Bingham Cienega Source Water Study

FINAL PROJECT REPORT

February 2001

Prepared by Pima Association of Governments for Pima County

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BINGHAM CIENEGA WATER SOURCE STUDY

PURPOSE

The purpose of this study was to determine the source of surface water in Bingham Cienega, a spring-fed wetland situated along the San Pedro River, east of the Santa Catalina Mountains and west of the Galiuro Mountains. The project included using the isotopic signatures for hydrogen and oxygen in combination with water chemistry data to determine similarities and differences between the waters at several locations within the study area. Determining the inputs from San Pedro River underflow and mountain-front recharge from the vicinity of Edgar Canyon Spring was the focus of this study. Water chemistry data from the Arizona Department of Environmental Quality database and previous studies were used to determine inputs from other canyons and the regional aquifer.

This three-year project was conducted by Pima Association of Governments (PAG) as part of the FY 1998-1999, FY 1999-2000, and FY 2000-2001 Work Programs with Pima County Flood Control District. Data collection occurred during the first two fiscal years of the project. The project was conducted by PAG under supervision of the Pima County Flood Control District.

BACKGROUND

Study Area

Bingham Cienega is a rare, perennial wetland located in Pima County, Arizona, approximately 2000 feet west of the lower San Pedro River, and 1/4 mile north of the settlement of Reddington (Figure 1). The Cienega is located within Township 11 South, Range 18 East, Sections 22, 23, 26, and 27 (Figure 2). It has been estimated that 95% of the low- to mid-elevation cienegas in Arizona have been lost (Hendrickson and Minkley, 1984). Bingham Cienega is located on the western side of the San Pedro River Valley, which is bounded by the Santa Catalina Mountains to the west and the Galiuro Mountains to the east. Canyons that open onto the San Pedro River between "The Narrows" and Bingham Cienega include Buehman and Edgar Canyons from the Santa Catalina Mountains, Teran Wash, Sierra Blanca Canyon, Hot Springs Canyon, Soza Wash, Aguja Canyon, and Redfield Canyon from the Galiuro Mountains, Kelsey Canyon from the Winchester Mountains, and Redrock Canyon, Roble Canyon, Paige Canyon, and Soza Canyon from the Rincon Mountains. In general, the canyons that originate in the Rincon and Santa Catalina Mountains are shorter and steeper than those that originate in the Galiuro and Winchester Mountains.

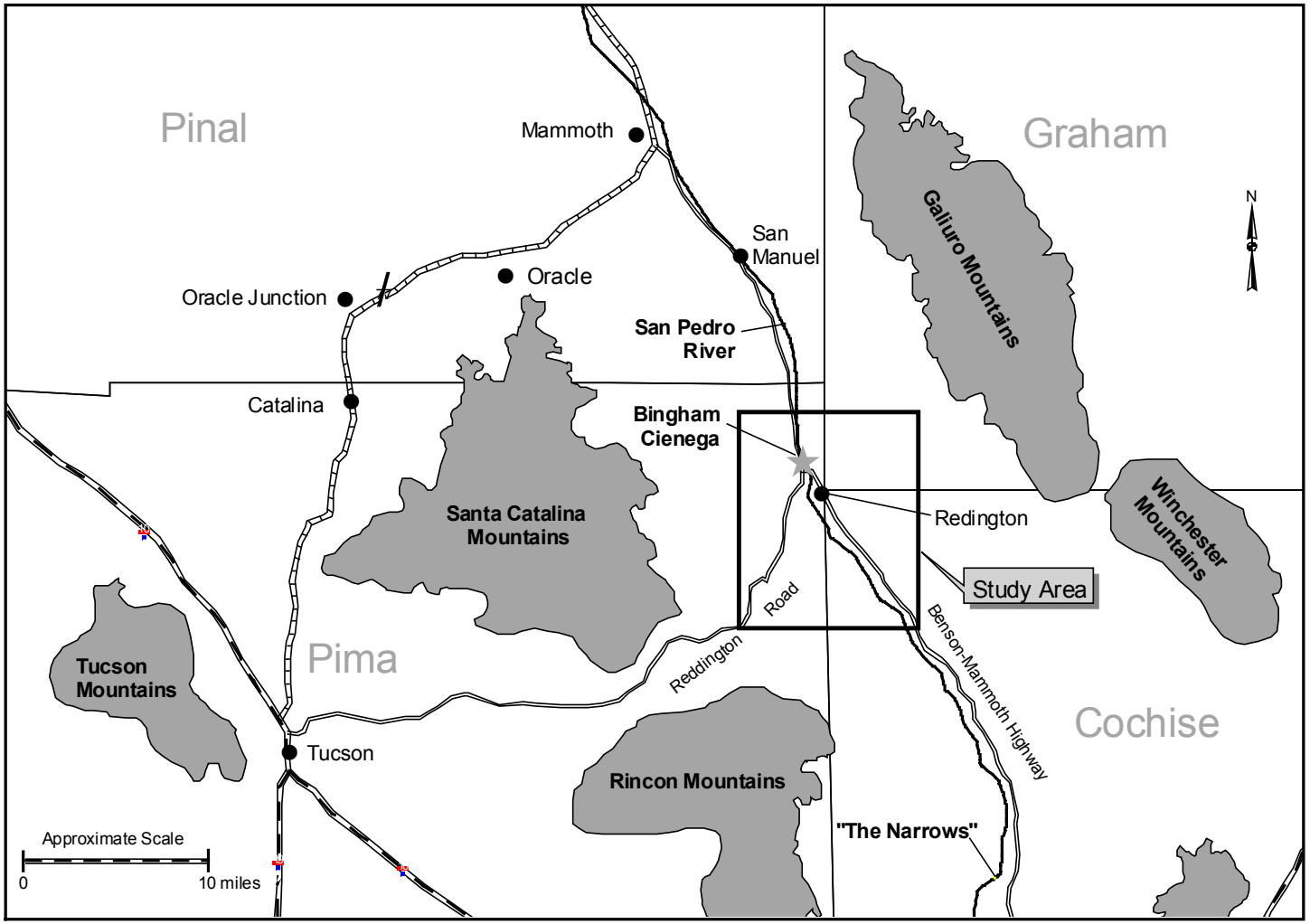
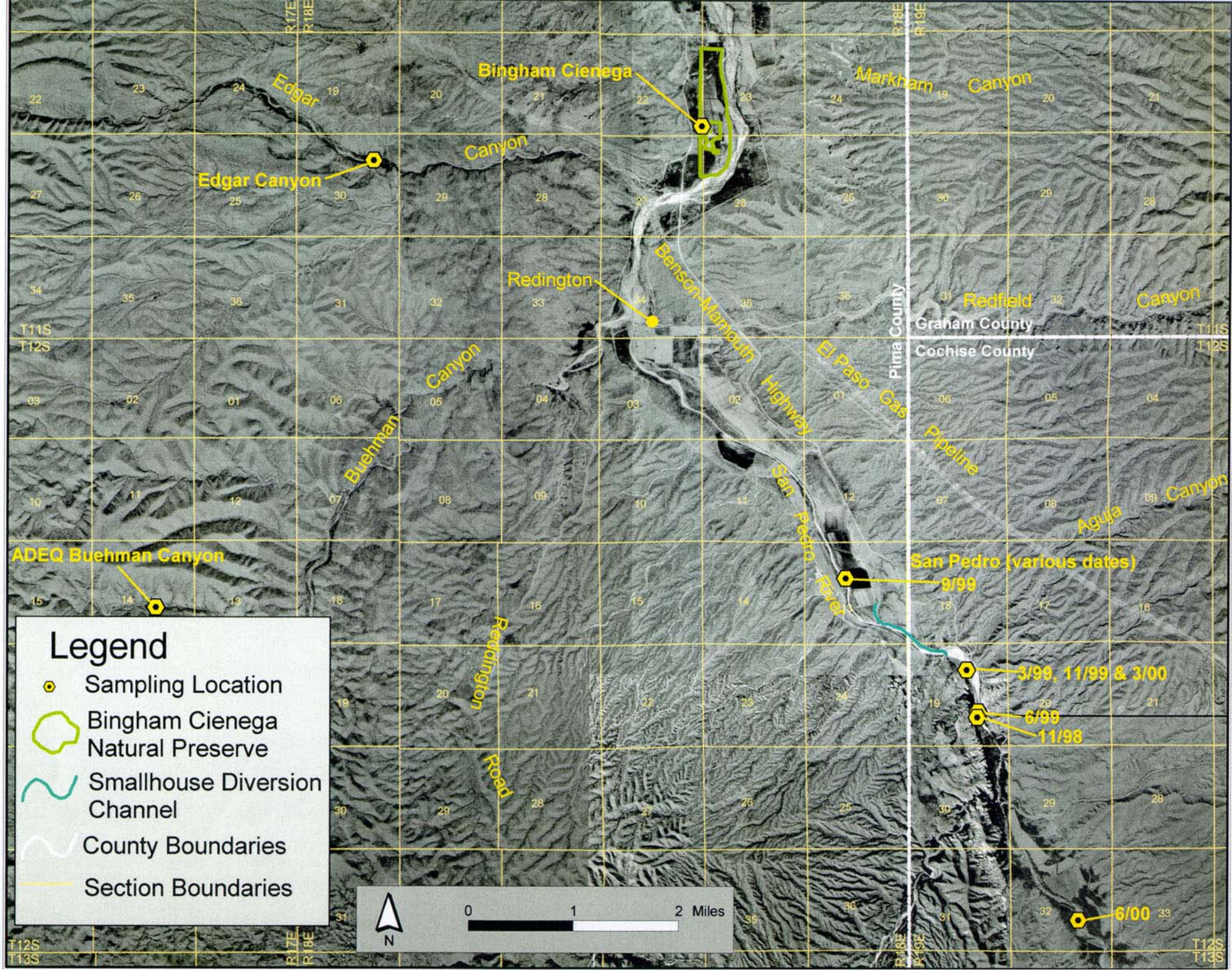


Figure 1. Study area location.


Bingham Cienega
Edgar Canyon
Redington
ADEQ Buehman Canyon
San Pedro (various dates)
9/99
3/99, 11/99 & 3/00
6/99
11/98
6/00
Edgar
Canyon
Markham
Canyon
Redfield
Canyon
Buehman
Canyon
Aguja
Canyon
Redington
Road
Benson-Mammoth
Highway
El Paso Gas
Pipeline
San Pedro River
Pima County
Graham County
Cochise County
T11S
T12S
T13S
R17E
R18E
R19E
Legend
Sampling Location
Bingham Cienega Natural Preserve
Smallhouse Diversion Channel
County Boundaries
Section Boundaries
N
0
1
2 Miles

Cienegas are low- to mid- elevation spring-fed wetlands, characterized by non-fluctuating shallow surface water. Soils associated with cienegas are permanently saturated, reducing Histisols. In general, cienega vegetation is usually dominated by herbaceous grass-like plants, although trees and shrubs are dominant in some areas (Hendrickson and Minkly, 1994). Springs in Bingham Cienega create riparian marshlands, ash swamps, and mesquite woodlands. Bingham Cienega supports populations of long-fin dace, lowland leopard frogs, and a wide variety of birds, reptiles and mammals (Baird et al., 1997). Dominant native and exotic plant species at Bingham Cienega include southern cattail (*Typha domingensis*), duckweed (*Lemna* sp.), watercress (*Rorippa nasturtium-aquaticum*), American bulrush (*Scirpus americanus*), cutleaf waterparsnip (*Berula erecta*), spikerush (*Eleocharis* sp.), willowherb (*Epilobium cilatum*), and Bermuda grass (*Cynodon dactylon*) (Baird et al., 1997). In the wooded area of the cienega, velvet ash (*Fraxinus velutina*) is the dominant tree species with willow (*Salix* sp.), cottonwood (*Populus fremontii*), buttonbush (*Cephalanthus occidentalis*), and yerba mansa (*Anemopsis californica*) as common associates (Personal Observation, PAG Staff). The woodland that surrounds the wetland area is dominated by velvet mesquite (*Prosopis juliflora*) (Personal Observation, PAG Staff, 2000).

Bingham Cienega and the surrounding area has historically been used for farming and ranching activities. In 1989, Pima County Flood Control District purchased the 28-acre Bingham Cienega along with 285 acres of surrounding land in order to restore natural ecological processes and to prevent floodplain development. The land is now managed for the District by The Nature Conservancy (Volunteers for Outdoor Arizona, 2000).

Previous Studies

Several geologic, hydrologic, and botanical studies have been conducted in the Lower San Pedro Valley near Bingham Cienega. Hydrological studies include: Arizona Department of Water Resources (1990); Anderson et al. (1992); Jahnke et al. (1995); Ronayne and Maddock (1996); Robertson (1991); and Robertson (1992). Geological mapping of the area is found in the following reports: Agenbroad (1967); Smith (1967); Halvorson (1984); Dickinson (1991); Dickinson (1998); and Richard et al. (2000). Baird et al. (1997) examined the vegetation of the cienega. Three previous studies included sections on the source of the cienega's surface water: Kenny (ND); Philips et al. (1994); and Ronayne and Maddock (1996).

Regional Geology

The project study area is located within the San Pedro River Valley, a fault-bounded trough that developed during late Miocene extension. Structural features of the region include a large, early-

Miocene detachment fault and associated hanging wall normal faults, both of which have been cross cut by basin-forming normal faults. Although the area is structurally complex, no faults have been mapped cutting basin-fill sediments in the Bingham Cienega area. Unexposed faults may exist in the underlying basement rocks.

Generalized depth-to-bedrock contours suggest that the bedrock surface below the valley-fill sediments forms two deep subsurface basins that are incompletely separated by a north-south-trending bedrock high (Richard et. al., 2000). This bedrock high is located within the PAG study area, and consists of Paleozoic and Cretaceous rocks exposed near Edgar Canyon. In addition, bedrock includes the regionally extensive Lower Miocene San Manuel Formation. Volcaniclastic rocks belonging to the Soza Canyon facies of the San Manuel Formation are exposed along the San Pedro River approximately 3.5 miles south of Redington. These rocks have been uplifted along one of the basin-bounding normal faults (Dickinson, 1998).

Mapping by Dickinson (1998) provided information about the valley-fill sediments in the Lower San Pedro Valley. In the Bingham Cienega project area, the basin-fill primarily consists of several facies of the Upper Miocene Quiburis Formation, which unconformably overlies the bedrock. Near Redington and Bingham Cienega, the Quiburis consists of an alluvial plain subfacies, which includes sandstone beds with interbedded reddish mudstone and carbonate nodules. This subfacies underlies and surrounds the San Pedro River flood-plain deposits. Flanking, and probably beneath, the alluvial plain subfacies is a gravelly alluvial-fan and braid plain subfacies of the Quiburis. This subfacies consists of conglomeratic streamflood and minor debris flow deposits.

Regional Hydrogeology

The hydrogeology of the San Pedro Basin near Bingham Cienega is complex and is known to include: 1) a flood-plain aquifer in the sediments along the San Pedro River and its tributaries; and 2) a deeper, underlying regional aquifer that is confined throughout most of the eastern portion of the basin (Ronayne and Maddock, 1996, Robertson, 1992). The regional confined aquifer is believed to hold approximately 84 million acre-ft of recoverable groundwater (Ronayne and Maddock, 1996). The water in this aquifer predominantly originates in the Galiuro Mountains and depths to groundwater near Bingham Cienega range from approximately 350 feet to 390 feet (Robertson, 1991 & 1992). Robertson (1992) suggested that the coarse-grained lower basin fill forms the regional aquifer and the overlying fine-grained basin fill serves as an aquitard and confining layer in the Lower San Pedro Basin.

The flood-plain alluvium that forms the matrix for the flood-plain aquifer is approximately 100 feet thick and is thought to contain approximately 1.3 million acre-ft of recoverable groundwater (Ronayne and Maddock, 1996). Bingham Cienega is underlain by streambed alluvium although it is outside the current channel area. The flood-plain aquifer underlies most of the river valley, which is approximately ¾ miles wide in this area (Robertson, 1992). The recent alluvial flood-plain aquifer in the Bingham Cienega area is directly underlain by the fine-grained upper unit of the Quiburis Formation, which is believed to be the confining layer for the regional aquifer. Within the flood-plain alluvial aquifer depths to water in wells near Bingham Cienega range from approximately 6 feet to 40 feet (Hill, 1998).

Geologic observations by PAG staff indicate that bedrock units in the lower San Pedro Valley are highly consolidated and probably do not form significant aquifers in the region. Ronayne and Maddock (1996) also concluded that the "crystalline and consolidated sedimentary rocks have a very low permeability and essentially act as hydrologic bedrock." Additionally Robertson's (1992) review of hydrogeology of the region does not contain any discussion of a bedrock aquifer system. Although it is possible that localized fracture aquifers exist near fault zones, no faults are exposed beneath or near Bingham Cienega. Unexposed faults may exist in underlying bedrock units.

Adjacent to Bingham Cienega, flow in the San Pedro River emerges at the surface and continues for a short distance almost directly north until it disappears below the surface. This surface/subflow regime is characteristic of the San Pedro River in the study area. The spring discharge that supports Bingham Cienega has ceased twice in this century. These events occurred from 1952 to 1953 and from 1974 to 1978, during times of drought in southern Arizona (Baird et al., 1997).

Edgar Canyon Spring, in the eastern foothills of the Santa Catalina Mountains west of Bingham Cienega, originates just upstream from the location where the Edgar Canyon streambed crosses the Quiburis/bedrock contact. Surface flow continues for a short distance until it percolates into the stream flood plain alluvium on the east side of the bedrock high.

Source Water Studies

Kenny (no date) examined the geology and geomorphology of the area of Bingham Cienega to determine the source for the spring. No travertine deposits were observed during the field inspection, suggesting that the spring water was not supersaturated with respect to calcium carbonate, which would be expected if the water had passed through carbonate rocks.

Kenny (no date) also noted that, the previous owner of Bingham Cienega said that the cienega had been too wet to cultivate in 1979 and 1984, two years of relatively high run-off in the San Pedro River. This evidence suggests that the source of Bingham Cienega's springs may not be the deep regional aquifer.

Robertson (1992) stated that the hydrologic flow in the San Pedro River Basin moves normal to the mountain ranges towards the basin axis. He used ^{14}C data to demonstrate that groundwater ages did not increase in a down-valley direction, the assumed direction of groundwater movement. He proposed that when water reaches the basin axis it is discharged mainly by evapotranspiration by the mesquite (*Prosopis* sp.) forests which extend along the entire axis of the basin. This proposal was based on measurements of tree density and size (Robertson 1992).

Phillips et al. (1994) demonstrated that the water in Bingham Cienega was not solely derived from a deep regional aquifer by comparing Robertson's (1992) radioactive isotope and water chemistry data from the regional confined aquifer with radioactive isotope and water chemistry data from Bingham Cienega and the flood-plain alluvial aquifer. ^{14}C analyses of water from wells drilled into the regional aquifer showed that water contained between 22.0 to 37.9 percent modern carbon (pMC). Calculated ages of the confined aquifer water, using $\delta^{13}C$ of -4.5‰ aquifer calcite, indicated that groundwater ages ranged between 5,200 and 10,600 years before present. Additionally, $\delta^{13}C$ analyses (-10.8‰ to -11.8‰) suggests that the carbon found in the confined aquifer is not from the dissolution of carbonate rocks, which would have yielded a isotopically heavier result (Robertson, 1992). Tritium analyses of the cienega sample (4.2 Tritium units, TU) and a nearby shallow well sample (5.5 TU) indicate that both the cienega and the shallow well water had at least some contribution from recent precipitation. The water from the regional confined aquifer did not contain any detectable amounts of tritium. The values for pH and bicarbonate (HCO_3^-) were lower in Bingham Cienega and the shallow well than in wells that had been drilled into the regional aquifer. Philips et al. (1994) suggested that the surface water originated from mountain-front recharge from the eastern slopes of the Santa Catalina Mountains.

Ronayne and Maddock (1996) modeled the hydrology of the Bingham Cienega area. The model assumed that a bedrock high in the area of the cienega forced San Pedro underflow to the surface resulting in surface flow at both Bingham Cienega and along a perennial reach of the San Pedro River. They based this assumption on a study by Agenbroad (1967). The model presented is only preliminary, but based on the results they suggest that San Pedro River underflow is responsible for spring discharge at Bingham Cienega.

Study Approach

This study attempts to determine the source of surface water in Bingham Cienega. The project approach involved sampling surface water at Bingham Cienega and at two potential source water locations and analyzing those samples for stable isotopes and the inorganic chemical composition of the water. Additionally, water chemistry data from this study is compared to data from previous studies (Robertson, 1992) and to data from the Arizona Department of Environmental Quality (ADEQ) surface water database. This work was supplemented by interpretations of available geologic maps of the region. Tracer tests and hydrogeologic models were not used in this study.

Stable isotopes of hydrogen (deuterium, D) and oxygen (^{18}O) are valuable indicators of a water's source. The deuterium and oxygen isotopic compositions of meteoric waters vary systematically with latitude, temperature, elevation and distance from oceanic source regions. Meteoric water isotopic variation closely follows the equation of the Meteoric Water Line, $\delta D = 8 * \delta^{18}O + 10$ (Craig 1961), where δ is a ratio of a sample relative to a standard and is reported in per mil: ‰ (parts per thousand). Kalin (1994) measured the isotopic signatures of various sources of precipitation in the Tucson basin as well as the values of water that infiltrated in two riparian corridors (Table 1). General trends in isotopic composition are that "lighter" (more negative δ values) are found in the winter/colder and mountainous/high-elevation precipitation, as would be expected.

Table 1. Isotopic composition of Tucson area precipitation (after Kalin, 1994). The average d-parameter (Gat, 1980) is the deuterium excess. The d-parameter of the Meteoric Water Line is 10 (see text). Values less than 10 are commonly indicative of evaporation, and values greater than 10 may be associated with snowfall.

Source	Average $\delta^{18}O$	Average δD	Average d parameter
Basin Summer Precipitation	-5.43 ‰	-38.63 ‰	4.98
Basin Winter Precipitation	-8.62 ‰	-57.76 ‰	11.14
Mountain Summer Precipitation	-7.20 ‰	-47.66 ‰	12.6
Mountain Winter Precipitation	-11.93 ‰	-71.44 ‰	24.0
Santa Cruz River Recharge	-8.60 ‰	-63.10 ‰	7.25
Rillito Creek Recharge	-9.20 ‰	-60.72 ‰	12.91

Evaporation affects the isotopic composition of surface waters. Through evaporation surface water becomes enriched with the heavier isotopes. However, such enrichment does not occur when water is lost through transpiration by plants (Clark and Fritz, 1997). Groundwaters inherits the isotopic composition of the parental waters (International Atomic Energy Agency, 1981). While

stable isotope data are useful in determining the source of meteoric water and the amount of evaporation the water has undergone, the interpretation of isotopic data can become complex due to post-infiltration processes. The conditions of the post-precipitation environment that may affect the isotopic and chemical composition of the groundwater include temperature, rock composition, water-rock ratio, fluid mixing, micro- and megascopic biochemical factors, and anthropogenic effects. Processes influential on water chemistry include water-rock interactions, including weathering of rocks and soil, and anthropogenic effects (Hem, 1985).

METHODOLOGY

Site Selection and Sampling Dates

For the study, one sampling site was established at Bingham Cienega and two sampling areas were established in potential source water areas (Figure 2). The Bingham Cienega sampling site was located in the southern portion of Bingham Cienega Natural Preserve near the spring discharge location. The first of the potential source water sites was located in Edgar Canyon approximately 2.8 miles upstream of the San Pedro River, and approximately 800 feet downstream of Edgar Spring, where the access road crosses the drainage. This site was chosen to represent the isotopic and ionic character of mountain-front recharge from the Santa Catalina Mountains. The second potential water source was the San Pedro River. Surface water samples were taken along a reach in the river between 5.7 and 8.2 miles upstream of Bingham Cienega. The location varied based on the downstream extent of surface flow, which either infiltrated into the streambed or was diverted by the Smallhouse Diversion Channel for irrigation purposes.

Surface water sampling was conducted over a two-year time span to capture any seasonal effects on the source of water found in Bingham Cienega. All three sites were sampled seven times: 11/23/1998, 3/19/1999, 6/15/1999, 9/10/1999, 11/20/1999, 3/30/2000, and 6/9/2000. Samples collected in September represent conditions during the summer rainy season. The November samples were collected to represent the dry fall season. June samples were taken during the dry spring season. The 1998/1999 and 1999/2000 winters were unusually dry causing samples to be collected in March, since substantial seasonal precipitation was not recorded earlier in the usually wet winter season.

Data from ADEQ's surface water database and from Robertson (1992) were used to better understand the potential contributions of water from various side canyons and the regional confined aquifer. These data can be found in Appendix C. Between the San Pedro sampling

reach and Bingham Cienega, four canyons enter the San Pedro: Edgar Canyon and the larger Buehman Canyon from the west and Aguja Canyon and Redfield Canyon from the east. Both of the western canyons have their headwaters in the Santa Catalina Mountains. Water chemistry data for Buehman Canyon were obtained from ADEQ to supplement the data collected by PAG for Edgar Canyon. The ADEQ samples were taken from a perennial reach of Buehman Canyon located in T12S R17E S14DB (Figure 2) on the following dates: 11/29/1995, 1/9/1996, 3/6/1996, 5/20/1996, 7/17/1996, 10/1/1996, 1/2/1997, 4/8/1997 (with duplicate), and 7/15/1997. Redfield Canyon is the larger of the two eastern canyons and drains the central portion of the Galiuro Mountains. ADEQ water chemistry data were obtained for two sites in Redfield Canyon. The downstream site is located at T11S R20E S31AC and was sampled three times on 2/4/1991, 4/29/1991, and 10/22/1991. The upstream site is located at T11S R20E S28BB and was sampled on 4/6/1992, 3/30/1993, 4/11/1994, and 4/29/1997. Neither of the ADEQ Redfield Canyon sites are shown on Figure 2 because they are outside of the depicted area.

Robertson's (1992) data for major ion and radioactive isotopes were used to represent the regional confined aquifer. Robertson's (1992) Sites 2,3,and 4 were used in this study. Cadastral locations for sites 2 and 4 are T11S R18E S26BBC and T11S R18E S03CDC respectively (Phillips et al., 1994). The cadastral location of site 3 is not given, but the site is reported to be less than three miles downstream of Bingham Cienega. Roberston sampled each site once: site 2 on 8/30/1981 and sites 3 and 4 on 8/7/1982.

Surface Water Sampling Procedures

In the field, PAG staff followed the procedures listed below for each sampling event:

1) Site selection based on availability of flow;
2) Measurement of field parameters;
3) Collection of isotope samples; and
4) Collection of water chemistry samples.

Upon arrival to the sampling area, PAG staff would locate appropriate sampling locations based on availability of flow. Variable flow availability at the San Pedro River site required samples to be taken at various locations along a 2.5 mile reach of the river (Figure 2). Bingham Cienega and Edgar Canyon sample locations were consistent, varying less than 50 feet for all seven sampling events (Figure 2).

Field parameters, including temperature, specific conductivity, and pH, were measured in the field and at the laboratory for each of the sampling events. For the first two sampling events

(11/23/1998 and 3/19/1999), PAG staff used a Hydac meter in the field. For subsequent sampling events (6/15/1999, 9/10/1999, 11/20/1999, 3/30/2000, and 6/9/2000), PAG staff used a Myron 6P Ultrameter. The change in parameter meter was necessary because the Hydac meter stopped working.

Bottles for water chemistry samples were prepared and pre-preserved by Turner Laboratories. Isotope bottles were prepared in the field by rinsing the bottle three times with sample water prior to filling to assure the bottle contained only the water being sampled. Except for the 6/9/2000 Edgar Canyon sample, water chemistry samples were filtered in the field using a 0.45-micron filter. The 6/9/2000 Edgar Canyon water chemistry sample was filtered by Turner Labs before analysis because filters failed in the field. The sample bottles for both isotope and water chemistry analyses were individually labeled in indelible ink with the sample name, date and time of collection. The samples were collected in containers that were tightly sealed, with minimal headspace, and chain-of-custody forms accompanied the samples from the field to the laboratory. Duplicate samples were collected for all sampling events. The samples for stable isotope analysis were hand delivered to the University of Arizona's Laboratory of Isotope Geochemistry. Water chemistry samples were stored in an ice chest until they were hand-delivered to Turner Laboratories in Tucson, Arizona for cation/anion analyses.

Laboratory Procedures & Quality Assurance/Control Procedures

Stable Isotopes

All stable isotope analyses were performed by the University of Arizona's Laboratory of Isotope Geochemistry in Tucson, Arizona. All $\delta^{18}O$ and δD measurements were made with a Finnegan DELTA-S mass spectrometer. $\delta^{18}O$ analyses were performed on carbon dioxide with which the water samples were equilibrated. δD analyses were performed on hydrogen that was liberated from the water samples by reaction with chromium. The laboratory calibrated relative to Vienna Standard Mean Ocean Water (V-SMOW), Standard Light Antarctic Precipitation (SLAP), and Greenland Ice Sheet Precipitation (GISP), which are international standards for stable isotope measurements in natural waters (Laboratory of Isotope Geochemistry, 1992; Laboratory of Isotope Geochemistry, 1997).

Water Chemistry

Samples were submitted to Turner Laboratories in Tucson, Arizona for analysis. Turner Laboratories conducted all water chemistry analyses except for the metals analyses for the

3/19/99, 9/10/99, and 11/20/99 samples, which were subcontracted to Severn Trent Laboratories in Pensacola, Florida. Severn Trent Laboratories were used because they could measure to a low enough practical quantitation limit (PQL) so that aluminum, potassium, and manganese could be measured in these waters. For each sample, analyses were run for silicon, calcium, magnesium, manganese, potassium, sodium, arsenic, sulfate, alkalinity (as $CaCO_3$), specific conductivity, pH, and total dissolved solids (TDS). Chloride was analyzed in all samples except for the 3/19/1999 sampling event when a chlorine analysis was erroneously requested. Barium, beryllium, chromium, copper, iron, nickel, silver, zinc, lead, and bromide were analyzed in the first sampling event. Because these ions were not detected in the first samples, they were dropped from the sample plan. Fluoride analysis was run for the 11/23/1998, 6/15/1999, 9/10/1999, 11/20/1999, 3/30/2000, and 6/9/2000 samples.

PAG staff completed a quality assurance/quality control analysis for each set of results from the water chemistry laboratories. This included a cation/anion balance analysis for each set of results, and comparison of duplicate sample results. Duplicate samples were taken at one of the sites during each sampling round. These samples were analyzed as a double check on the water quality results. Duplicate samples showed excellent correlation, indicating that the data consistency was high. Variations in the cation/anion balance probably reflect the absence of one or more ions from the analysis. Only analyses for the selected ions were conducted. All of the samples were within the accepted range of less than 5% for the charge balance, except for the 3/19/1999 San Pedro River sample, which had a charge imbalance of 9.26%, probably due to the absence of chloride analysis, and the 6/9/2000 Edgar Canyon sample which had a charge imbalance of 7.43%, probably due to the absence of another ionic analysis.

RESULTS AND DISCUSSION

Stable Isotopes

δD and $\delta^{18}O$ values for the Bingham Cienega, Edgar Canyon and the San Pedro River are included on Table 2 and are plotted separately on Figures 3 and 4. The δD vs. $\delta^{18}O$ values are plotted on Figure 5. All but one of the δD vs. $\delta^{18}O$ values of Bingham Cienega and Edgar Canyon plot very near the meteoric water line, which suggests that the water has not undergone evaporation. This was expected since both sites were sampled very close to the point where the water emerges from the ground. The 6/9/2000 Bingham Cienega data indicated that the sample

Table 2. Isotope analysis results, 11/1998-6/2000.

Sample	Bingham Cienega			Edgar Canyon			San Pedro River		
Date	O-18	D	d-par	O-18	D	d-par	O-18	D	d-par
11/23/1998	-9.3	-63.5	10.9	-9.8	-68.5	9.9	-9.3	-65.5	8.9
3/19/1999	-9.4	-66	9.2	-9.8	-71	7.4	-9.4	-68	7.2
6/15/1999	-9.6	-65	11.8	-9.7	-68	9.6	-9.0	-63	9.0
9/10/1999	-9.5	-65	11	-10.0	-70	10	-8.9	-63.5	7.7
11/22/1999	-9.4	-68	7.2	-10.1	-73	7.8	-9.4	-70	5.2
3/30/2000	-9.5	-66	10	-10.0	-70	10	-8.6	-67	1.8
6/9/2000	-8.6	-63	5.8	-9.6	-69	7.8	-9.5	-67	9.0
Average	-9.3	-65.2	9.4	-9.9	-69.9	8.9	-9.2	-66.3	7.0

Note: All isotope measurements in o/oo V-SMOW.

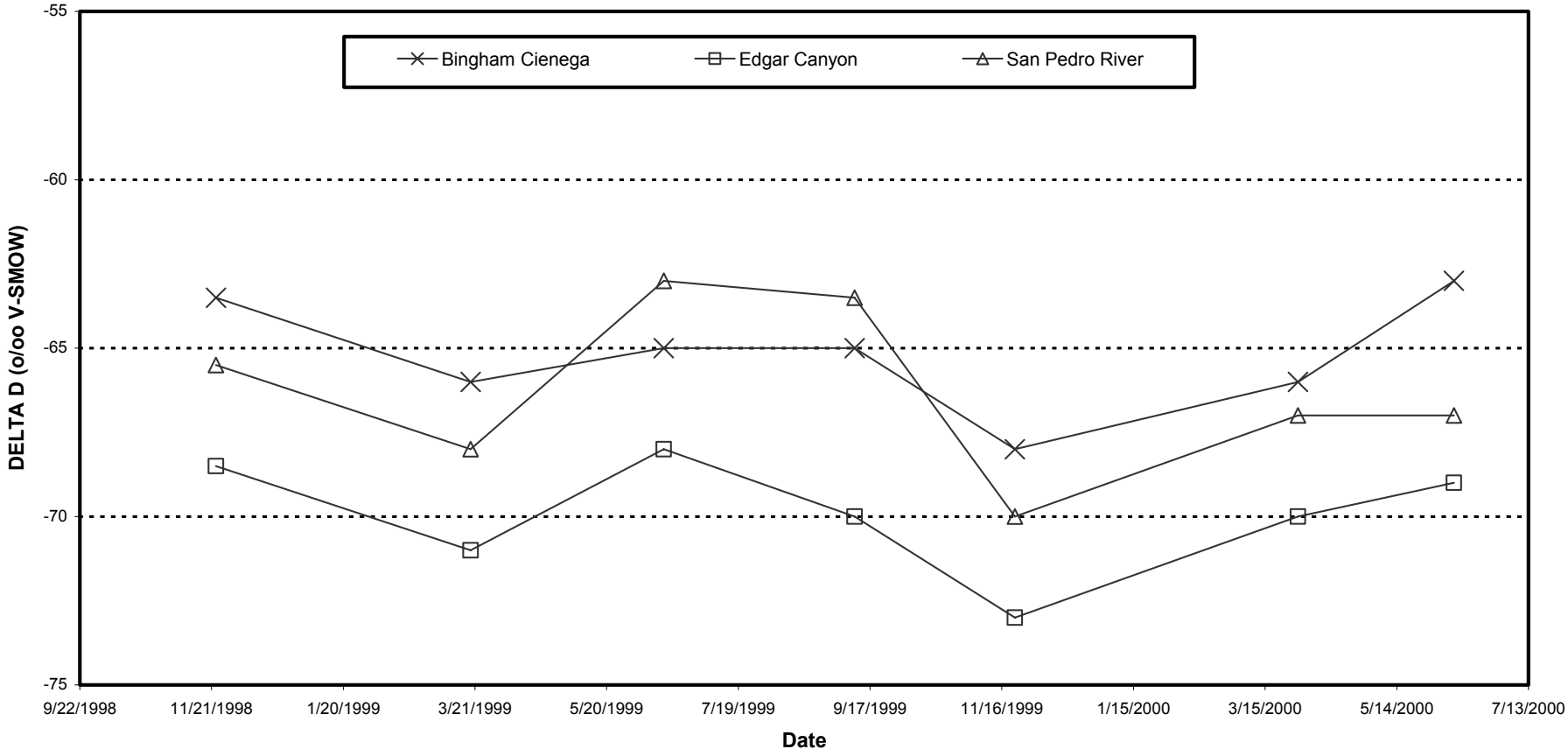


Figure 3. Deuterium isotope results, 11/1998 - 6/2000.

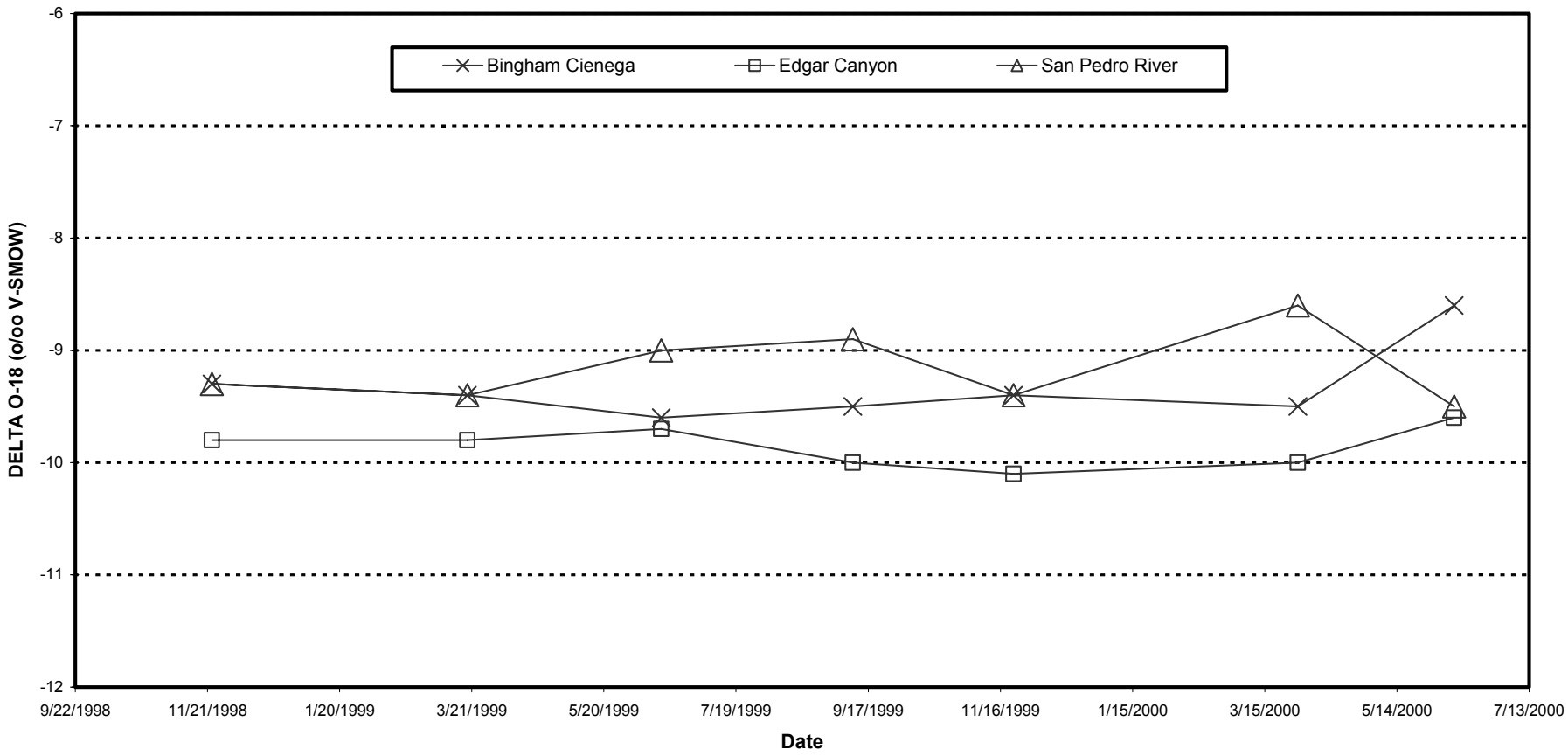


Figure 4. Oxygen-18 isotope results, 11/1998 - 6/2000.

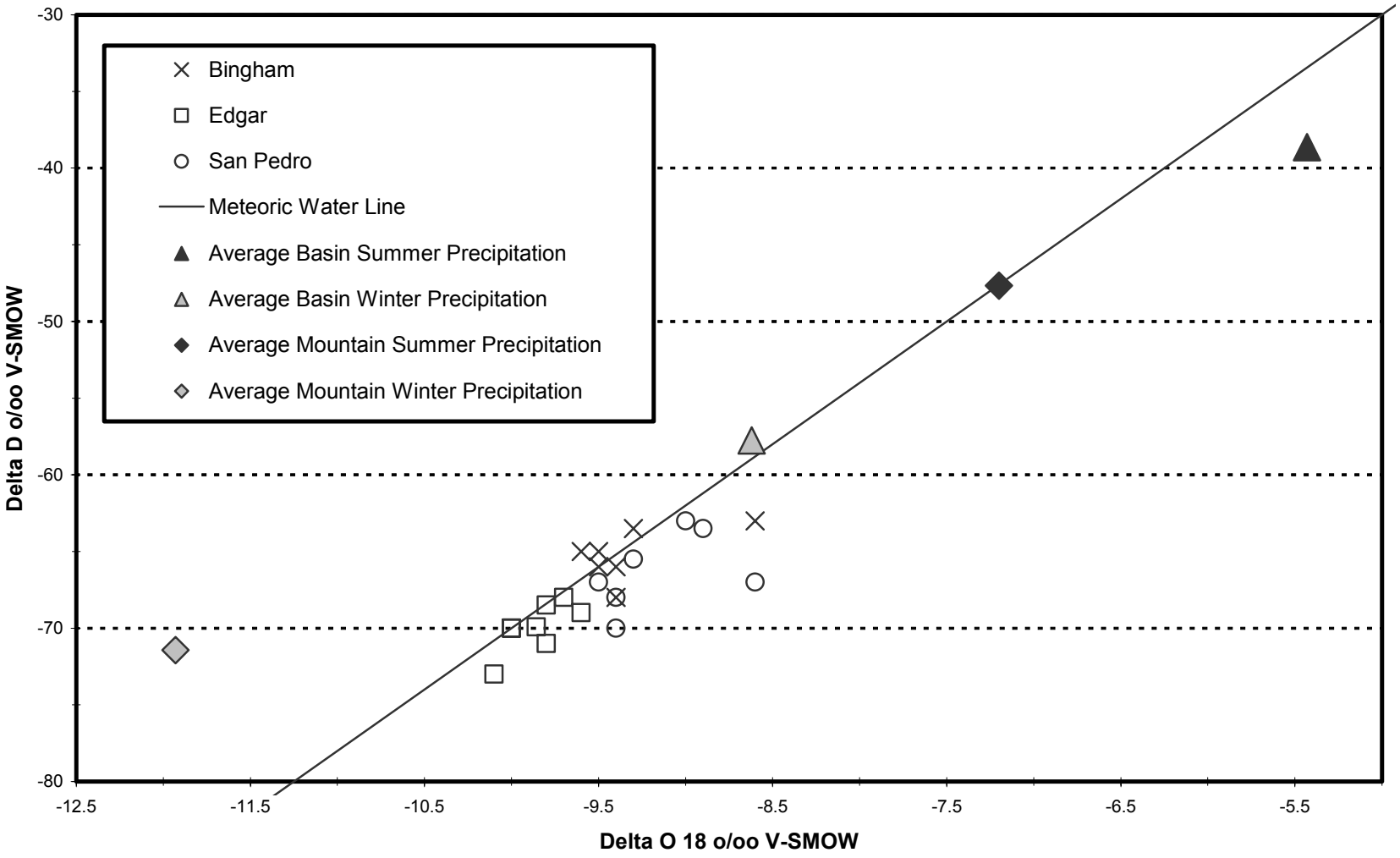


Figure 5. δD vs. $\delta^{18}O$, 11/1998 - 6/2000. Average values are from Kalin (1994).

had undergone evaporation. This sampling event occurred when discharge from the spring at the cienega had ceased and the sample was taken from a standing pool. This sample was not considered in the statistical analysis because it was not representative of the site. The San Pedro samples are highly variable but are consistently below the meteoric water line which is characteristic of the partially evaporated surface water in semi-arid to arid regions.

The isotopic values for Bingham Cienega and the two potential source waters fall in the range of local mountain precipitation reported by Kalin (1994). Statistical analysis (analysis of variance or ANOVA) was conducted on the δD and $\delta^{18}O$ values from each of the samples. This was done to determine if a significant difference in the isotopic signatures existed between the different sampling locations. The statistical analysis was conducted using SYSTAT 9.0 (SPSS, 1999) software. When the values were grouped by site, significant differences ($p<0.05$) were found in both oxygen and hydrogen isotope ratios. Subsequent pairwise Bonferroni adjusted comparisons were conducted to determine which sites were different from each other. Pairwise comparisons of δD and $\delta^{18}O$ values showed significant differences between Edgar Canyon and the other two sites. Edgar Canyon samples are isotopically the lightest, suggesting that water in Edgar Canyon is derived from the highest elevation precipitation. Significant differences were also found between the $\delta^{18}O$ values for Bingham Cienega and the San Pedro River. Bingham Cienega water is isotopically lighter than the water sampled from the San Pedro River.

San Pedro samples exhibited more variability in isotopic ratios than Edgar Canyon and Bingham Cienega. Standard deviations of San Pedro $\delta^{18}O$ and δD were 0.33 and 2.48 compared to 0.10 and 1.50 for Bingham Cienega and 0.18 and 1.69 for Edgar Canyon. The greater variability in the San Pedro isotopic ratios suggests that the large catchment region for the river provides water derived from different sources at different times. Additionally, the effects of evaporation on the isotopic signature of the San Pedro samples were variable because of differences in temperature and distance between the location where the sample was taken and the point of emergence. The relatively constant $\delta^{18}O$ and δD values for Edgar Canyon and Bingham Cienega indicate that both waters are derived of either a homogeneous precipitation source or a well blended mixture of different precipitation sources.

Based on a graph of δD vs. $\delta^{18}O$ (Figure 5), the stable isotopic composition of Bingham Cienega surface water could not be derived solely from either Edgar Canyon surface flows. Additionally due to differences in $\delta^{18}O$ values, Bingham Cienega is not soley derived from the San Pedro River. However, Bingham Cienega water appeared to have an isotopic signature similar to δD and

$\delta^{18}O$ values that would be expected either for San Pedro River surface water that had not been evaporatively enriched, or for a mixture consisting of un-evaporated San Pedro water and an amount of Edgar Canyon water. Perhaps underflow along the San Pedro floodplain aquifer would not be subject to as much evaporative enrichment as the water that PAG sampled at the surface, particularly since the samples were taken close to the end of flow in a losing reach of the river. A plausible interpretation of the stable isotope data may be that the source of Bingham Cienega surface water is either San Pedro underflow, or a mixture of San Pedro underflow and water from mountain-front recharge that is isotopically similar to Edgar Canyon spring water.

Another set of ANOVAs was run to determine if any seasonal trend was present in the data. The differences from site mean were examined by season of sampling (summer monsoon, dry fall, winter rainy, and dry spring). No significant differences ($p<0.0.5$) were found in the data. However, the sampling period was of limited duration so the test may not be powerful enough to detect seasonal differences with such a small data set. In addition, the exceedingly dry winters during the study period would have a homogenizing effect on the data.

Water Chemistry

The water chemistry data gathered for this report are summarized on Table 3. Laboratory-measured parameters are graphed on Figure 6 and average anion and cation concentrations are depicted by site in Figures 7-8. Ion concentrations for each monitoring event by site are found in Appendix A. One-way ANOVAs were conducted to determine if significant differences existed between sampling sites for ionic concentrations and general parameters. If significant differences were found, post-hoc pairwise Bonferrioni tests were run to determine which sites were significantly different from each other.

Laboratory-measured parameters are depicted (Figure 6) because the parameter meter used in the field initially malfunctioned. pH was lowest at Bingham while no significant differences could be found between Edgar Canyon and San Pedro River. Electric conductivity (EC) was lowest at Edgar Canyon and was highest at San Pedro. When the Bingham Cienega 6/9/2000 (the uncharacteristic evaporated sample, as per isotopic analysis) analysis was removed, the one-way ANOVA performed on TDS values showed significant differences. The post-hoc Bonferrioni comparisons found that the San Pedro samples had significantly higher TDS levels than either Bingham Cienega or Edgar Canyon; however, Bingham Cienega and Edgar Canyon were not significantly different from each other (Figure 6).

Table 3. Water chemistry summary, 11/1998 - 6/2000.

Bingham Cienega

	11/23/1998	03/19/1999	06/15/1999	09/10/1999	11/20/1999	03/30/2000	06/09/2000
Silicon (Si)	15	14	12	14	13	16	17
Aluminum (Al)	0	0	0	0	0	–	–
Calcium (Ca)	67	67	55	60	63	62	73
Magnesium (Mg)	13	13	10	12	12	12	14
Manganese (Mn)	0.11	0.05	0	0.16	0.19	0.035	0
Potassium (K)	0	4.4	0	3.6	3.9	0	0
Sodium (Na)	45	45	32	42	42	39	38
Arsenic (As)	0.0063	0.008	0	0.006	0	0	0.01
Chloride (Cl)	11.3	–	10.2	11	11	10	11
Sulfate (SO_4)	69.8	63.7	48.4	53	56	50	50
Fluoride (F)	1.1	–	–	1.2	1.3	1	1.1
Alk. as $CaCO_3$	234	238	204	200	220	210	230
Lab TDS	250	320	310	230	250	200	400
Lab Conductivity	580	570	520	590	560	560	600
Lab pH	7.4	7.7	6.9	6.8	7.1	7.3	7.6

San Pedro River

	11/23/1998	03/19/1999	06/15/1999	09/10/1999	11/20/1999	03/30/2000	06/09/2000
Silicon (Si)	14	13	13	13	12	15	15
Aluminum (Al)	0	0	0	0	0	–	–
Calcium (Ca)	65	74	52	55	73	58	68
Magnesium (Mg)	15	17	14	16	16	16	15
Manganese (Mn)	0	0.01	0	0	0	0	0
Potassium (K)	0	4.6	0	6.6	4	0	0
Sodium (Na)	50	56	51	56	56	56	60
Arsenic (As)	0.0054	0.005	0	0.005	0	0	0
Chloride (Cl)	15	–	17.2	19	19	18	17
Sulfate (SO_4)	81.8	89.8	92.5	99	100	83	85
Fluoride (F)	0.8	–	–	0.8	1	1	1
Alk. as $CaCO_3$	230	224	212	180	250	230	230
Lab TDS	370	370	390	300	340	250	390
Lab Conductivity	590	630	620	670	630	610	680
Lab pH	8.2	8.6	7.9	8	8	8	8

Edgar Canyon

	11/23/1998	03/19/1999	06/15/1999	09/10/1999	11/20/1999	03/30/2000	06/09/2000
Silicon (Si)	17	16	19	20	16	18	21
Aluminum (Al)	0	0	0	0	0	–	–
Calcium (Ca)	62	70	56	67	71	67	58
Magnesium (Mg)	14	15	14	16	16	14	14
Manganese (Mn)	0	0	0	0.07	0	0	0.021
Potassium (K)	0	2.7	0	2.8	2.4	0	0
Sodium (Na)	26	24	24	22	22	21	26
Arsenic (As)	0	0	0	0	0	0	0
Chloride (Cl)	6.3	–	7.7	8	7.9	5.8	5.9
Sulfate (SO_4)	20.8	22.4	20.9	14	21	18	13
Fluoride (F)	0.4	–	–	0.5	0	0.56	0.47
Alk. as $CaCO_3$	242	254	228	250	260	230	200
Lab TDS	290	270	320	270	290	310	260
Lab Conductivity	470	500	490	540	490	460	450
Lab pH	7.9	8.2	7.5	7.7	7.9	8	7.8

NOTE: "0" = constituent was not detected at the Pratical Quantitation Limit (PQL) used by Turner or Severn Trent Laboratories.

"–" = constituent was not included in the analysis.

All measurements are in mg/l except for conductivity which are in mmhos, and pH.

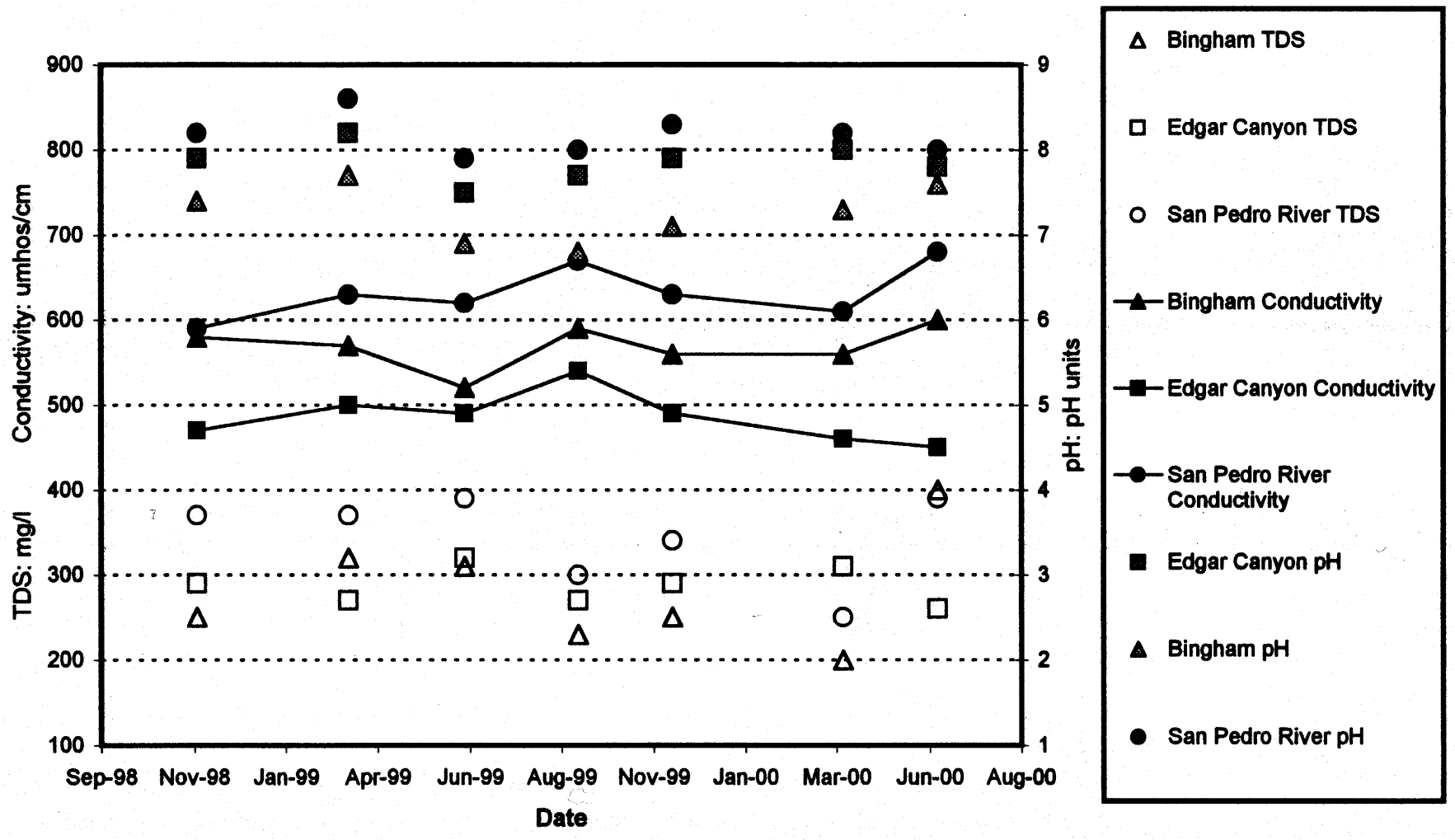


Figure 6. Laboratory TDS, Conductivity, and pH, 11/1998-6/2000.

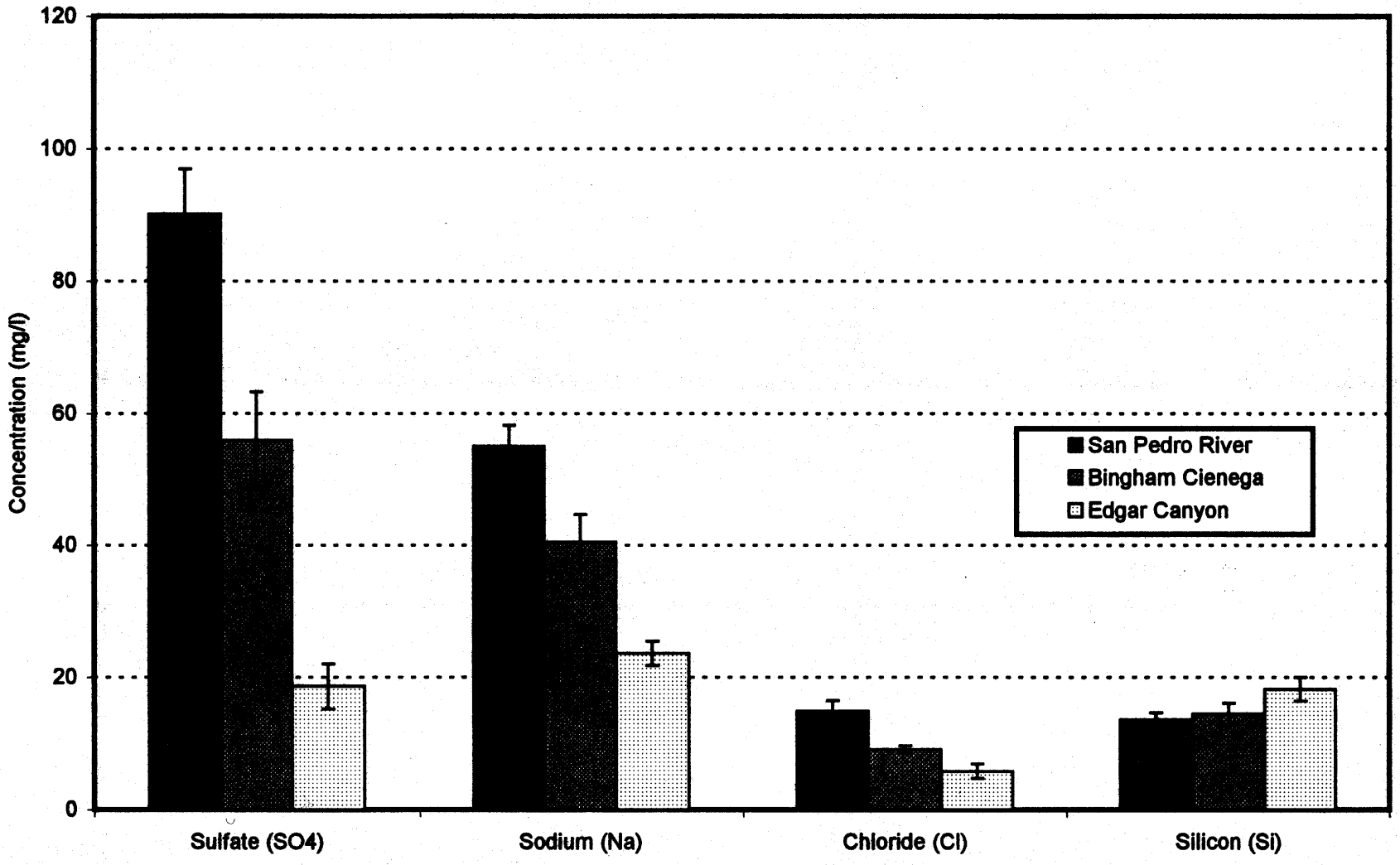


Figure 7. Average sulfate, sodium, chloride, and silicon concentrations by site. Error bars indicate the limits of 95% confidence intervals above and below the mean.

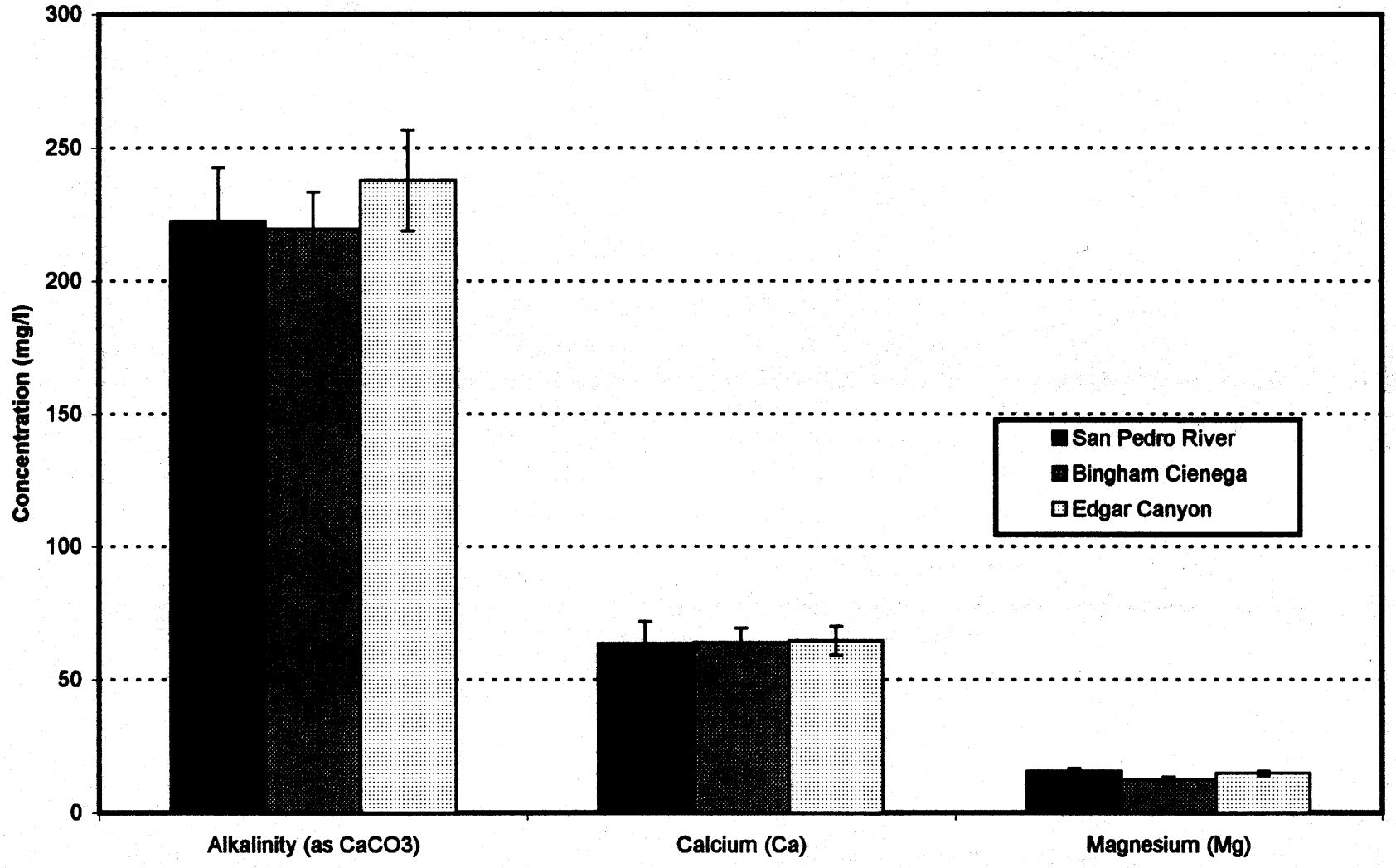


Figure 8. Average calcium, sodium, and alkalinity (as $CaCO_3$) concentrations by site. Error bars indicate the limits of 95% confidence intervals above and below the mean.

Sulfate (SO_4), sodium (Na), and chloride (Cl) ion concentrations all show similar patterns (Table 3, Figure 7). The concentrations of these ions at Bingham Cienega are between the concentrations at the two potential source water sites. The differences between all three sites are significant ($p<0.05$). Because these ions have high solubility, they would be concentrated in water by evaporation. The higher concentrations found in San Pedro samples therefore support the interpretation from the stable isotope data, that the water in the San Pedro has been affected by evaporation more than the other two sites. Silicon (Si) concentrations were the highest at Edgar, but differences did not exist between the Bingham and San Pedro sites (Figure 7).

Calcium (Ca) concentrations were very similar between sites, ranging from 52 mg/l to 74 mg/l. The highest and lowest values were both from the San Pedro site. No significant differences between sites could be found in calcium (Figure 8). No significant differences existed for alkalinity (as $CaCO_3$) concentrations between sites. Alkalinity (as $CaCO_3$) averaged approximately 220 mg/l (Figure 8). Magnesium (Mg) concentrations were lowest at Bingham but the other two sites were not significantly different from each other (Figure 8).

Average concentrations of manganese (Mn) were significantly higher at Bingham Cienega than concentrations at either the San Pedro River and Edgar Canyon sources (Table 3). This was probably due to the reducing environment of the cienega. Mn is only found dissolved in reducing environments (Hem, 1985).

Other low-concentration ions of interest include fluoride (F), potassium (K), and arsenic (As). Fluoride analyses were conducted for five of the seven sampling events (Table 3). Fluoride levels for Buehman Canyon ADEQ surface water database samples were significantly higher than all other sites, using post-hoc Bonferroni adjusted pairwise comparisons (Intercooled Stata 6.0). The next highest levels of fluoride were found in the samples from Bingham Cienega and Robertson's (1992) confined aquifer sites (Robertson 1992); however the concentrations at Bingham Cienega were not significantly higher than concentrations found in the San Pedro River. Both Bingham Cienega and confined aquifer samples had significantly higher fluoride levels than Edgar and Redfield Canyons. That fluoride levels for Bingham Cienega fall between different surface water sources (lower than Buehman Canyon and higher than the San Pedro River as well as Edgar and Redfield Canyons) suggests that the potential source waters could be combined to result in a water with a fluoride concentration similar to that of the Bingham Cienega samples. However, the fluoride data do not rule out potential contributions to Bingham Cienega from the regional aquifer.

To compare potassium concentrations, the data from the 3/19/99, 9/10/99 and 11/20/99 were examined. Severn-Trent Laboratory, who conducted the metals analyses for these sampling events, has a PQL of 1.0 mg/l in comparison to the 5.0 mg/l PQL of Turner Laboratories who conducted the metals analyses for the other sampling events. All values from the Severn-Trent analyses were below 5.0 mg/l. A one-way ANOVA (Intercooled Stata 6.0) conducted of the three Severn-Trent analyzed sampling events found significant differences between the three sites, and post-hoc Bonferroni adjusted pairwise comparisons found that the San Pedro River samples contained significantly higher potassium concentrations than did the Edgar Canyon samples.

For all sites, arsenic levels in the samples were either below or barely above the PQL of 0.005 mg/l. For all seven sampling dates, arsenic concentrations at Edgar Canyon were below the PQL. San Pedro samples contained measurable levels of arsenic in three of the seven sampling events, and Bingham Cienega samples contained measurable levels of arsenic in four of the seven sampling events. No statistically significant differences (One-way ANOVA, Intercooled Stata 6.0) could be found between the arsenic concentrations of the three sites, because non-detects were treated as zeros.

The water chemistry data (excluding the 03/19/1999 sampling event when chloride was not analyzed) were plotted onto a Piper Diagram (Figure 9) using the HydroChem (Rockware, Inc., 1998) software package. Data from the ADEQ surface water database for the Buehman Canyon site and the two Redfield Canyon sites are included on the diagram. These data were included because both Redfield and Buehman Canyons have large catchments, have significant perennial reaches, and intersect the San Pedro River downstream of the PAG sampling site. The Piper Diagram also includes data from Robertson (1992) for wells drilled into the regional confined aquifer, to evaluate whether Bingham Cienega water could have originated from upward leakage from the confined aquifer. Robertson's (1992) sites 2, 3, and 4 were included because of their proximity to Bingham Cienega.

The Bingham Cienega, San Pedro River, Edgar Canyon, and Buehman Canyon samples cluster on the Piper Diagram, indicating similar chemistry. However, each site clusters independently along a linear pattern with end members being Edgar Canyon (relatively higher in calcium and carbonate and lower in sulfate and sodium) and the San Pedro River (relatively higher in sulfate and sodium while lower in calcium and carbonate). Bingham Cienega plots slightly closer to the San Pedro cluster and Buehman Canyon plots closer to Edgar Canyon. The general position of each of the individual clusters suggests (as per Hounslow, 1995) that mixing of these waters could

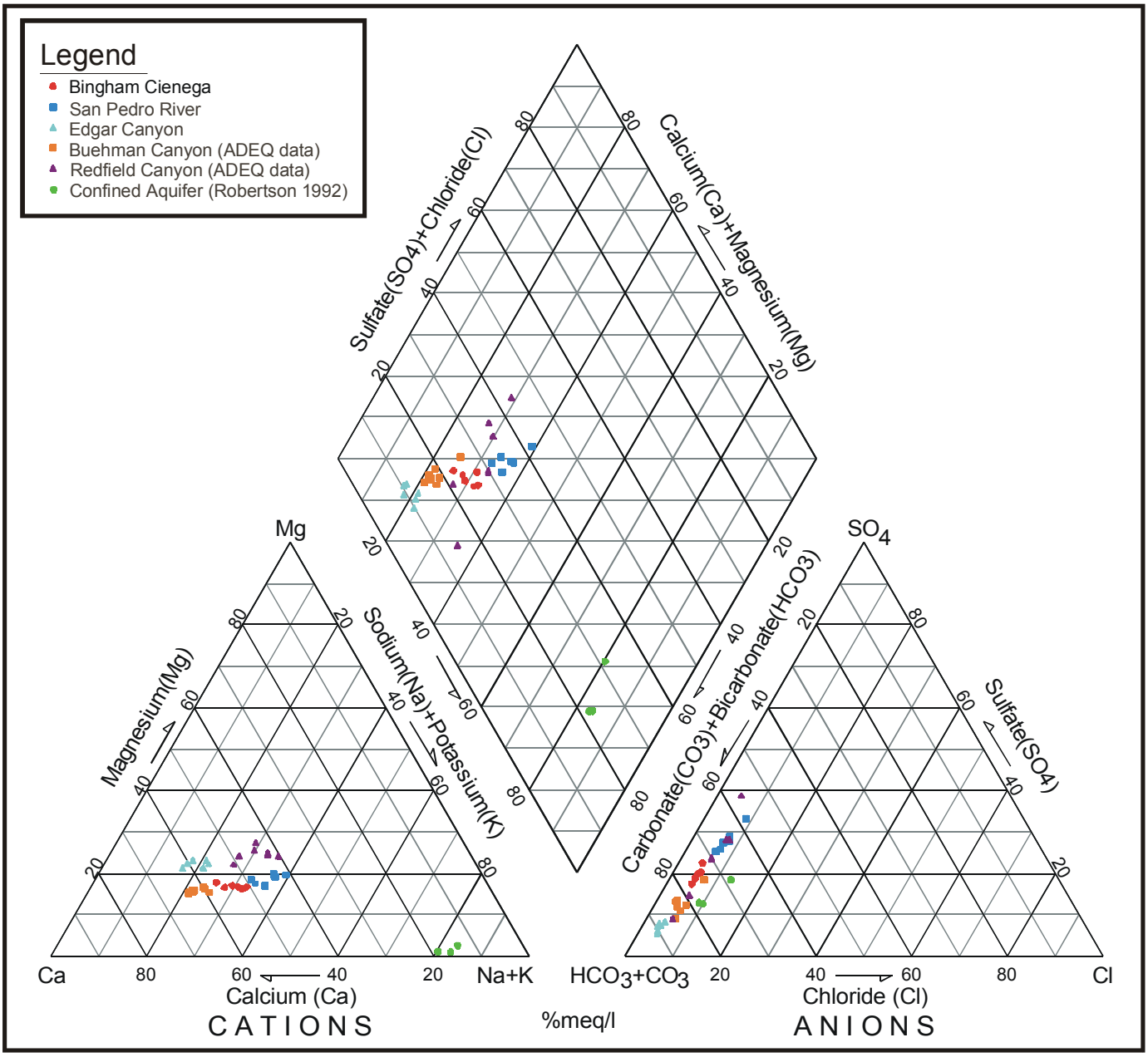


Figure 9. Piper diagram of samples, 11/1998-6/2000 with ADEQ Buehman and Redfield Canyons samples and confined aquifer samples from Robertson (1992).

be responsible for the chemistry of Bingham Cienega. The Redfield Canyon data is more variable than the other four sites, but the averaged ionic concentration for Redfield Canyon plots within the cluster of samples from Bingham Cienega.

The regional confined aquifer data (Robertson, 1992) plotted in a distinctly different area than the surface waters on the Piper Diagram. Anion differences between samples from the confinedaquifer and surface water samples were small although the confined aquifer had more chloride in solution. The confined aquifer had relatively lower magnesium and calcium concentrations and relatively higher sodium concentrations than the surface water. Robertson (1992) attributed the low magnesium and calcium concentrations in the confined aquifer to removal by montmorillonite and calcite precipitation. It is unlikely that enough sodium for calcium cation exchange could occur during percolation of confined aquifer water to the surface, for the groundwater to be transformed into a water with a chemical composition of Bingham Cienega water. Additionally, fluoride concentrations in the confined aquifer are approximately twice (average of three well samples 1.9 mg/l) that of the Bingham Cienega samples (average 1.1 mg/l ignoring non-detections).

CONCLUSIONS

Several possible sources of the surface water in Bingham have been suggested: upward leakage from the deep regional confined aquifer; mountain-front recharge from the Santa Catalina Mountains (Phillips et al., 1994); or San Pedro River underflow along the floodplain aquifer (Kenny, ND; Ronayne and Maddock, 1996). This study attempted to test the validity of the three hypotheses using major and minor ion and stable isotope data. PAG's water chemistry and stable isotope sampling was designed to evaluate the inputs to Bingham Cienega from San Pedro underflow and from mountain-front recharge.

It is unlikely that upward leakage from the confined aquifer is the source of water for Bingham Cienega. The cienega has gone dry twice in the past century during times of drought, which would not be likely if upward leakage were the source of the cienega surface water. In addition, the ionic signature of the cienega's water was considerably different from the ionic signature of the regional confined aquifer. Also carbon-14, tritium, pH, temperature, TDS, and bicarbonate data support the hypothesis that Bingham Cienega could not be solely derived from a deep regional aquifer (Phillips et al. 1994).

The available stable isotope data for Bingham Cienega, Edgar Canyon, and the San Pedro River

suggest that a simple mix of water from the San Pedro and Edgar Canyon cannot be responsible for the isotopic signature found in the cienega samples. However, if the San Pedro subflow was less evaporated than the surface flow, a mixture of the subflow and the water from Edgar Canyon could result in water isotopically similar to that found in Bingham Cienega. The San Pedro samples were taken near the end of flow in a losing reach of the stream. Since the stream in this reach is not receiving continuous contributions from the subflow, the surface water would become more and more evaporatively enriched (*sensu* Allison et al., 1983, Allison and Hughes, 1983). In contrast, the subflow would be primarily affected by transpiration by plants, which leaves the residual water in the soil isotopically unchanged (Clark and Fritz, 1997).

Stable isotope data indicated that waters from Edgar Canyon, Bingham Cienega, and the San Pedro River were derived from precipitation sources of similar elevations. These waters were also similar chemically, indicating similar geologic environments along their respective flow paths. However, the waters are sufficiently distinct, both isotopically and chemically, to conclude that neither of the two sites that PAG sampled was the sole source of the water in Bingham Cienega. We suggest that water in Bingham Cienega is derived from San Pedro underflow that has been augmented by inputs from several side canyons: Buehman Canyon, Edgar Canyon, Aguja Canyon, and Redfield Canyon. The chemical data from this study and from the ADEQ surface water database allow that Bingham Cienega could be derived from San Pedro River water if it were mixed with subflow from Buehman Canyon and Edgar Canyons and potentially Redfield Canyon. Fluoride concentrations also suggest mixing because the potential source waters have values both above and below the value found at Bingham Cienega. However, additional data is needed to prove that the surface water at Bingham Cienega is derived from the San Pedro subflow with contributions of water from one or more side canyons.

RECOMMENDATIONS

The following investigations could be pursued to obtain a better understanding of the connection between various parts of the Bingham Cienega hydrologic system.

1) Future study would be needed to determine if the water found in Bingham Cienega is isotopically and chemically distinct from the water in the adjacent perennial reach of the San Pedro. A one-time sampling event for major ions and stable isotopes might be sufficient to determine if these waters are derived from the same source.

2) Future study of the stable isotopic signature of the deep confined aquifer could be used to determine if there is an input from the deep confined aquifer to the surface water at Bingham Cienega. Stable isotope data has not been examined outside of this study.

3) Future study would be needed to determine the contributions of the various canyon systems to the San Pedro River subflow. All of these canyons probably contribute water to the San Pedro subflow and therefore probably contribute to the spring discharge in Bingham Cienega. The USGS PHREEQC model could be used to model sequential additions of water from the various canyons, and could potentially determine the approximate contributions of each canyon system to the San Pedro River subflow. This modeling effort would be improved by collecting limited additional data for major ions and stable isotopes.

4) Determining the elevation of the spring in Bingham Cienega in relation to the streambed of the San Pedro River would help prove that the shallow San Pedro River streambed aquifer is a possible source for the cienega.

REFERENCES

Agenbroad, L.D. 1967. Cenozoic Stratigraphy and Paleohydrology of the Reddington-San Manuel Area, San Pedro Valley, Arizona. Doctor of Philosophy Dissertation, University of Arizona, Tucson, Arizona.

Allison, G.B., C.J. Barns, and M.W. Hughes. 1983. This distribution of deuterium and ^{18}O in dry soils; 2. Experimental. Journal of Hydrology 64: 377-397.

Allison, G.B., and M.W. Hughes. 1983. The use of natural tracers as indicators of soil-water movement in a temperate semi-arid region. Journal of Hydrology 60: 157-173.

Anderson, T.W., G.W. Freethey, and P. Tucci. 1992. Geohydrology and water resources of the alluvial basins in south-central Arizona and parts of adjacent states: U.S. Geological Survey Professional Paper 1406-B.

Arizona Department of Water Resources. 1990. Hydrographic survey report for the San Pedro water shed, Volume 1:General Assessment. Arizona Department of Water Resources, Phoenix, Arizona.

Baird, K.J., M.J. Ronayne, and T. Maddock III. 1997. Preliminary vegetation and hydrological analyses for Bingham Cienega, HWR No. 97-040. Department of Hydrology and Water Resources, University of Arizona, Tucson, Arizona.

Clark I.D. and P. Fritz. 1997. Environmental isotopes in hydrogeology. CRC Press & Lewis Publishers, Boca Raton, Florida.

Craig, H. 1961. Isotopic variation in meteoric waters. Science 113: 1702-1703.

Dickinson, W.R. 1998. Facies map of Post-Mid-Miocene Quiburis Formation, San Pedro Trough, Pinal, Pima, Gila, Graham, and Cochise Counties, Arizona, Arizona Geological Survey, Contributed Map CM-98-A.

Dickinson, W.R. 1991. Tectonic setting of faulted Tertiary strata associated with the Catalina core complex in southern Arizona. Geological Society of America Special Paper 264.

Dickenson, W.R. 1987. General Geologic Map of Catalina Core Complex and San Pedro Through, Arizona. Arizona Bureau of Geology and Mineral Technology.

Gat, J.R. 1980. The isotopes of hydrogen and oxygen in precipitation. Pp. 21-47 *in* Fritz, P. and J.C. Fontes, eds., Handbook of Environmental Geochemistry. Elsevier Scientific Publishing Company, Amsterdam, The Netherlands.

Halvorson, P.H.F. 1984. An exploratory gravity survey in the San Pedro Valley, southeastern Arizona. Master of Science Thesis, University of Arizona, Tucson, Arizona.

Hem, J.D. 1985. Study and interpretation of the chemical characteristics of natural water. Third edition. United States Geological Survey Water Supply Paper 2254. United States Government Printing Office, Washington, DC.

Hendrickson, D.A. and D.A. Minkley. 1984. Cienegas: Vanishing climax communities of the American southwest. Desert Plants 6:131-175.

Hill, E. 1998. Interoffice memorandum to J. Fonseca, Bingham Cienega Well Inventory. Pima County, Department of Transportation & Flood Control District.

Hounslow, A.W. 1995. Water quality data analysis and interpretation. Lewis Publishers. Boca Raton, Florida.

International Atomic Energy Agency. 1981. Stable isotope hydrology - Deuterium and oxygen-18 in the water cycle. Technical Reports Series No. 210.

Jahnke, P., T. Maddock III, and D.P. Braun. 1995. Modeling of groundwater flow and surface/groundwater interactions for the San Pedro river basin from Fairbank to Redington, Arizona. University of Arizona, Department of Hydrology and Water Resources HWR-95-010.

Kalin, R.M. 1994. The Hydrogeochemical evolution of the groundwater of the Tucson Basin with application to 3 dimensional groundwater flow modeling. Doctor of Philosophy Dissertation, University of Arizona, Tucson, Arizona.

Kenny, R. No Date. Site and background report: Bingham Cienega.

Laboratory of Isotope Geochemistry. 1997. Oxygen isotopes in water: Procedures manual. Version February 10, 1997. University of Arizona, Department of Geosciences.

Laboratory of Isotope Geochemistry. 1992. Hydrogen isotopes in water: Procedures manual. Version March 6, 1992. University of Arizona, Department of Geosciences.

McKenna, J.J. 1966. Buehman Canyon Paleozic Section, Pima County, Arizona. Master of Science Thesis, University of Arizona, Tucson, Arizona.

Pima Association of Governments. 2000. Sonoran Desert Conservation Plan, GIS coverage of perennial streams, intermittent streams, and areas of shallow groundwater.

Philips, W.M., F.N. Robertson, L. Wirt, and J. Fonseca. 1994. Origin of water to springs in Bingham Cienega, Lower San Pedro Basin, Arizona. Abstract presented at Arizona Riparian Council Annual Meeting, Phoenix, Arizona, April, 1994.

Richard, S. M., J.E. Spencer, and P.A. Pearthree. 2000. Geologic Map of Arizona: Arizona Geological Survey Map 35, 1 sheet, scale 1:1,000,000.

Robertson, F.N. 1992. Radiocarbon dating of groundwater in a confined aquifer in southeast Arizona. Radiocarbon 34 : p. 664-676.

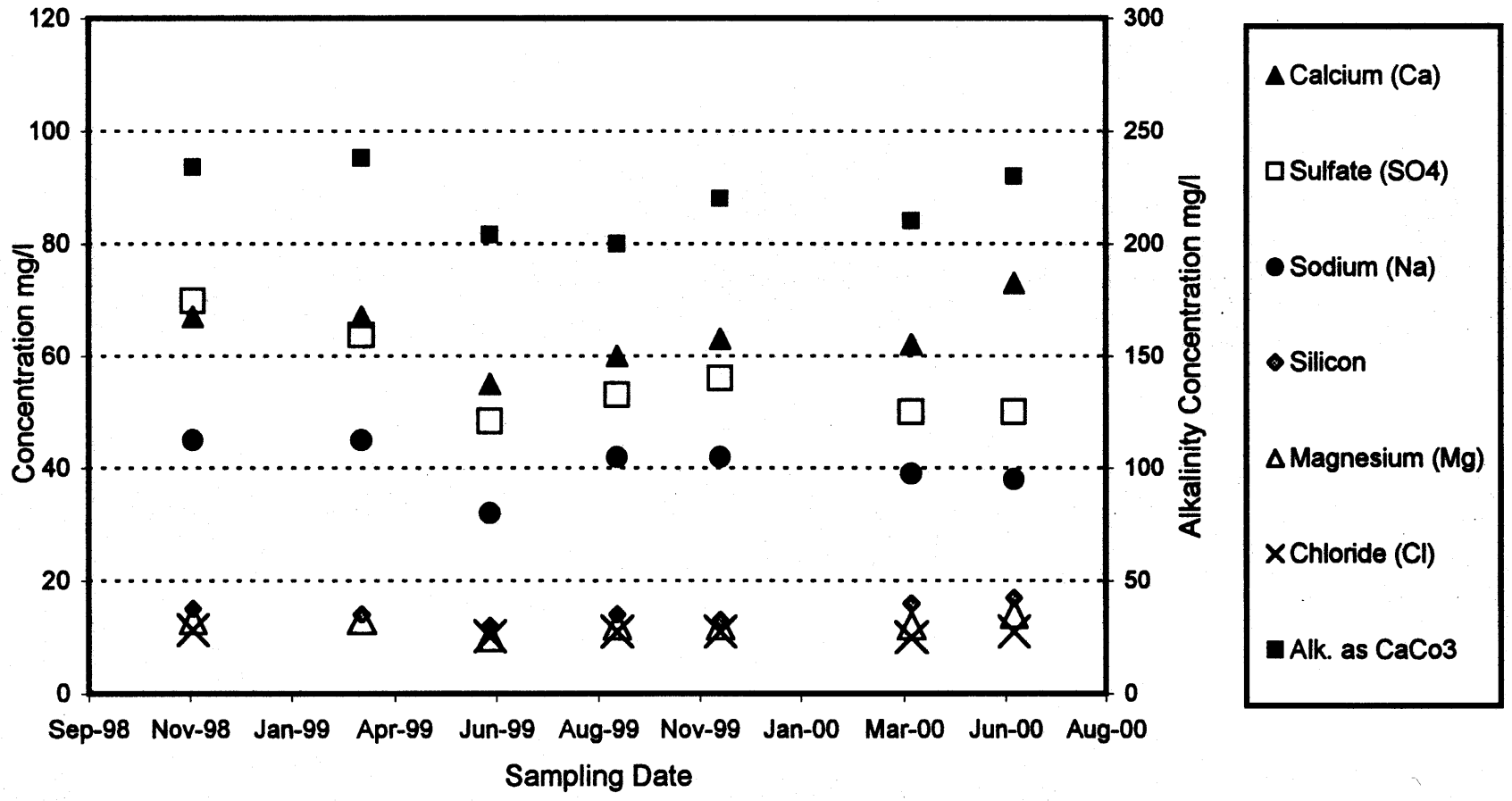
Robertson, F.N. 1991. Geochemistry of ground water in alluvial basins of Arizona and adjacent parts of Nevada, New Mexico and California. U.S. Geological Survey Professional Paper 1406-C. United States Government Printing Office, Washington, D.C.

Ronayne, M.J. and T. Maddock III. 1996. Flow model for the Bingham Cienega area, San Pedro Basin, Arizona: a management and restoration tool, HWR No. 96-050. Department of Hydrology and Water Resources, University of Arizona, Tucson, Arizona.

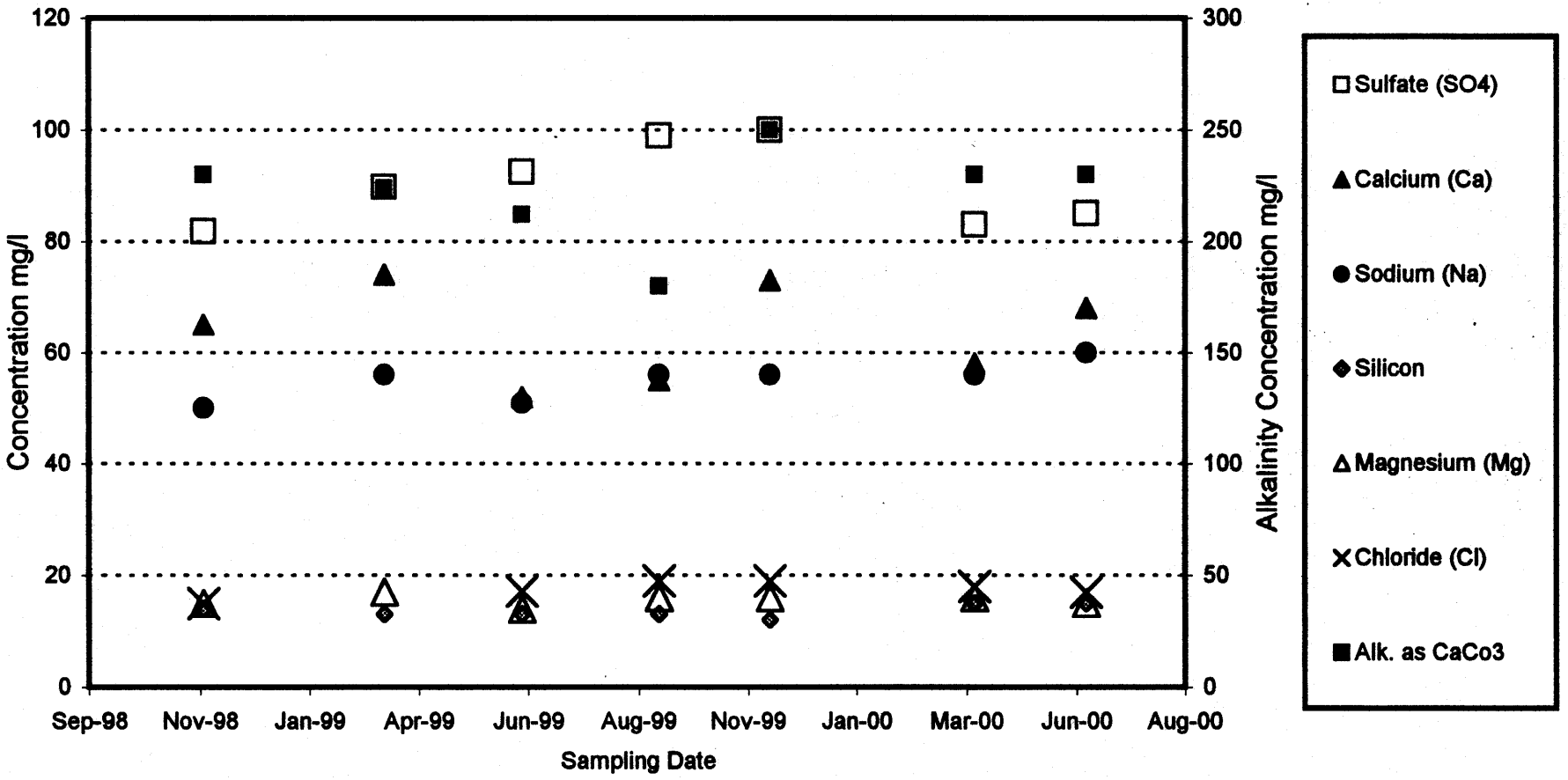
Smith, W.J. 1967. Cenozoic stratigraphy near Redington, Pima County, Arizona. Master of Science Thesis, University of Arizona, Tucson, Arizona.

Volunteers for Outdoor Arizona. 2000. Bingham Cienega Natural Preserve Restoration Plan. http://www.dgcenter/orgvoa/BCNP_Plan.htm.

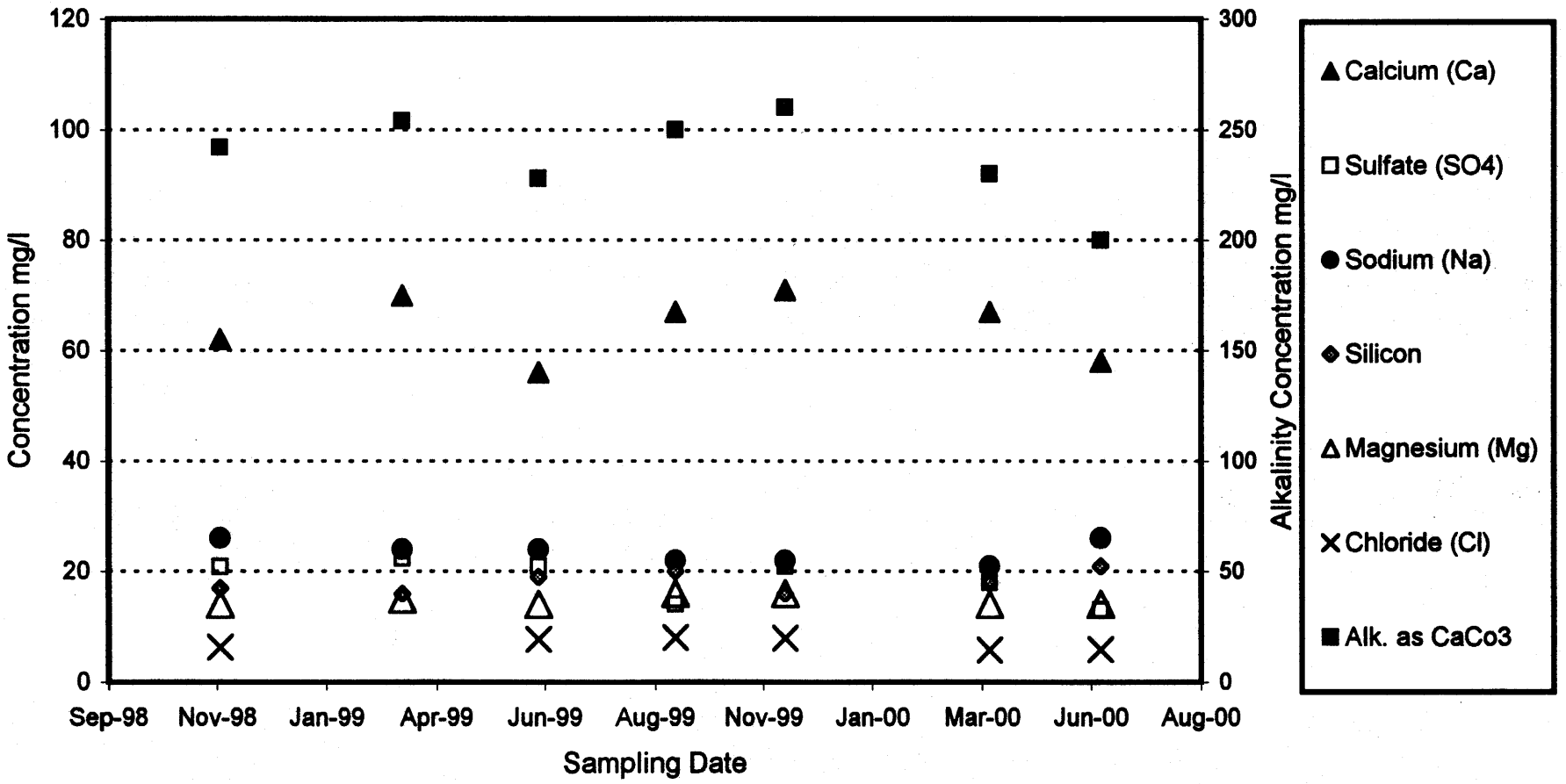
APPENDIX A. Time Series Plots of Ion Concentrations at Various Sites.



Appendix A Figure 1. Water chemistry data for Bingham Cienega, 11/1998-6/2000.



Appendix A Figure 2. Water Quality Data for San Pedro River, 11/1998-6/2000.



Appendix A Figure 3. Water Chemistry Data for Edgar Canyon, 11/1998-6/2000.

APPENDIX B. Site Photographs.

Appendix B Figure 1. Bingham Cienega sampling point, 6/9/2000.

Appendix B Figure 2. Edgar Canyon sampling site, 6/9/2000.

Appendix B Figure 3. Edgar Canyon, sampling location is on the right (west) of tree line in the canyon.

Appendix B Figure 4. San Pedro River sampling site, 6/9/2000.

Appendix B Figure 5. San Pedro River, 6/9/2000 sampling site is near the center of the photo.

APPENDIX C. Data From Other Sources Used In This Study.

Appendix C. Data from other sources used in this study. Values are in mg/l.

Site	Source	Date	HCO_3	Ca	Cl	F	Mg	K	Na	SO_4
Redfield Canyon #1	ADEQ*	10/22/91	216	42.2	8	0.93	15.3	3.7	40.5	18
Redfield Canyon #1	ADEQ*	4/29/91	116	29.6	6	0.39	10.6	2.4	25	31
Redfield Canyon #1	ADEQ*	2/4/91	114	27.4	6	0.42	9.7	1.8	23.4	30
Redfield Canyon #2	ADEQ*	4/29/97	150	36	6.8	--	9.6	1.9	21	22
Redfield Canyon #2	ADEQ*	4/11/94	130	32.1	9	0.32	9.7	2.52	19.1	45.3
Redfield Canyon #2	ADEQ*	3/30/93	93	31.3	5.9	0.22	7.4	2.71	14.6	31.7
Redfield Canyon #2	ADEQ*	4/6/92	62	15.8	3.1	0.24	6.1	1.72	11.1	33.7
Buehman Canyon	ADEQ*	7/15/97	210	52	10	2.6	8.8	2.3	22	25
Buehman Canyon	ADEQ*	4/8/97	165	46	9.5	1.53	7.3	2	22	33
Buehman Canyon	ADEQ*	1/2/97	215	58.3	9	2.79	8.5	2	20.8	18.1
Buehman Canyon	ADEQ*	10/1/96	210	56.9	9	3.05	8.3	2.11	20.5	22.1
Buehman Canyon	ADEQ*	7/17/97	209	55.5	8.8	3.11	8.4	1.97	21.1	22
Buehman Canyon	ADEQ*	5/20/96	210	53.9	7.2	3.01	8.4	1.91	20.8	23.9
Buehman Canyon	ADEQ*	3/6/96	212	58	5.7	2.96	8.8	2.04	21.3	26.6
Buehman Canyon	ADEQ*	1/9/96	210	58.3	10.1	2.92	9	2.16	21.8	25.1
Buehman Canyon	ADEQ*	11/29/95	210	51.5	6	2.7	8.6	2.18	22.3	27.1
Well No. 2	Robertson#	8/30/81	146.3	13	16	1.69	0.51	1.6	64	31
Well No. 3	Robertson#	8/7/82	136	9.3	9.1	1.9	0.41	1.6	59	17.8
Well No. 4	Robertson#	8/7/82	146	10	11	2	1.1	1.8	64	19

ADEQ* - Data from Arizona Department of Environmental Quality Surface Water Database. Additional data available include Alkalinity as phenolphthalein, Ammonia as nitrogen, dissolved and total antimony, dissolved and total arsenic, dissolved and total barium and compounds, dissolved and total beryllium and compounds, dissolved and total boron (boron and borates only), dissolved and total cadmium, calcium carbonate, carbonate, dissolved and total chromium, dissolved and total copper, dissolved oxygen, EDTA, fecal coliform, fecal streptococci, flow, hydroxide, dissolved and total iron, Kjeldahl nitrogen, dissolved and total lead and compunds, dissolved and total manganese, dissolved and total elemental mercury, dissolved and total molybdenum, dissolved and total nickel, nitrate, nitrite, pH, phosphorus, dissolved and total selenium, dissolved and total silver, specific conductivity, stream depth, stream width, dissolved and total strontium, temperature, dissolved and total thallium, TDS, TSS, turbidity, and dissolved and total zinc.

Robertson# - Data from Robertson, F.N. 1992. Radiocarbon dating of groundwater in a confined aquifer in southeast Arizona. Radiocarbon 34:p 664-676). Additional data available are well depth, TDIC, $\delta^{13}C$, ^{14}C, ^{3}H, temperature, field pH, TDS, nitrate, and silicon.