connected to the Rio Mesquites system, but no data exist to test the possibility.

Starting at the source spring, Poza Churince, and comparing to Laguna Intermediate, only slight changes in the chemistry were observed (Tables 2 and 9 and Figure 26). Much of the chemical composition of Poza Churince remained approximately the same or increased very slightly as the water traveled to Laguna Intermediate. The water flows as surface flow and groundwater flow from Churince to Intermediate. Only alkalinity, iron, nitrogen, and zinc decreased slightly along the path. The pH, ionic strength, boron, chloride, manganese, lithium, sodium and sulfur increased slightly.

No surface flows exist from Poza Bonita. However, it is nearly identical in chemical composition to Poza Churince, but with slightly higher concentrations of calcium, and sodium; and slightly lower concentrations of barium, iron, manganese, and zinc (Table 9). Poza Intermediate is very close in chemical composition to Poza Bonita as well. Laguna Intermediate has slightly higher bromine, choloride, boron, iron, alkalinity, sodium, and sulfate. It has lower concentrations of barium, nitrate, and zinc. The saturation indices for calcite, gypsum, and magnesium phases at Laguna Intermediate are higher than those at Poza Bonita.

The chemical pathway between Laguna Intermediate and Laguna Grande is more pronounced. The only chemical parameters that decrease along this path are barium, nitrogen, and zinc. Fluoride remains nearly the same, with a slight increase, while the other species increase noticeably. Boron, bromine, chloride, potassium, and magnesium increase by nearly an order of magnitude. Laguna Grande is the terminal lake in the flow system. The concentration vs. distance plot shows that the major

Units in Moles	Poza Churince	Poza Bonita	Laguna Intermediate	Percent error LagunaIntermediate/ Churince
Alk	2.90E-03	2.91E-03	4.64E-03	37.51
Ba	1.28E-07	8.38E-08	9.99E-08	-28.40
Br	6.16E-06	6.20E-06	6.84E-06	9.92
Ca	8.50E-02	9.27E-03	8.71E-03	-876.23
Cl	2.96E-03	3.01E-03	3.31E-03	10.46
F	1.40E-04	1.45E-04	1.52E-04	7.52
K	2.05E-04	2.32E-04	2.05E-04	0.00
Li	8.64E-05	9.12E-05	9.85E-05	12.33
Mg	4.40E-03	4.70E-03	4.46E-03	1.32
Na	6.36E-03	6.71E-03	6.90E-03	7.80
S	1.27E-02	1.33E-02	1.47E-02	13.51
Si	9.95E-05	1.12E-04	1.07E-04	7.32
Sr	1.73E-04	1.77E-04	1.79E-04	3.41

Units in Moles	Percent error Laguna Intermediate/ Bonita
Alk	37.34
Ba	16.16
Br	9.36
Ca	-6.40
Cl	9.07
F	4.35
K	-13.15
Li	7.45
Mg	-5.29
Na	2.75
S	9.50
Si	-4.10
Sr	0.78

Table 9: Percent differences between the springs in the Churince System.

cations and anions increased along the flow system, except nitrate and alkalinity (Figure 28).

GARABATAL- BECERRA- RIO MESQUITES SYSTEM

The Rio Mesquites system is far more complicated than any of the other systems in the basin. Its source springs most likely include Poza Becerra, Poza Juan Santos, Poza Tierra Blanca, and Poza Mojarral Oeste (Poza Azul) (Figure 29). Poza Escobeda and Poza Tio Candido also contribute water via routing from subsurface flows into the Rio Mesquites. However, Poza Tio Candido mainly contributes to the Hundidos system. All of the Rio Mesquites source springs originate along the Sierra San Marcos at the northwest and northeast flank, close to the mountain. Another source was collected from a cave at the northwest tip of the Sierra San Marcos, which is representative of the source water. The springs discharge enough water to create a surface stream (once called Rio Garabatal), disappears into subsurface flow, and most likely flows through conduits into the Rio Mesquites.

Due to the karst nature of this system, several other sources of groundwater must also contribute to the Rio Mesquites along its flow path (i.e., the cave at the tip of the Sierra San Marcos, unknown conduits beneath the basin floor, etc.). However, for the sake of simplicity, I concentrate on the samples collected in the field. Several samples were collected along the stream Rio Mesquites, including Rio Mesquites-Palapas, Rio Mesquites- Escobeda, Rio Mesquites- Las Salinas (not to be confused with Las Salinas the terminal lake), and the canal at the outlet of the basin to measure changes along its flow path. Pools in the Rio Mesquites system that were sampled include Poza Mojarral Este, Poza de Tonta, Puente Colorada, Los Corales, Canal Don

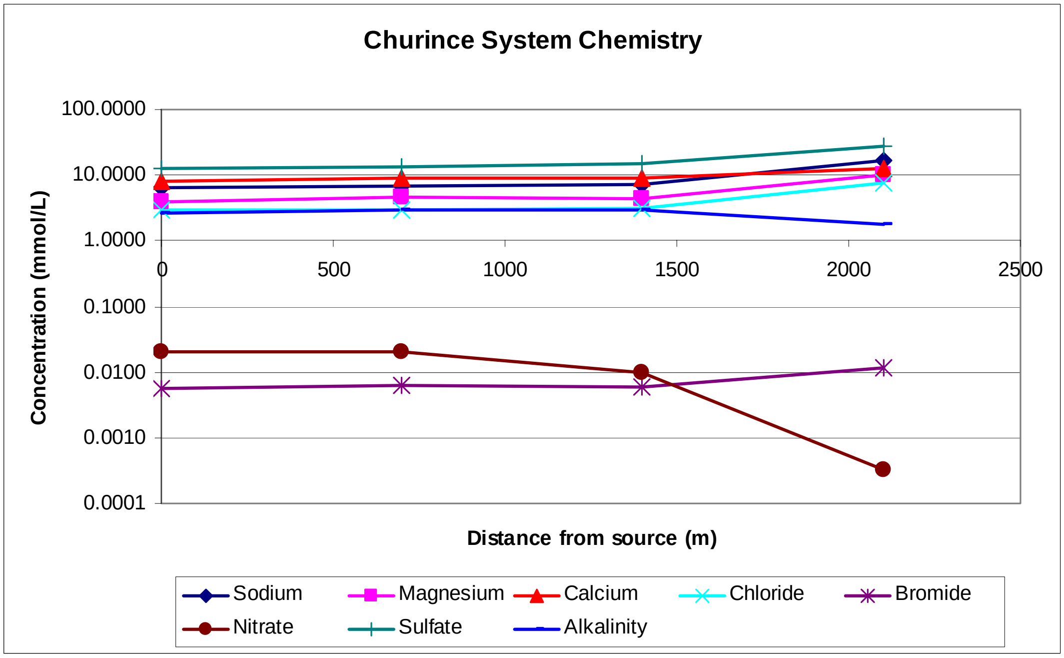

Figure 28: Concentration vs. distance plot for the Churince system.

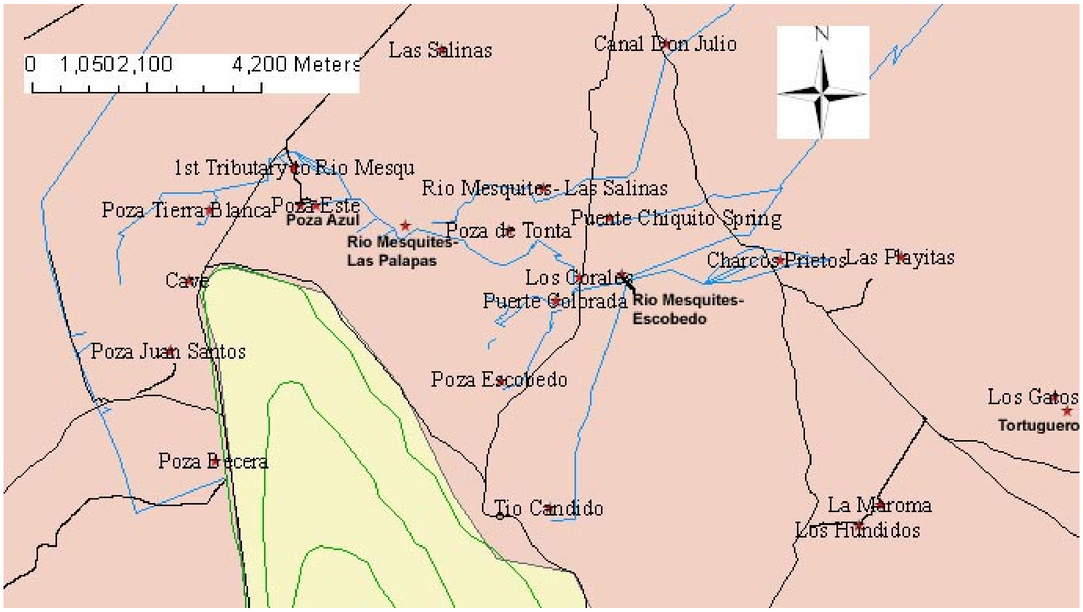

Figure 29: Map of the Rio Mesquites and Tio Candido/Hundidos systems.

Julio, Los Charcos Prietos, and Puente Chiquito. These pools are located along the length of the Rio Mesquites (Figure 29). The terminal lakes in this system include Las Salinas and Las Playitas.

Source waters for the Rio Mesquites system include Poza Becerra, Poza Juan Santos, the cave sample, Poza Tierra Blanca, and Poza Escobedo. These waters generally had the lowest concentrations of all the chemical species except nitrate and alkalinity (Table 4, 5, and Figure 24). The nitrate and alkalinity tended to decrease along the projected flow path. The first sample along the flow path downstream of the source springs is Rio Mesquites- Las Palapas. In relation to Poza Becerra and Poza Tierra Blanca, only nitrogen decreased from both sources. From Poza Becerra, the water at Las Palapas had a higher pH and higher concentrations in everything, except nitrate and barium. From Poza Tierra Blanca the pH, and bromine, sodium, and silica concentrations increased slightly, but there was relatively little change in chemistry from one site to the other. The saturation indices (SI) for calcite, aragonite, and dolomite increased from Poza Becerra to Palapas and from Poza Tierra Blanca to Palapas.

The river encounters a three-way fork downstream of Rio Mesquites- Las Palapas (Figure 29). The surface water forks north to Rio Mesquites- Las Salinas, or south to Los Corales. It may also travel directly east through conduits to Poza de Tonta. Poza de Tonta is a spring that was discovered in June 2004, during the collection of the samples. In this section of the river, the flowing Rio Mesquites disappears traveling downstream, and reappears at Poza de Tonta. The chemistry from Rio Mesquites- Las Palapas to Poza de Tonta had virtually no change from one to the other. Bromide increased slightly, along with chloride, while nitrate and alkalinity decreased slightly.

Starting at the north fork, the Rio Mesquites- Las Salinas site receives water from surface flows in the Rio Mesquites. Upstream of the site is the Rio Mesquites- Las Palapas. From Las Palapas, there is little change in the chemistry of the water. Most of the elements increase slightly. Compared to Poza de Tonta, the Rio Mesquites- Las Salinas was nearly identical as well. Most of the elements increased slightly, except nitrate.

Canal Don Julio lies downstream of the Rio Mesquites- Las Salinas sample on the north fork of the river. Canal Don Julio was slightly more concentrated and had a higher temperature than the Rio Mesquites- Las Salinas. However, alkalinity, magnesium, sodium, and nitrate decreased as the water flowed downstream. The SI's between the two sites were nearly the same.

Continuing on to the middle fork, starting with Poza de Tonta, the next site downstream was the Puente Chiquito Spring. The chemistry between the two sites is very similar. Most of the elements increased, but barium and nitrate decreased. The pH and temperature also decreased. The Rio Mesquites - Las Salinas water may contribute to this site via conduit flow as well. Concentrations from Rio Mesquites- Las Salinas to Puente Chiquito increased more dramatically than that from Poza de Tonta, though barium and nitrate also decreased.

From Las Palapas, forking to the south, the next downstream sample was Los Corales. The change in chemistry between the two samples was very slight. Only the elements nitrate, alkalinity, and lithium decreased in Los Corales. The pH also decreased slightly. Most of the other elements increased slightly. The SI's for calcite, dolomite, and aragonite increased from Las Palapas to Los Corales. Los Corales is also very similar in chemistry to Poza de Tonta. The chemical concentrations increased slightly from Poza de Tonta to Los Corales, but the changes were miniscule. Puente Colorada is located upstream of Los Corales and may also contribute to its chemistry. The chemistry between Los Corales and Puente Colorada was nearly identical with nitrate and alkalinity decreasing from Puente Colorada to Los Corales.

Puente Colorada lies along the canal that was constructed to route Poza Escobeda into the Rio Mesquites. Though the canal flow is consumed by a sink, the water from Poza Escobedo must contribute to the Puente Colorada chemistry via subsurface flow. Along the flow path from Poza Escobeda to Puente Colorada, every element except nitrate and barium increased slightly.

On the south fork at Los Corales, the next downstream sample was at the Rio Mesquites- Escobedo inlet. This sample was collected along the Rio Mesquites, downstream of the Poza Escobedo canal. Its name was associated with Escobedo only because it was accessed in the field by hiking from Escobedo. Otherwise, there is no relationship between the two sites. The chemistry of the Rio Mesquites-Escobedo had nearly the same composition as Los Corales. However, alkalinity and nitrate decreased from one to the other. The temperature in the river increased by four degrees Celsius from Los Corales to Rio Mesquites- Escobedo. This site is located upstream of the canal from Poza Tio Candido. The Rio Mesquites- Escobedo chemistry was more concentrated than for Poza Tio Candido. However, barium, nitrate, and the temperature were slightly lower.

Slightly downstream of the Rio Mesquites- Escobedo site, the canal Saca Salada at Puente Cuatas carries much of the water from the Rio Mesquites to the outlet of the basin. However, some of the water gets past the diversion for the canal and travels through conduits or shallow surface flows to Charcos Prietos and Las Playitas. Compared to the Rio Mesquites- Escobedo, Charcos Prietos is noticeably more concentrated in every element except barium, alkalinity, and nitrate. The temperature increased from 30.2 degrees Celsius to 34.6 degrees Celsius and the pH increased from 7.76 to 8.07. Saturation indices for gypsum, calcite, aragonite, and dolomite were higher than those in the Rio Mesquites.

The natural terminal lake for this system is Las Playitas. From Charcos Prietos to Las Playitas, concentrations of the major elements increased noticeably. Nitrate and alkalinity were exceptions and were lower in concentration than in Charcos Prietos. The temperature remained constant at 30.2 degrees Celsius, and the pH increased to 8.33.

The manmade termination point for the Rio Mesquites is at the canal Saca Salada. This canal receives the inflow of the Santa Tecla canal before leaving the Cuatro Cienegas valley. combines flows from the Rio Mesquites canal and the Santa Tecla canal. Therefore, the Antiguos Mineros system, though not naturally part of the flow system, mixes with the Rio Mesquites water before the canal leaves the basin. The outlet to the basin, downstream of the confluence of the canals, was compared to the chemical composition of Puente Chiquito, Rio Mesquites- Escobedo, Don Julio, and Antiguos Mineros. Compared to Puente Chiquito, the outlet water is more dilute. Compared to the Rio Mesquites- Escobedo site, most of the elements are higher at the outlet, including pH. Compared to Don Julio, the outlet is more concentrated, but

Don Julio is closer in composition to the outlet than the Rio Mesquites- Escobedo. Antiguos Mineros varies the most in chemical composition. Most of the elements were higher at the outlet. Most of the Rio Mesquites samples were below the detection limit for iron, but it is detectable at the outlet to the basin.

Finally, Las Salinas is another natural terminal lake in the system. It is the most highly concentrated pool in the basin. It has virtually no alkalinity. Compared to Playitas, the terminal lake for the main channel of the Rio Mesquites, the chloride, sodium, and magnesium concentrations are one and a half to two orders of magnitude higher, and nitrate is two orders of magnitude lower. The pH is the same as in Playitas. Gypsum and barite had an SI of .33 and .38, respectively.

In summary, karst terrain introduces a large amount of uncertainty in the precise flow paths from the springs. However, the pools along each probable flow path become more concentrated as their distance increases from their source. The Rio Mesquites system increases in nearly every element as it travels downstream (Figure 30). The compounds that consistently decrease along the flow path are nitrate and alkalinity. Las Salinas probably received flow until canal construction diverted water elsewhere. The exact source of this water is unknown. Along with Las Playitas, it is a terminal lake for the system.

TIO CANDIDO- HUNDIDOS SYSTEM

The Tio Candido- Hundidos system is extremely similar in chemical composition to the Rio Mesquites system (Table 6 and Figure 23). However, the source springs have a different terminal lake than the Rio Mesquites system. The source springs for this system include Poza Escobeda and Poza Tio Candido (Figure

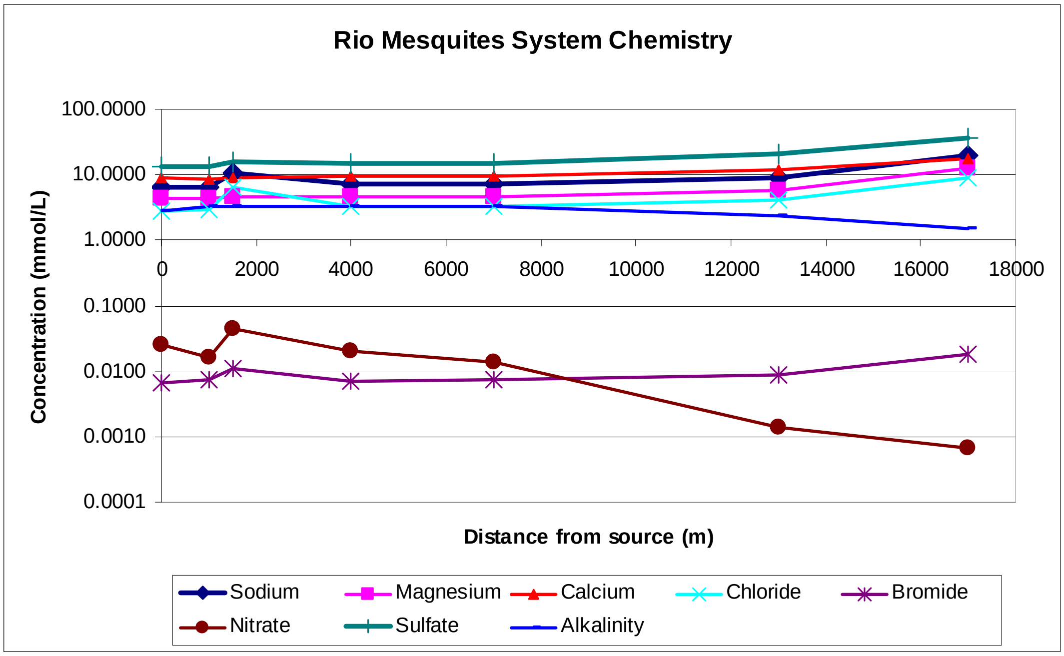

Figure 30: Concentration vs. distance plot for the south fork of the Rio Mesquites system.

29). These springs originate on the eastern flanks of the Sierra San Marcos. Man-made canals have been constructed to direct the spring water from these two sources into the Rio Mesquites system. However, due to the complex nature of the karst system in the basin, it is probable that the spring water travels through conduits into the middle of the basin along its previously undisturbed underground flow path. Springs in the middle of the system include Poza Los Hundidos and Poza La Maroma. The terminal lakes for this system include Los Gatos and Tortuguerra, which are located immediately adjacent to one another.

Two samples for this system, located in the middle of the system (La Maroma and Poza Los Hundidos), were obtained in April, 2004; therefore, the temperatures were slightly lower than what would be expected in June. The charge balance on these two sites was out of the range for reliability (13.6 and 18.6 percent error). Regardless of this fact, it appears that both samples were even higher in concentration than Los Gatos, which is the terminal lake for this system. The two samples were especially distinct in their high alkalinity concentrations (higher than the source springs and terminal lakes). Both La Maroma and Los Hundidos were supersaturated with respect to calcite (SI: 0.8 and 1.27) and dolomite (SI: 1.51 and 2.42) and were slightly supersaturated with respect to gypsum (SI: 0.14 for both). The exact concentrations cannot be trusted because the charge balance error is high in these samples. However, the results give an estimate for the range of concentrations that can be expected. Due to its error, this system needs more evaluation.

SANTA TECLA SYSTEM

The Santa Tecla system is located in the south east portion of the basin. The springs originate along the southeast flanks of the Sierra San Marcos (Figure 31). The major pozas in this system include Poza Antiguos Mineros, Pozas Azules, Laguna Quintero, Laguna Los fresnos, and Laguna Santa Tecla (Johannasson et. al., 2004). The only sample obtained for this study was Poza Antiguos Mineros (Table 7). The relationship of this poza to the outlet of the Rio Mesquites was given above in the Rio Mesquites system section. This sample was one of the least concentrated in the basin.

ANTEOJO SYSTEM

The Anteojo system is located in the northernmost portion of the basin, near the town of Cuatro Cienegas (Figure 32). Poza Anteojo is located on the southern flanks of Sierra La Madera, the tallest of the mountains surrounding the basin. Samples obtained for this system included Poza Anteojo, a well in the town of Cuatro Cienegas (Pozo de Sandra), and Canal Angostura (Table 8 and Figure 33). Pozo Anteojo is the main spring for this system. It had a temperature of 27.6 degrees Celsius at the time of collection (one of the cooler springs in the basin). It is much less concentrated than the other source springs in the basin. Canal Angostura, thought to be part of the Rio Mesquites system, was slightly less concentrated than Poza Anteojo. It had a higher pH and was slightly more concentrated in chloride, sodium, sulfate, and silica. However, it was very close in composition to Poza Anteojo. Pozo de Sandra, the water well at a residence in town, varied slightly from the other water. Its heavy metal concentrations (iron and zinc) were 1-1 ½ orders of

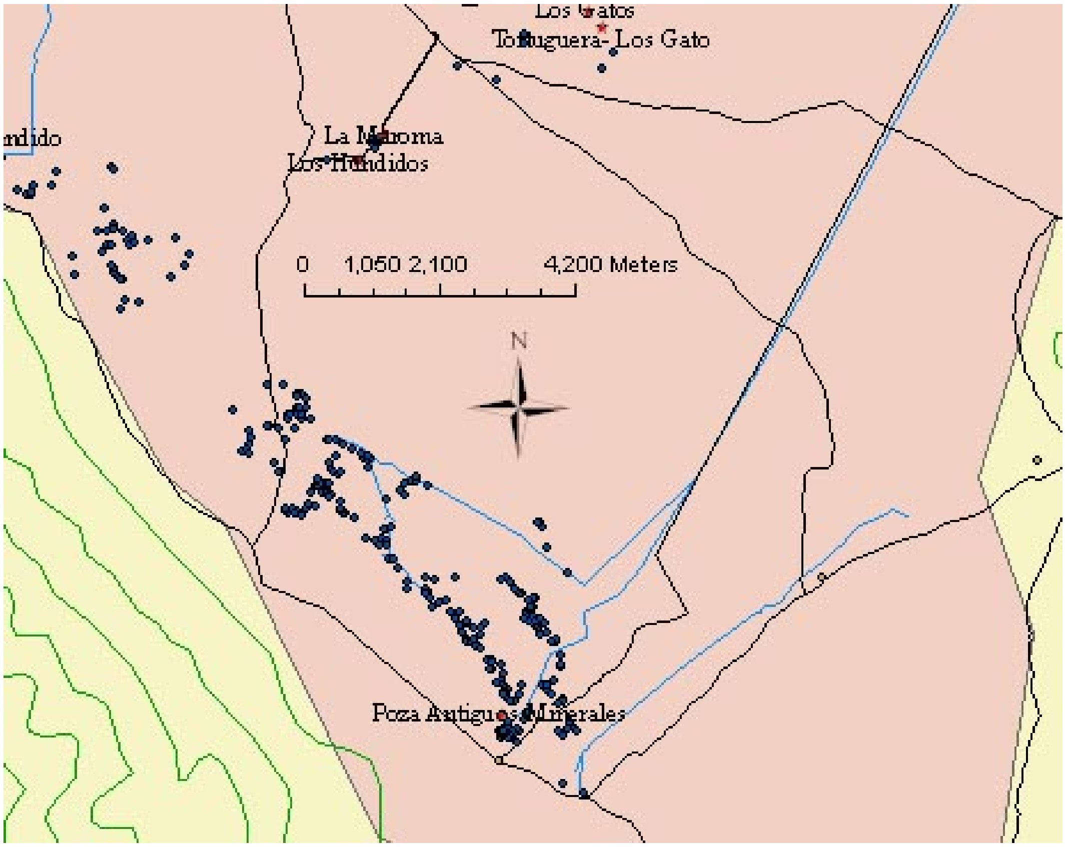

Figure 31: Map of the Santa Tecla system. Only Poza Antiguos Mineros was sampled in the Santa Tecla system.

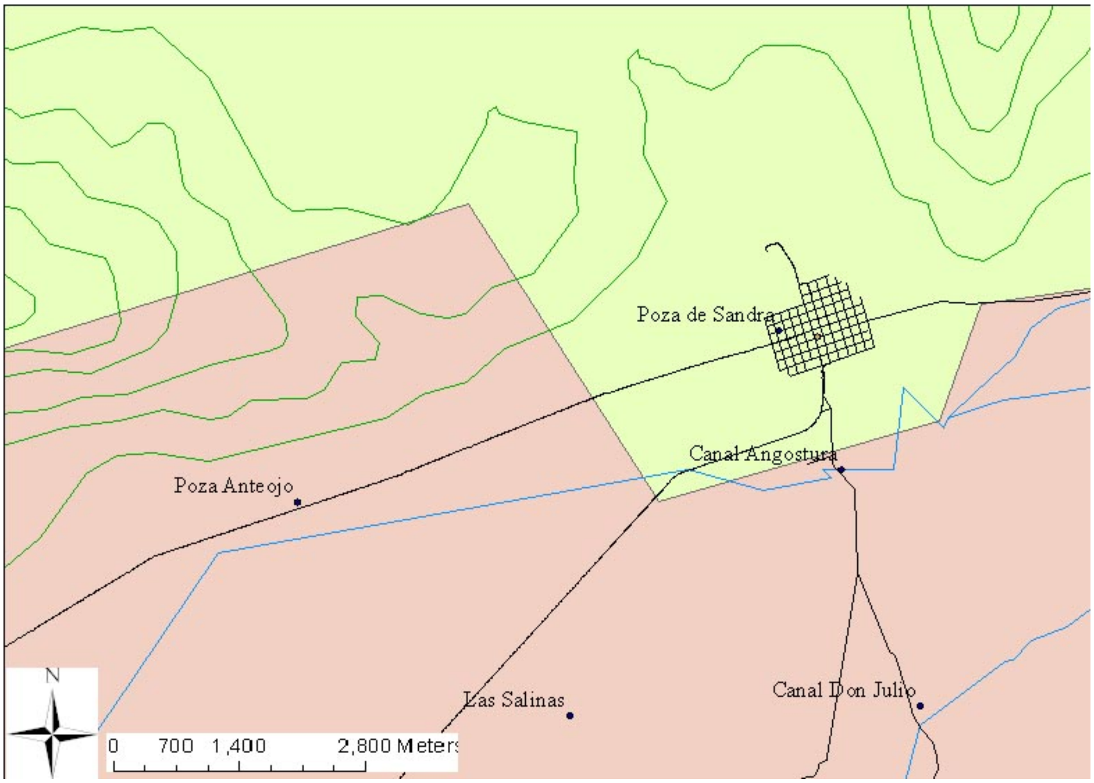

Figure 32: Map of the Anteojo system.

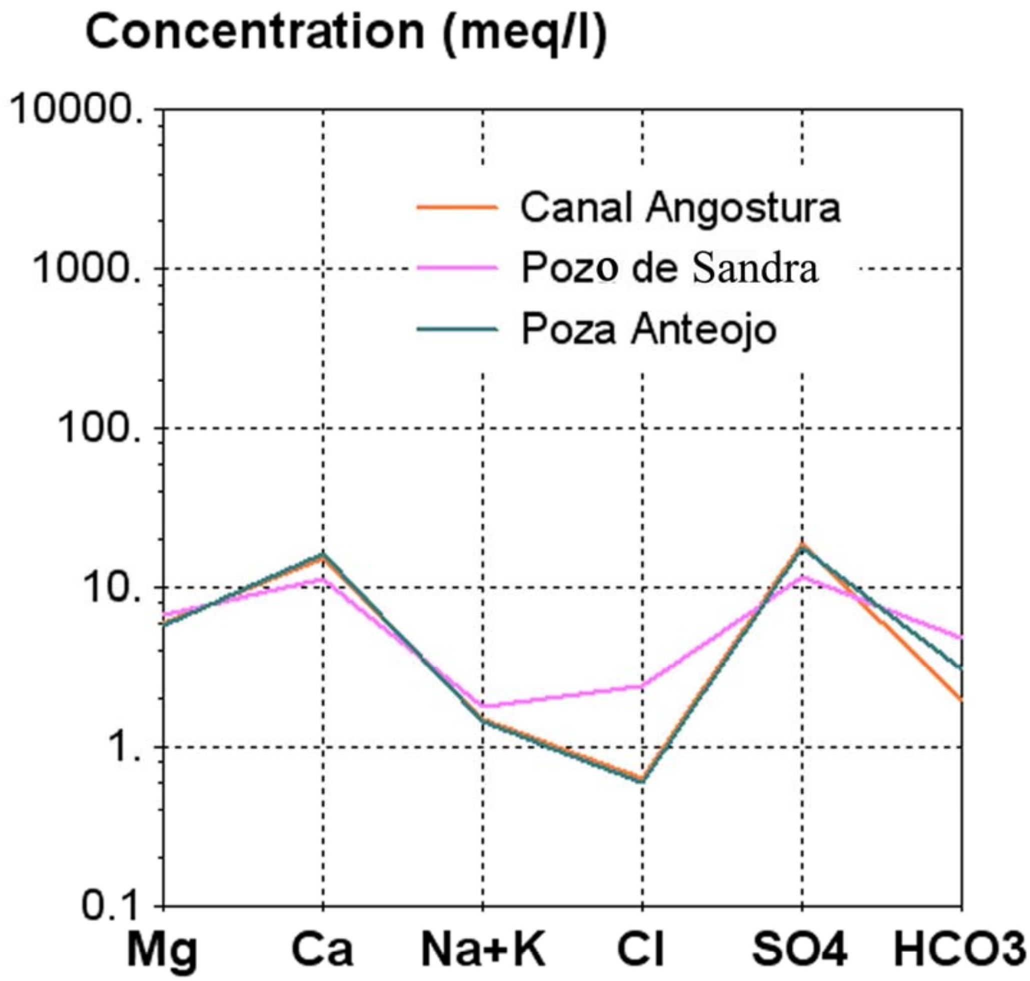

Figure 33: Schoeller Plot of the Anteojo system.

magnitude larger than those found in Poza Anteojo. It was also more concentrated in most chemical species.

CHAPTER 4: INTERPRETATION AND DISCUSSION

General Chemical Analysis

The scatter plots demonstrate the overall processes occurring within the basin better than other figures. The chloride ion is generally a conservative species in natural waters because it does not readily participate in water-rock interactions except in extremely saline waters (Drever, 1982). Therefore, increasing chloride concentrations are generally due to evaporation from rainwater. Plotting other ions against the chloride ion demonstrates the extent to which evaporation controls the system. The two increase linearly on a log-log plot as evaporation of water increases, if evaporation is the only controlling factor (Drever, 1982). The Na^+ vs. Cl^- plot (Figure 13) is useful for determining how close the sample is to rainwater, and for determining if the waters have undergone significant evaporation. The waters from the basin plot on the 1:1 evaporation line, demonstrating that evaporation controls the basin. Seawater was plotted on the diagram to demonstrate its resemblance to the Cuatro Cienegas waters, suggesting that the source of the water comes from recharging rainwater, rather than halite.

The Cl^- vs. Br^- ratios can show the origination of the water since both are conservative for evaporation. If the mass ratio between the two is 288, there is a seawater source. A ratio of more than 1000 indicates a halite signature. The Cl^- vs. Br^- plot shows that the Cuatro Cienegas waters are evaporation controlled and the mass ratio shows that they are closely related to seawater, not halite (Figure 17). The rainwater to the system most likely originates in the Gulf of Mexico or the Pacific Ocean.

The Mg^{2+} vs. Cl^- plot (Figure 14) is useful in determining if processes other than evaporation have occurred to reach specific magnesium concentrations. Magnesium, assuming no inputs from an outside source, will also behave conservatively and increase linearly with chloride. The plot shows that magnesium values in the basin have more scatter and are higher than what would be found if the concentration were solely a result of evaporation. Therefore, magnesium concentrations are not only a result of evaporation, but also originate as a result of dissolution processes (mainly dolomite phase). The stratigraphic units surrounding the basin contain dolomite, which is the most likely contributor to magnesium concentrations in the basin. Its chemical reaction is $Ca^{2+} + Mg^{2+} + 2CO_3^{2-} \Leftrightarrow CaMg(CO_3)_2$.

Sulfate is the major anion for the water in Cuatro Cienegas and therefore, needs to be evaluated against chloride. The scatter plot of sulfate vs. chloride (Figure 15) illustrates the evidence evaporation and gypsum/anhydrite precipitation. The samples plot in a nearly perfect 1:1 line, but the samples plot below the line as the concentration increases. The units surrounding the basin contain gypsum beds, which most likely contribute to the initially high concentration of sulfate in the water. Evaporation is controlling the concentrations of sulfate in the basin to a point, since the ratio of sulfate to chloride remains nearly the same throughout the basin. However, in the most concentrated water bodies, gypsum and/or anhydrite precipitation controls the water chemistry (gypsum: $Ca^{2+} + SO_4^{2-} + 2H_2O \Leftrightarrow CaSO_4 \cdot 2H_2O$; anhydrite: $Ca^{2+} + SO_4^{2-} \Leftrightarrow CaSO_4$).

An indicator that precipitation of gypsum and/or anhydrite controls the sulfate species is the scatter plot for the modeled Saturation Index (SI) for gypsum vs. sulfate

(Figure 16). At high sulfate concentrations, the SI is greater than zero. Evaporation is the control mechanism allowing sulfate concentrations to increase above equilibrium with the gypsum phase, allowing gypsum/anhydrite to precipitate. In natural waters, it is unusual for gypsum to be supersaturated. Since the only samples in the basin close to, or at equilibrium, were at the end of flow systems or terminal lakes, this is a clear indicator of the dominating influence of evaporation.

The carbonate system is important in the Cuatro Cienegas Basin. The Ca^{2+} + Mg^{2+} vs. HCO_3^- plot shows that the most concentrated water bodies have a higher ratio of calcium and magnesium to bicarbonate, and fall above the 1:2 line (Figure 19). This is a result of increased Ca^{2+} concentrations from the contribution of gypsum in the most highly concentrated water bodies. If the calcium that is contributed from the gypsum species were removed, the points would lie on the 1:2 line. The Ca^{2+} vs. Mg^{2+} scatter plot shows a 2:1 relationship with calcium concentrations almost twice as high as magnesium concentrations (Figure 18). This relationship reverses in the terminal lakes where the Mg^{2+} concentrations are equal or twice as high as the Ca^{2+} concentrations. This is due to calcite precipitation occurring in the most concentrated water bodies, allowing the magnesium from the dolomite to dominate.

The precipitation of calcite controls calcium and bicarbonate concentrations in the basin, (calcite: $CaCO_3 + H_2O + CO_2(g) \Leftrightarrow Ca^{2+} + 2HCO_3^{2-}$). As the water in the basin becomes more concentrated with respect to chloride, the calcite and dolomite SI increases to equilibrium or a super-saturated state (Figures 20 and 21). Dolomite precipitates kinetically more slowly than calcite, so calcite precipitation dominates over the precipitation of dolomite (Stumm, et. al., 1970). Minckley and others have documented active travertine deposition in the basin, demonstrating that calcite precipitation is occurring. Therefore, declining alkalinity concentrations are due to the precipitation of calcite with increased salinity.

In summary, the scatter plots show that evaporation is controlling the system, but other processes are involved. Calcite precipitation actively occurs in the basin, generally as travertine. The highest saturation indices for calcite occur at the terminal lakes for the systems. High magnesium concentrations are due to initial dolomite dissolution and subsequent evaporation. Gypsum precipitation controls the sulfate concentrations at high chloride concentrations.

The Piper plot shows that the water type for most of the water bodies in Cuatro Cienegas is calcium-sulfate (Figure 12). Deviation from the calcium-sulfate water occurs at the most highly evaporated terminal lakes. Investigating this further leads to an understanding of the chemical divides occurring with evaporation. Hardie et. al. (1970) studied the evaporation of closed-basin brines. They found that with continued evaporation, depending on the molar ratios of various chemical elements, various mineral phases will precipitate, slowly removing elements from the dissolved system (Figure 34). The first mineral to precipitate upon evaporation is calcite. From the Piper plot, the Las Salinas sample deviated the most from the other samples in the basin. This is the most highly evaporated pool in the basin. It is a magnesium, sodium, sulfate, chloride water. Comparing this to the evaporation chemical divides, it shows that calcite and gypsum must precipitate to achieve this composition. Looking at the molar ratios of Ca^{2+}:HCO_3^- and Ca^{2+}:SO_4^{2-}, this is the expected result of evaporation for Poza Becerra, one of the source springs for this pool. This projected pathway is true for the source springs in the basin, though it is less

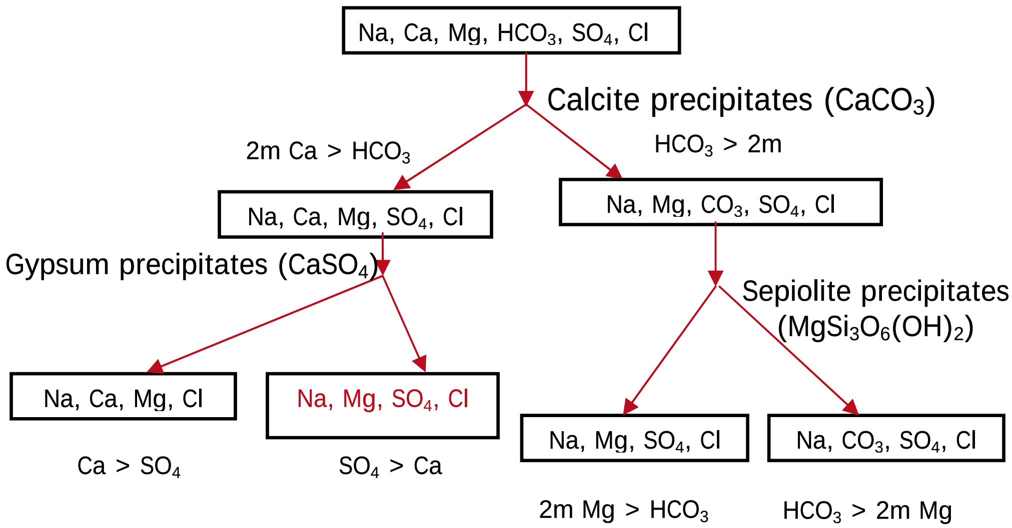

Figure 34: Chemical divides that occur during evaporation (modified from Drever, 1982 and Hardie, et. al., 1970). The Cuatro Cienegas springs trend is toward a Na, Mg, SO_4, Cl terminal signature, as evidenced by the terminal lake Las Salinas.

pronounced in the Santa Tecla and Anteojo systems since their ratios of Ca^{2+}:HCO_3^- and Ca^{2+}:SO_4^{2-} are lower than the other systems.

A study in Lake Magadi in Kenya was one of the first to employ the chemical divides concept to understanding the chemical evolution of closed basin brines (Eugster, 1970). Though this site is a sodium, carbonate, sulfate, chloride brine, it's evolution is similar to that of Cuatro Cienegas. It is located in an arid, closed basin, fed by thermal springs. The extraordinary feature of the Cuatro Cienegas Basin is that the chemical evolution of the system may be readily observed by comparing the water chemistry from the source springs to the terminal lakes. The chemical divides are made clear though chemical analysis.

Flow System Chemistry

From the general chemical analysis, the major processes within the basin have been illuminated. The increase in concentration along the flow paths is primarily due to evaporation. Nitrate and alkalinity consistently decrease along the flow path. The alkalinity decreases due to the precipitation of calcite minerals, mainly travertine. The decrease in nitrate concentrations is most likely due to the reduction of nitrate to nitrogen gas. While the reduction of nitrate to nitrogen gas in the presence of organic matter produces alkalinity ($2.5CH_2O + 2NO_3^- \Leftrightarrow N_2 + 2.5HCO_3^- + 0.5H^+ + H_2O$), in the Cuatro Cienegas Basin, alkalinity decreases with increased salinity. The rate at which nitrate decreases is significantly greater than that for bicarbonate. Though bicarbonate is produced in the denitrification reaction, the precipitation of calcite in the basin controls the bicarbonate concentration, causing it to decline.

The Rio Mesquites Schoeller plot shows a clear example of evaporation in a single flow system (Figure 24). By analyzing the trends of the chemistry in this plot, and comparing each sample signature to locations determined by the GIS, it is clear that the source springs had the lowest concentrations in the system (are located at the bottom of the plot), and springs became more concentrated as distance from the sources increased (moved toward the top of the plot). Due to the fact that the basin is located in the Chihuahuan Desert and evaporation rates are high, there is no doubt that the systems are evaporation controlled. The plot helps to confirm this relationship that was established by the Cl^- scatter plots. The other systems show the same trend as the Rio Mesquites system.

SOURCE SPRINGS

The first question needing evaluation to investigate the flow system chemistry is what the chemical pathways are for the evolution of rainwater to spring water. In order to assess the possible pathways of the chemical evolution of the rainwater, PHREEQC was utilized. From the graphical results of the chemistry, it is evident that evaporation is the most important process occurring, but is not the only control of water chemistry. The main source spring samples (Becerra, Antiguos Mineros, and Anteojo) are the low evaporation end members. Therefore, using PHREEQC, rainwater was evaporated and equilibrated with several minerals to mirror these springs. The percent difference between the actual spring, and the evaporated water chemistry was calculated. Results with less than ten percent error were considered acceptable models. A large amount of error is associated with this type of model because the PRHEEQC evaporation is highly dependent on the chloride concentrations. With only a small increase in chloride concentrations in the rainwater, the number of times the water must be evaporated may drastically decrease in the model. The results from the PHREEQC models give an approximate amount of concentration for the springs in the basin and are not precise.

The amount of carbon dioxide in the springs (pCO_2) is important for mineral equilibria, especially calcite and dolomite. A system left open to the atmosphere has a pCO_2 of $10^{-3.5}$, or SI -3.5. However, when water recharges and interacts with organic matter in soil and rocks, the pCO_2 generally increases due to root respiration (Kehew, 2001). Typical pCO_2 for groundwater is between 10^{-3} and 10^{-1}. Higher pCO_2 values will contribute to calcite dissolution ($CaCO_3 + H_2O + CO_2 \Leftrightarrow Ca^{2+} + 2HCO_3^-$). All of the PHREEQC models take the partial pressures of CO_2 in the water into account.

The main spring, representative of the average water chemistry for the basin is Poza Becerra. This spring is representative for the Rio Mesquites, Churince, and Tio Candido/Hundidos sytems. Therefore, the rainwater was modeled to this spring. After various simulations, two models closely fit the Poza Becerra chemistry (Table 10). The first evaporated the rainwater by a factor of 990 at atmospheric pCO_2 ($10^{-3.5-}$), equilibrated the water to a pCO_2 of $10^{-1.5}$ and dolomite, albite (1 mmol), and kaolinite equilibrium, and finally equilibrated the water to a pCO_2 of $10^{-1.93}$, which is the partial pressure at Poza Becerra, and brought to calcite equilibrium. Sodium, calcium, and magnesium concentrations did not converge as well as hoped. However, sodium and chloride are controlled seasonally with variations in temperature and evaporation throughout the year. Such error is not unexpected.

Units in moles	Poza Becerra (M)	Rainwater (M)	Evaporate 990 x, Equilibrate CO2: -1.5, dolomite, albite, kaolinite, Equilibrate CO2:-1.93, calcite	Percent difference
Ca	8.95E-03	1.85E-05	1.83E-02	-104.76
Cl	2.86E-03	2.82E-06	2.79E-03	2.41
Mg	4.48E-03	9.46E-07	2.40E-03	46.54
Na	6.37E-03	3.87E-06	4.33E-03	32.00
S	1.32E-02	1.22E-05	1.21E-02	8.71

Table 10: PHREEQC model results for rainwater to Poza Becerra.

Cation exchange with clays may also contribute to this error. Sodium/calcium exchange must also take place. This would increase the sodium levels, decrease the calcium, and cause dolomite dissolution, which would increase the magnesium concentration. This model is reasonable for this site.

The model to evaporate the rainwater to Poza Anteojo differed from that of Poza Becerra. In order to match the chemical concentrations in Poza Anteojo, the rainwater was evaporated 215 times at atmospheric CO_2 pressure, equilibrated to a pCO_2 of $10^{-1.5}$ and calcite and dolomite equilibrium, then equilibrated to a pCO^2 of $10^{-1.99}$. Gypsum and calcite were precipitated to an SI of -0.41 and -.28, respectively (Table 11). The sodium value did not converge for this model. Cation exchange with calcium would decrease the calcium concentration and increase the sodium concentrations. However, all other species converged nicely, within an 11 percent error.

The rainwater was also modeled to Poza Antiguos Mineros in the Santa Tecla system (Table 12). The rainwater was evaporated 440 times at atmospheric CO_2, and then equilibrated to a pCO_2 of $10^{-2.0}$ and dolomite, albite (0.5 mol), and kaolinite equilibrium. Next, it was and equilibrated with a pCO_2 of $10^{-2.43}$ and calcite equilibrium. The calcium concentration was high, and the magnesium low. As stated before, this may be due to cation exchange. Under calcium, sodium exchange, the calcite will decrease, sodium will increase, and dolomite will dissolve, increasing the magnesium concentration. Several trials were run, but this was the most reasonable model. This portion of the basin has a much thicker alluvial fan than the other systems. This may allow a higher residence time and more cation exchange.

Units in Moles	Poza Anteojo	Rainwater	Evaporate 215 x, Equilibrate CO2:-1.5, dolomite, calcite; Equilibrate CO2:-1.99, Precipitate gypsum -0.41, calcite 0.28	Percent difference
Ca	8.02E-03	1.85E-05	8.89E-03	-10.84
Cl	6.00E-04	2.82E-06	6.06E-04	-1.12
Mg	2.93E-03	9.46E-07	2.90E-03	1.23
Na	1.37E-03	3.87E-06	8.32E-04	39.25
S	9.00E-03	1.22E-05	7.97E-03	11.47

Table 11: PHREEQC model results for rainwater to Poza Anteojo.

Units in Moles	Poza Antiguos Mineros	Rain	CO2:-3.5, Evaporate 440 x, Equilibrate CO2:-2.0, dolomite, albite, kaolinite, Equilibrate CO2:-2.43, calcite	Percent difference
Ca	4.67E-03	1.85E-05	8.05E-03	-72.25
Cl	1.29E-03	2.82E-06	1.24E-03	3.65
Mg	2.34E-03	9.46E-07	1.25E-03	46.49
Na	2.60E-03	3.87E-06	2.20E-03	15.20
S	5.50E-03	1.22E-05	5.36E-03	2.49

Table 12: PHREEQC model results for rainwater to Poza Antiguos Mineros.

CHURINCE SYSTEM

Poza Churince and Laguna Intermediate are very close in proximity to one another and the changes in chemistry were so slight, only a small amount of evaporation, dissolution, or precipitation takes place between the two (Table 9). According to the model calculated in PHREEQC, Poza Churince must be evaporated 1.08 times, equilibrated to a pCO_2 of $10^{-2.88}$, and must precipitate gypsum to an SI of -0.28 to match Laguna Intermediate's chemistry (Table 13). Poza Bonita is a second spring that contributes to Poza Intermediate and Poza Grande, though no surficial flow can be observed. The chemical composition of Poza Bonita is so close to that of Laguna Intermediate that the most likely explanation is that both Poza Bonita and Poza Churince contribute to Laguna Intermediate.

As the terminal lake of the system, Laguna Grande has undergone significantly more evaporation over time than the other pozas in the system because it does not discharge to any other known location (Table 14). In the PHREEQC model, Laguna Intermediate was evaporated 2.45 times and equilibrated to a pCO_2 of $10^{-2.96}$. Calcite and gypsum were precipitated to an SI of 0.78 and 0.03, respectively, to match the values at Laguna Grande. The model converged as hoped. Evaporation, and calcite and gypsum precipitation occur in this water body. The presence of gypsum dunes off of the western banks of the lake indicates that this lake has undergone significant evaporation as a playa lake. This system is the most isolated one in the basin. It is the ideal model for an evaporation pathway system.

Units in Moles	Churince	Laguna Intermediate	Percent difference Churince/Intermediate	Evaporate 1.08, CO2: -2.88, Precipitate gypsum SI -0.28	Percent difference
Br	5.77E-06	6.03E-06	4.39	6.23E-06	-3.25
Ca	7.99E-03	9.24E-03	13.48	9.04E-03	2.14
Cl	2.93E-03	3.17E-03	7.78	3.16E-03	0.41
F	1.37E-04	1.45E-04	5.98	1.48E-04	-1.58
K	1.85E-04	1.92E-04	3.81	1.99E-04	-3.91
Mg	4.02E-03	4.38E-03	8.42	4.34E-03	1.09
N(5)	2.02E-05	9.63E-06	-109.47	2.18E-05	-126.28
Na	6.60E-03	7.14E-03	7.58	7.13E-03	0.17
S	1.26E-02	1.46E-02	13.74	1.40E-02	4.03
Sr	1.49E-04	1.61E-04	7.21	1.61E-04	-0.19

Table 13: PHREEQC model results for Churince to Laguna Intermediate.

Units in Moles	Laguna Intermediate	Laguna Grande	Percent difference Intermediate/Grande	Evaporate 2.45, CO2: -2.96	Percent difference
Ca	9.24E-03	1.27E-02	27.28	2.26E-02	-78.19
Cl	3.17E-03	7.75E-03	59.02	7.78E-03	-0.37
K	1.92E-04	5.01E-04	61.69	4.70E-04	6.15
Mg	4.38E-03	9.91E-03	55.78	1.07E-02	-8.33
Na	7.14E-03	1.71E-02	58.26	1.75E-02	-2.28
S	1.46E-02	2.85E-02	48.67	3.58E-02	-25.75

Units in Moles	Precipitate Calcite 0.78, Gypsum 0.03	Percent difference
Ca	1.43E-02	-12.76
Cl	7.78E-03	-0.37
K	4.70E-04	6.15
Mg	1.07E-02	-8.33
Na	1.75E-02	-2.28
S	2.82E-02	0.98

Table 14: PHREEQC model results for Laguna Intermediate to Laguna Grande.

RIO MESQUITES SYSTEM

Generally speaking, the waters in this system increase in concentration from the source springs to the terminal lakes for the system. This relationship becomes more complex toward the middle of the basin, in the middle of the flow system. It is more difficult to determine which pozas contribute to one another after the river splits at Las Palapas. The flow paths modeled for this system were from Poza Becerra to the Rio Mesquites- Las Palapas, Las Palapas to Los Charcos Prietos, and Charcos Prietos to Playitas.

The first model, from Poza Becerra to Rio Mesquites-Las Palapas required an evaporation factor of 1.15 at a pCO_2 of $10^{-2.74}$ (Table 15). The pCO_2 for the Rio Mesquites site was higher than that of Poza Becerra ($10^{-1.99}$) because the water travels as surface flow that receives subsurface flow and is equilibrating with atmospheric CO_2. For this length of the system, evaporation dominates over any other process occurring. The model results had less than 11 percent error for each species. Only a small amount of chemical change is occurring at this point in the system. From Rio Mesquites- Las Palapas, the existence of subsurface conduits contributing to the system complicates the system. Subsurface flow increases the pCO_2 of the water, thereby affecting the chemical equilibrium. Much care was taken to account for this in the models, but not every site could be modeled.

Poza de Tonta is very closely related to the Rio Mesquites- Las Palapas. Its closest water source is the Las Palapas site. The water must travel through underground conduits from the Rio Mesquites to the spring site. Therefore, it undergoes relatively little evaporation. Mineral dissolution and precipitation from its source to the spring are relatively small due to its proximity to the Rio Mesquites.

Units in Moles	Poza Becerra	RM- Las Palapas	Percent difference	CO2:-2.74, Evaporate 1.17 x	Percent difference
Ca	8.95E-03	9.68E-03	7.55	1.04E-02	-7.67
Cl	2.86E-03	3.38E-03	15.25	3.35E-03	0.86
K	2.30E-04	2.47E-04	6.88	2.69E-04	-8.94
Mg	4.48E-03	4.74E-03	5.32	5.25E-03	-10.79
Na	6.37E-03	7.25E-03	12.16	7.46E-03	-2.77
S	1.32E-02	1.51E-02	12.40	1.55E-02	-2.45

Table 15: PHREEQC model results for Poza Becerra to Rio Mesquites- Las Palapas.

Rio Mesquites - Las Salinas receives much of its water from surface flows from a separate tributary of the Rio Mesquites, and much from the Las Palapas site via surface/subsurface flows due to its striking chemical resemblance to Rio Mesquites - Las Palapas. Its quick travel time allows for little evaporation or interaction with the banks. This site may also receive some flow from underground conduits with similar chemistry surfacing in the river. Poza de Tonta may provide some water to this site through conduit flow. Unmapped spring inflows to the river may provide a source of dilution for the water, canceling out the effects of evaporation.

Las Palapas also supplies water to Los Corales as the river forks to the south. Los Corales receives most of its water from this source due to its similar chemical composition. However, it also receives inflow from Puente Colorada, which lies along the canal constructed from Poza Escobeda. Like the Rio Mesquites - Las Salinas site, it may receive flow from Poza de Tonta through conduits surfacing in the Rio Mesquites. Little change in composition occurs between these springs due to their proximity. However, evaporation is causing the water to become slightly more concentrated.

The Rio Mesquites - Escobedo site is located downstream, very close in proximity to Los Corales. The main difference between the sites was the change in temperature. Therefore, the majority of the flow at this point in the Rio Mesquites comes from Los Corales. The sample location was directly downstream of the Poza Escobedo inlet from the canal. Due to the rapid velocity of the flow, the water in the river at this point has not had time to change in chemical composition. However, the change in temperature at this point in the river shows that the input from Poza Escobedo has reached the river.

Due to the similarity in chemical concentrations for the samples in the Rio Mesquites system, not all could be modeled. However, the water was modeled from the Rio Mesquites- Las Palapas site to Charcos Prietos, which had large enough chemical differences to model. Using the model, Las Palapas was evaporated 1.23 times at a pCO_2 of $10^{-2.97}$, with very good results (Table 16). The pCO_2 was slightly higher at Charcos Prietos than at Rio Mesquites- Las Palapas.

The final path modeled was from Charcos Prietos to Las Playitas, the terminal lake for the system. The water was evaporated 2.15 times at a pCO_2 of $10^{-3.5}$ (Table 17). The partial pressure of carbon dioxide has equilibrated to atmospheric levels in this lake. In order to fit the calcium and sulfur values, the calcite and gypsum were precipitated to an SI of 1.12 and 1.25, respectively. The PHREEQC model results converged well. This terminal lake has precipitated calcite and gypsum upon evaporation, comparable to the terminal lake in the Churince System (Laguna Grande).

TIO CANDIDO- HUNDIDOS SYSTEM

Due to the canal construction and close communication of the Rio Mesquites system and the Hundidos system, the two have similar chemistry. Large karst features in this area of the basin indicate that subsurface flow and karst dynamics control this system, making it difficult to predict its source waters. While charge balance errors prohibited a full analysis of this system, it was clear from the large difference in chemistry from the other springs in the basin, that La Maroma and Poza

Units in Moles	RM-Palapas	Charcos Prietos	Percent difference	CO2: -2.97, Evaporate 1.23	Percent difference
Br	7.37E-06	8.91E-06	17.38	9.06E-06	-1.62
Ca	9.68E-03	1.21E-02	20.08	1.19E-02	1.73
Cl	3.38E-03	4.15E-03	18.55	4.15E-03	-0.19
F	1.59E-04	2.08E-04	23.51	1.95E-04	5.92
K	2.47E-04	2.85E-04	13.26	3.04E-04	-6.67
Mg	4.74E-03	5.79E-03	18.13	5.83E-03	-0.69
Na	7.25E-03	9.28E-03	21.85	8.92E-03	3.88
S	1.51E-02	2.06E-02	26.69	1.86E-02	9.82

Table 16: PHREEQC model results for Rio Mesquites- Las Palapas to Charcos Prietos.

Units in Moles	Charcos Prietos	Las Playitas	Percent difference	Evaporate 2.15, CO2: -3.5	Percent difference
Br	8.91E-06	1.84E-05	51.48	1.92E-05	-4.30
Ca	1.21E-02	1.79E-02	32.35	2.60E-02	-45.42
Cl	4.15E-03	8.91E-03	53.47	8.91E-03	-0.04
K	2.85E-04	6.24E-04	54.30	6.13E-04	1.75
Mg	5.79E-03	1.26E-02	54.12	1.24E-02	1.35
Na	9.28E-03	1.99E-02	53.38	2.00E-02	-0.25
S	2.06E-02	3.68E-02	44.16	4.42E-02	-20.06

Units in Moles	Precipitate to calcite SI 1.12, Gypsum SI 1.25	Percent difference
Br	1.92E-05	-4.30
Ca	1.82E-02	-1.68
Cl	8.91E-03	-0.04
K	6.13E-04	1.75
Mg	1.24E-02	1.35
Na	2.00E-02	-0.25
S	3.74E-02	-1.52

Table 17: PHREEQC model results for Charcos Prietos to Las Playitas.

Los Hundidos are not directly related to the Rio Mesquites system. The high alkalinity concentrations separate these two springs from all others in the basin. The system also has separate source springs and terminal lakes. Therefore, it is a separate system in the basin.

SANTA TECLA SYSTEM

The Santa Tecla system was separated from the others due to its generally lower specific conductance in the springs. While there were no samples taken toward the end of the flow system, and no terminal lake exists for this system, Poza Antiguos Mineros was distict from all other source springs in its alkalinity concentration and total dissolved solids. It is similar to the Rio Mesquites and other systems due to its location at the foot of the Sierra San Marcos in the south east lobe of the basin, but differs in its chemical composition. Its waters originate from this mountain, but travel paths and evolution of the water were distinctly isolated from the other water in the basin. This may be due to a fault lying along the western side of the Sierra San Marcos, starting at Poza Azules and traveling just south of Poza Antiguos Mineros, creating a larger alluvial fan than seen anywhere else in the basin (Johannesson, et. al., 2004). The greatest temperature differences in the basin occur in this system. Pools in this system may have a temperature difference of 10 degrees Celsius within a 15 meter distance, according to personal communication with Suzanne Pierce, Department of Geological Sciences at The University of Texas. This may be due to karst flow controlling the spring locations. The deeper source springs have a higher temperature than the springs with shallower source water.

ANTEOJO SYSTEM

The Anteojo system is a distinct system in the north portion of the basin. Its springs are lower in overall concentrations and are not closely related to the systems originating from the Sierra San Marcos. This system originates from the Sierra de la Madera, which peaks higher than the Sierra San Marcos. According to isotope studies conducted by K. Johannesson et. al. (2004), this system most likely has a higher source altitude than the other systems; therefore, attributing to its higher carbonate concentrations. Furthermore, it had been thought that the Canal Angostura originated from the Rio Mesquites. However, due to the proximity and similarity of chemical composition of the canal to Poza Anteojo, it is clear that it is more closely related to the Anteojo system than the Rio Mesquites system.

CHAPTER 5: CONCLUSIONS AND FUTURE WORK

The Cuatro Cienegas Basin is a unique and complex valley. Its endemic and endangered fauna rely on the complex groundwater systems in the basin. Delineating the flow systems and discovering their chemical relationships will facilitate a complete hydrogeologic characterization of the basin. Future studies of all facets are dependent on investigations of the groundwater systems in the basin. This study details the type of water in the springs to the terminal lakes, and establishes the relationship between the springs and their source (rainwater), the springs and their terminal lakes, and the systems in respect to one another.

Evaporation controls the chemical pathway for evolution of the flow systems in the basin. The dominant water type is calcium-sulfate, and tends toward a sodium, magnesium-sulfate, chloride water with evaporation. Source springs have solute concentrations between 200 and 1000 times that of rainwater. As the rainwater is evaporated, several factors affect the chemical signature at the spring, such as the partial pressure of carbon dioxide, temperature, and contact with rocks and minerals along the flow path. The primary minerals participating in the chemical evolution are calcite, dolomite, and gypsum. Rainwater is evaporated, and reacts with dolomite and calcite prior to its reappearance as spring-flow. Its pCO_2 increases as the rainwater infiltrates through the subsurface, providing a catalyst to mineral dissolution. The end result is a spring water with a seawater signature, confirming that it was derived from the rainwater.

Within the basin, the spring water flows on the surface and through subsurface conduits. Karst in the basin introduces complexity within each flow system, and between the flow systems, making it difficult to compartmentalize each water body to one system. Furthermore, subsurface flows increase the pCO_2 of the water and affects mineral equilibrium. This is an arid wetland and much of the flow occurs beneath the land surface as groundwater flow. Surface flows occur, but a much more complex system exists than what an observer may see.

With a significant amount of evaporation, the water approaches various chemical divides, depending on the molar ratios of the major ions in the water. The Cuatro Cienegas water tends to precipitate calcite with evaporation. As the evaporation factor increases, gypsum may begin to precipitate as well to result in a sodium, magnesium- sulfate, chloride water. An example of this magnitude of evaporation is the most concentrated pool in the basin, Las Salinas.

While the water becomes more concentrated as the water travels further from its source spring, nitrate and alkalinity consistently decrease in every system. The alkalinity decreases as a result of calcite precipitation as the water reaches a chemical divide that occurs with cumulative evaporation. Nitrate decreases due to the uptake from the vegetation or chemical reduction as a result of extreme evaporation.

Five flow systems are confirmed to exist within the Cuatro Cienegas basin: the Churince, Rio Mesquites, Tio Candido/Hundidos, Santa Tecla, and Anteojo systems. Though it is not a requirement, an indicator of separate flow systems is the presence of terminal lakes at the end of a flow system and springs at the source of a system. Distinctly differing chemical compositions is another indicator of separate systems. Specific conductance increases from the source to the terminal lake of unique systems.

The systems located along the Sierra San Marcos (Rio Mesquites, Churince, and Tio Candido/Hundidos) are similar in composition. However, each of these systems has separate sources and terminal lakes that delineate them into separate systems. More study is needed in the Poza Hundidos area to determine a precise source for these waters. Karst flow dominates in this area, so that exact flow paths difficult to determine.

The Santa Tecla system is the exception along the Sierra San Marcos. It is most likely controlled by an isolated fault located on the eastern flank of the Sierra, though this hypothesis has not been tested. A large alluvial fan is associated with this portion of the mountain. This, along with karst flow, contributes to the evolution of this system because it may increase the residence time in the subsurface for water/rock interaction. It has a distinctly lower specific conductance than the other systems originating from the sierra, which separates it from the other systems.

The system originating off of the Sierra La Madera, the Anteojo system, is distinct from all other systems and has a higher source altitude. It has the lowest conductivity of all of the systems in the basin and has undergone the least amount of evaporation. Its geographic separation and chemical distinction separate it from the other systems in the basin. More research on this system could reveal a close relationship to the adjacent valley to the north, Ocampo.

Future isotopic studies with ^{18}O would be useful to evaluate and quantify evaporation within the basin. These data would be compared to the Johannesson et. al. (2004) study to determine if the data in the terminal portion of the basin matches with the projected evaporation line. Isotopes could be a key indicator of separate flow systems, and may help determine a relationship to the adjacent valleys, especially the valley to the south of Cuatro Cienegas, Valle Los Hundidos. This type of study would be useful to determine whether a hydrogeological connection exists between them. This will be important in determining an accurate water balance for the basin.

Appendix A

GIS SAMPLE LOCATIONS:

OBJECTID	SITE	SAMPLE__	EASTING	NORTHING	ELEV
1	**Poza Becera**	SBE-1	784203.00	2976305.00	759
2	**Laguna Intermediate**	SBE-2	783882.00	2972890.00	773
3	**Laguna Grande**	SBE-3	783254.00	2973179.00	774
4	**Poza Churince**	SBE-4	784812.00	2971974.00	790
5	**Poza Juan Santos**	SBE-5	783386.00	2978294.00	773
6	**Poza Antiguos Mineros**	SBE-8	798066.00	2966454.00	724
7	**Tio Candido**	SBE-9	790256.00	2975443.00	734
8	**Poza Escobedo**	SBE-10	789393.00	2977756.00	742
9	**Rio Mesquites- Escobedo**	SBE-11	791561.00	2979680.00	733
10	**Rio Mesquites- Las Salinas**	SBE-12	790187.00	2981239.00	724
11	**Puente Colorada**	SBE-13	790370.00	2979205.00	716
12	**Los Corales**	SBE-14	790795.00	2979629.00	716
13	**Puente Chiquito Spring**	SBE-15	791344.00	2980687.00	715
14	**Las Playitas**	SBE-16	796639.00	2979978.00	722
15	**Charcos Prietos**	SBE-17	794432.00	2979933.00	730
16	**Canal Don Julio**	SBE-18	792362.00	2983865.00	737
17	**Poza de Tonta**	SBE-19	789520.00	2980480.00	721
18	**Poza Bonita**	SBE-20	784179.00	2971608.00	771
19	**Poza Anteojo**	SBE-23	785145.00	2986221.00	751
20	**Rio Mesquites- Las Palapas**	SBE-24	787637.00	2980555.00	736
21	**Poza Tierra Blanca**	SBE-26	784091.00	2980835.00	713
22	**Poza Churince**	SBE-30-4/	784812.00	2971974.00	790
23	**Poza Juan Santos**	SBE-31-5/	783386.00	2978294.00	773
24	**Canal Angostura**	SBE-21	791454.68	2986606.82	null
25	**Poza de Sandra**	SBE-22	790728.22	2988235.69	null
26	**1st Tributary to Rio Mesqu**	SBE-29-3	785630.25	2981606.64	null
27	**Cave**	SBE-35-9	783706.16	2979565.85	null
28	**Los Gatos**	SBE-6	799428.16	2977463.49	703
29	**Tortuguera- Los Gatos**	SBE-7	799643.35	2977190.37	701
30	**Rio Mesquites-outlet**	SBE-25	811102.91	2991002.42	672
31	**Poza Azul (Mojarral Oeste)**	SBE-27-1	785736.33	2980920.41	null
32	**Poza Mojarral Este**	SBE-28-2	786032.52	2980922.71	null
33	**Las Salinas**	SBE-32-6	788301.96	2983741.49	null
34	**La Maroma**	SBE-33-7	796248.02	2975503.49	null
35	**Los Hundidos**	SBE-34-8	795853.30	2975116.02	null

DETAILS ON INTEGRATION OF SAMPLES INTO GIS:

Building a geodatabase and basemap

A geodatabase was created for the basin and named CCproj. Six feature datasets were created within the geodatabase for each spatial projection encountered in the data (Figure 3). All base files for the Cuatro Cienegas basin and Mexico were obtained from Jennifer Howeth and A. Moline. The data was in both geographic coordinates (North American Datum-1927) and projected coordinates (Universal Transverse Mercator- UTM, Zone 13). The CuatroC and Mexico feature datasets were in NAD-1927, CuatroCUTM13 and UTM13 were in UTM Zone 13, and CuatroCUTM14 and UTM14 were in UTM Zone 14. All of the data were ultimately gathered into the UTM Zone 13 projection for the ease of study.

Integrating geochemical sample locations into the GIS

The chemical data, field data, and GPS data were entered into an Excel database upon return from the field. Each sample location was recorded using a handheld GPS device. The GPS was not utilized for samples taken in April. Locations for samples from the Angostura Canal and Pozo de Sandra were not obtained due to weather conditions at the site. The GPS took readings in UTM (Universal Transverse Mercator) mode. Most of the samples were in UTM Zone 13, while 3 were in UTM Zone 14. Due to the variability in data availability, the spreadsheet was divided into 4 new databases (DBF4 files). The first and largest of these was for the samples taken in UTM Zone 13 (GPS13). A feature class was created in ArcCatalog for the GPS13 points, and uploaded into the CuatroCUTM13 feature dataset. The second was for the location points located in Zone 14 (GPS14).

A feature class was created for this database, and was uploaded into the CuatroCUTM14 feature dataset. This feature class was then imported into the CuatroCUTM13 feature dataset.

The sample sites with no GPS data were separated into two databases. These final two databases were more complicated in their integration into GIS. One that had sample locations with known latitude and longitude coordinates that were imported by hand from an existing data base from Suzanne McGaugh (UTMNoData), and one with sample locations that had never previously been located using a GPS device (NeedXY). The UTMNoData database sample locations were imported as latitude and longitude coordinates (NAD-1927). These data were converted into a feature class (GPSNoData) and imported into the CuatroC feature dataset, then into the CuatroCUTM13 feature dataset. A new point feature class (GPSXY) was created for the NeedXY table in the CuatroCUTM feature dataset. In order to populate the empty feature class, the editor tool bar was utilized in ArcMap. First, the CuatroCUTM feature dataset and the NeedXY table were added to a new map. The editor toolbar was opened and sketch tool chosen and set to create a new feature in the GPSXY layer. After zooming in on the basin to add points to the map, four points were added to the map for the Canal de Angostura, Pozo de Sandra, 1st tributary to Rio Mesquites, and Cave sample locations. In the attribute table, a new field called "Relate" was created. The null values were edited to numbers 1-4, based on the ObjectID of the corresponding sample in the NeedXY table. Finally, using the "Join" feature, the attributes from the NeedXY table were joined to the GPSXY feature class. The resulting feature and attributes were stored as a separate layer (XYGPS).

The final four layers containing the geochemical data and spatial locations were the GPS13, GPS14, GPSData, and GPSXY. In order to interpolate the chemical data for the basin, the layers were combined into one layer with all of the attributes of the four layers. For each layer containing the chemical data in the UTM Zone 13 projection, coordinates were added as fields in the attribute table using the Add XY tool in ArcToolbox. The data was then exported as database files, opened in Excel, copied and pasted into a new Excel spreadsheet. The final combined spreadsheet was saved as a database file (FinalGPS.dbf). A feature class was created from the database file using the XY coordinates as the location input. The feature class was added to the map and saved as a layer.

Viewing the chemical data in the GIS

Using the Spatial Analyst toolbar in GIS, the chemical data in the FinalGPS data layer was interpolated to a raster using the inverse distance weighted, spline, and kriging methods. All three methods were utilized to determine which had the most realistic results. They were utilized to create temperature and alkalinity rasters for the basin as well.

Appendix B

ANION RESULTS FROM RE-ANALYSIS OF SAMPLES WITH LARGE CHARGE BALANCES.

SAMPLE DESCRIPTION	Fluoride	Acetate	Formate	Chloride	Nitrite-N	Bromide
Detection Limits (1X)	<0.005	<0.005	<0.005	<0.005	<0.002	<0.002
All concentrations are in ppm (ug/g)						
SBE - 3 #1 (20X)	12.81	<0.10	<0.10	796.7	<0.05	3.413
SBE - 3 #2 (20X)	12.76	<0.10	<0.10	795.4	<0.05	3.463
SBE - 27 (5X)	2.296	0.11	<0.025	60.05	<0.010	0.262
SBE - 28 (5X)	2.377	0.08	0.07	86.55	<0.010	0.31
SBE - 30 (5X)	5.546	<0.025	<0.025	204.9	<0.010	0.823
SBE - 33 (5X)	4.319	<0.025	<0.025	326.5	<0.010	1.353
SBE - 34 (5X)	5.729	<0.025	0.041	257.7	<0.010	1.026

SAMPLE DESCRIPTION	Nitrate-N	Bi-Carbonate	Sulfate	Oxalate	Phosphate
Detection Limits (1X)	<0.001	<1	<0.010	<0.005	<0.002
All concentrations are in ppm (ug/g)					
SBE - 3 #1 (20X)	0.157	1167	5893	<0.10	<0.05
SBE - 3 #2 (20X)	0.073	1170	5866	<0.10	<0.05
SBE - 27 (5X)	0.862	249	907.4	0.242	<0.010
SBE - 28 (5X)	0.995	312	1223	<0.025	<0.010
SBE - 30 (5X)	0.057	394	3040	<0.025	<0.010
SBE - 33 (5X)	0.072	402	2928	<0.025	<0.010
SBE - 34 (5X)	0.101	412	3108	<0.025	<0.010

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Vita

Shanna Beth Evans was born in Sabetha, Kansas on August 4, 1878 to Robert and Mona Evans. After graduating from Westlake High School in Austin, Texas in 1996, she attended Baylor University in Waco, Texas. She received a B. S. in Geology in December, 2000, graduating cum laude. Her undergraduate thesis was written under Dr. Peter Allen, entitled The Effectiveness of an Artificial Wetland in Controlling Pollution. After graduating, she took an internship with Joshua Expeditions to lead educational eco-tours through the rainforests of Costa Rica. Upon her return to the U. S. A. the summer of 2001, she accepted a job as an Environmental Investigator at the Texas Commission on Environmental Quality (TCEQ) in the Edwards Aquifer Protection Program (EAPP).

Shanna entered the John A. and Katherine G. Jackson School of Geosciences Masters program at The University of Texas at Austin in the fall of 2003. She researched under the supervision of Dr. John M. Sharp, Jr. As a student, she was a teaching assistant for entry-level geology labs, and an upper-level Intro to Hydrology class. She presented her graduate research at the International Congress for Researchers in Cuatro Cienegas, Coahuila, Mexico in August 2004, at the Chihuahuan Desert Research Institute (CDRI) Symposium in October 2004, and the Texas State University (TSU) Groundwater: Towards Sustainability Conference in February 2005. She received best student poster awards at two of these conferences: the CDRI and TSU Groundwater: Towards Sustainability. She served as the Cookie Czar for the department during the Spring of 2005. Shanna also received the

Outstanding Teaching Assistant award at the end of the spring semester, 2005 for her assistantship in the Intro to Hydrology class. After graduation, Shanna will start a job with ERM, an environmental consulting firm in Austin.

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