Chapter 1

1-1 Introduction

The availability of fresh water of sufficient quantity and quality is one of the most important issues in arid and semi-arid areas. Northern Arizona, as a semi-arid area, has been dealing with this problem for a long time, especially during the current drought. In this area, most rivers and washes flow only seasonally, with some sections of the Little Colorado River containing water throughout the year. Therefore, there is a substantial dependence on ground water to support domestic and agricultural needs.

Two major types of aquifers are recognized in the Navajo and Hopi lands in northern Arizona. The first type is the bedrock aquifers composed of sedimentary rocks such as the D-, N- C- aquifers (Cooley et al. 1969). The second type is the alluvial aquifers found marginal to and beneath many washes.

Alluvial aquifers are typically located at the base of mountains, where rapid erosion transports the sediments down to steep slopes to broad depositional fans. An alluvial aquifer is formed by the deposition of weathered materials such as gravels, sand and silt particles. The water flow in these aquifers can be very fast to very slow (Schwartz and Zhang, 2003).

Alluvial aquifers are routinely used because they are relatively shallow, less expensive to drill, and generally contain acceptable water quality. However, these shallow aquifers are dependent mainly on local recharge from precipitation, which makes them vulnerable to drought. The surface exposure of these aquifers also renders them vulnerable to contamination. The quality of water in this type of reservoir depends on many factors, including human-sourced contaminants and pollutants, water-sediment interactions, and evaporation. The quantity of water depends on precipitation, the permeability of alluvial sediments, water recharge from adjacent aquifers, and the discharge from the aquifer, which may happen naturally as springs or discharge to neighboring aquifers, and by withdrawals for agriculture and domestic use. Careful management of water extraction from alluvial aquifers in arid and semi-arid areas is necessary to avoid damaging the quality and quantity of the water supply. Increased salinity, changes in pH or Eh states, and increased concentrations of toxic elements such as arsenic and heavy metals are common examples of the lowered quality of water that may happen when aquifer usage is not managed. Studies of aqueous geochemistry help us to better understand possible chemical reactions that affect the quality of the water in aquifers.

This investigation focused on the upper 40 kilometers of the course of the Pueblo Colorado Wash (PCW). The paleo-incised valley beneath the PCW is one of many in northern Arizona that has been infilled with alluvial and eolian sediments to form aquifers along the Little Colorado River and its lower order drainages. Many small communities in northern Arizona and the Navajo reservation are dependent on the Pueblo Colorado and similar alluvial aquifers.

1-2 Purpose

The purpose of this study is to determine the variation in the chemical composition of ground water in the Pueblo Colorado Wash alluvium and attempt to explain the major controls on the inorganic chemical composition of ground water. To achieve this goal, two objectives are addressed:

The first objective is to sample and analyze water from wells and springs producing water for use by residents of the study area. Thirteen wells and springs had been sampled during the previous work conducted by the U.S. Geological Survey. Twenty-six wells and springs were sampled in this study. All water samples were analyzed for major cations and anions as well as trace metals; δD, $\delta^{18}O$ and $\delta^{13}C$ composition of selected samples was also determined. Field measurements include pH, specific conductance, temperature, dissolved oxygen, dissolved ammonia and hydrogen sulfide. Moreover, the composition of water in bedrock aquifers located near Pueblo Colorado Wash was evaluated to assess the interaction of the alluvial and bedrock aquifers

The second objective is to use the chemical and isotopic composition of the water to identify processes that account for the observed spatial compositional variations. Among the processes considered are mineral dissolution and precipitation, redox changes, cation exchange and water mixing. Stable isotope data help reveal the role of evaporation, possible water mixing, and biological contributions to the Pueblo Colorado Wash aqueous system. The modeling program WATEQA4 was used to mathematically evaluate mineral saturation states and speciation of trace elements.

1-3 Significance of the study

Pueblo Colorado Wash aquifer is currently the major domestic water supply for several communities on the Navajo Indian Reservation, including Greasewood, Indian Wells, Dilkon, White Cone, Teesto and Jadito (figure 1-1). In the Greasewood area, the water to supply livestock also largely comes from Pueblo Colorado Wash alluvium. Residents have reported that the salt content of some wells has increased in the recent past. In addition, water quality testing being done by Navajo Tribe Utility Authority has detected high concentrations of some toxic and carcinogenic elements such as arsenic (announced in a public warning posted in chapter fire stations in June 2004). These problems are of greater concern when we consider the population in this area is increasing at a high rate (table 1-1). This study attempts to determine the possible reasons for these changes in water quality. The results of this study will be given to the Navajo Tribe Utility Authority and the chapter houses to inform them of water quality problems in wells and springs used by the public and/or livestock. The database created by this study will also be given to the USGS office in Flagstaff for future studies.

1-4 Study Area

The Navajo Nation is located in northeastern Arizona, Utah and New Mexico. The Navajo land has an area of approximately 70,000 square kilometers. Pueblo Colorado Wash is one of the several washes draining into Little Colorado River in the western Navajo Nation. The upper part of Pueblo Colorado Wash was chosen for this study. The study area starts in Kinlichee Navajo Tribal Park where several streams join to make the Pueblo Colorado Wash. The study area continues to southwest and ends near Twin Buttes (see the map in appendix 1).

Chapter	1990 Population	1990 Water Demand acre-feet/year	2000 Population	2020 Population	2020 Water Demand acre-feet/year	2040 Population	2040 Water Demand acre-feet/year
Dilkon	1996	356	2164	4142	742	6761	1212
Teesto	1006	180	925	2093	375	3416	612
Indian Wells	1330	239	958	2781	498	4540	814
Lower Greasewood	1345	238	1391	2769	496	4520	810
White Cone	986	177	1383	2057	369	3357	602

Table 1-1: The population increase and the projected water demand in the Dilkon-Ganado Area. The water demand is in acre-feet/year (modified from Economic Benefit of the Three Canyon Water Supply Water Project, Navajo Nation, James P. Merchant, David Dornbusch & Company, Dec 1999. The population of year 2000 is a total derived from all the chapters' websites).

1-5 Climate and Vegetation

The climate of the region is semi-arid. The average summertime daily maximum temperature varies from 20 to 30°C and in the winter from a minimum of -10°C to maximum of 20°C (Sellers et al., 1985). The average annual precipitation in the region ranges from 150 to 380 millimeters (Arizona Department of Water Resources, 1989). Precipitation in the region occurs as the result of two distinct processes:

1-Winter precipitation results from storms originating in the Pacific Ocean and falls mostly as snow in the higher elevations. These winter storms produce the majority of the usable surface and recharge water.

2-Summer precipitation is the result of small-scale, locally intense convective storms. The Gulf of California and the Gulf of Mexico are the primary sources of moisture for these high intensity storms.

The Colorado Plateau is one of the windiest regions in Arizona. This wind, combined with high temperatures and low humidity at the lower elevations, produces evaporation rates exceeding 1400 millimeters per year (Arizona Department of Water Resource, 1989).

The vegetation of the Navajo Nation has been divided into two broad zones by Hicks (1969):

a- The grass-shrub zone, which is below 1720 meters above sea level and consists of sparse grassland-browse vegetation types and is characteristic of the flood plain of the Pueblo Colorado Wash.

b- The pinon-juniper zone ranges from 1720 to 2340 meters above sea level and is dominated by woodland-browse species. This vegetation is typical of the area near Kinlichee and ridges surrounding the Wash.

c- In addition to the two above-mentioned classes, a narrow band of shrubs and trees grow on banks of the active channel of the wash, primarily consisting of invasive Russian olive (*Elaeagnus angustifolia*).

1-6 Landscape

The dominant landscape forms adjacent to the Pueblo Colorado are buttes, mesas, and extensive plains. The northern part—from Kinlichee spring to the south of Ganado—is marked by steep slopes adjacent to the wash compared with the broad flat areas along the central and southern parts. The average slope of the drainage along the northern part of the study area (from Kinlichee to Ganado) is about 3%. The flood plain is absent or is very narrow from Kinlichee to Ganado whereas the central and southern parts of the wash have gentler slopes—the average slope from Cornfield to Twin Buttes is about 0.7%—and the adjacent flood plain, is locally as wide as 5 km.

The current geomorphology of the study area is the product of processes that affected the Colorado Plateau. Scarborough (2000) states that, along the Little Colorado River and the eastern parts of Grand Canyon, the continuous uplift and erosion during Neogene time resulted in the current morphology of the area. Therefore, Pueblo Colorado Wash is considered the result of cut and refill and/or infill of the older formations during the uplift of the edges of Colorado Plateau. In the northern parts—from Kinlichee spring to south of Ganado— the alluvium is thin—less than 10 meters—and in some parts, especially near Kinlichee, the channel is cut directly into bedrock. In the central parts of the wash—between Cornfield and north of Greasewood—the alluvium is thick—more than 50 meters—and the extent of the alluvium is broad. The thickness of alluvium decreases to about 20 meters at Greasewood. South of Greasewood, the thickness of alluvium increases to about 60 meters then decreases abruptly to zero northeast of Twin Buttes. The width of the also wash decreases slightly to the south (table 1-2).

Sample #	NTUA #	Depth (m)	Lon.	Lat.	Location
04PWW3	17M91A	35	109 40.998	35 38.945	Cornfield
04PWW5	17K367	70	109 44.599	35 36.265	S. Cornfield
04PWW6	17K338	30	109 45.945	35 35.047	S. Cornfield
04PWW17	17M340	35	109 52.164	35 29.379	S. Greasewood
TSN03	17K306	55	109 53.186	35 24.276	Twin Buttes
N/A	17T-526A	45	109 49.733	35 32.950	N. Greasewood
N/A	17T-526B	44	109 49.600	35 32.95	N. Greasewood
N/A	17T-526C	43	109 49.500	35 32.917	N. greasewood
N/A	17T-526D	41	109 49.383	35 32.927	N. Greasewood
N/A	17T-526E	52	109 49.267	35 32.867	N. Greasewood
N/A	17T-526F	42	109 49.183	35 32.817	N. Greasewood
N/A	17T-526G	30	109 49.083	35 32.767	N. Greasewood
N/A	17T-526H	33	109 48.967	35 32.733	N. Greasewood
04PF13 ?	GRWD PM1	28	109 51.265	35 31.227	S. Greasewood
04PF14 ?	GRWD PM3	20	109 51.197	35 31.273	S. Greasewood
04PF15 ?	GRWD PM4	22	109 51.044	35 31.423	S. Greasewood
04PF16 ?	GRWD PM 5	30	109 50.794	35 31.641	S. Greasewood

Table 1-2: The depth of alluvium in some wells in the study area. To match samples 04PF13, 04PF14, 04PF15 and 04PF16, with the NTUA numbers, longitudes and latitudes of samples were used and the NTUA wells numbers were not observed at the sampling sites. Data for the first five sites are from Davis et al. (1963), other data is derived from well logs provided by the U.S.G.S, Water Science Centers at Denver and Flagstaff.

1-7 Human Habitation and Water Usage

The area of the Navajo and Hopi reservations has hosted Native Americans for more than 8000 years (Powell and Gumerman 1987). The Navajo people are relatively recent residents and have been in the area for less than 1000 years. The current population of the Navajo Nation is more than 175,000 (US Census Bureau, 2000). The study area includes several small communities, in which water from Pueblo Colorado Wash Aquifer is used. During 2002, about 93 million gallons was pumped by NTUA from wells 1, 2, and 3 (correspondent to samples 04PN20, 04PN21, 04PN22 of this study) (Navajo Nation Water Management Branch records, Window Rock, AZ). The population of the area was 6000 in 1990 and has been projected to increase to about 14000 in 2020 and 23000 in 2040 (Water Resource Development Strategy For the Navajo Nation, 2000). In addition to the residents of the area, several boarding schools, ranches, one hospital and some small industries depend on the Pueblo Colorado Wash water.

1-8 Hydrologic Setting

In addition to alluvial aquifers, bedrock aquifers are important water supplies in the study area. The most important bedrock aquifers are the C-aquifer, which provides water for Ganado (Hart et al. 2002), the N-aquifer and the D-aquifer are located to the north of the study area, beneath Black Mesa (Lopes and Hoffman 1997). To the east side of Pueblo Colorado Wash aquifer, the Defiance Plateau also consists of bedrock units which produce water (see section 1-10).

The Pueblo Colorado Wash aquifer is neighbored by the Steamboat Wash alluvial aquifer in the west, which joins Pueblo Colorado Wash near Twin Buttes, Snake Flat aquifer to the north and the Defiance Plateau aquifer in the east. These alluvial aquifers are defined based on the morphology, presence and absence of exposed bed rock, change in the direction of the topographic slopes, and the location of the crest lines. The Steamboat aquifer and the Snake Flat aquifer are alluvial aquifers whereas the Defiance Plateau aquifer is a bed-rock aquifer. The overall topography in the study area slopes from north to south. Pueblo Colorado Wash, and

Steam Boat Wash drain to Cottonwood Wash and then to the Little Colorado River. The density of wells in the alluvium of Pueblo Colorado Wash is greater than in the neighboring bedrock and alluvial aquifers. The increased number of wells in PCW is an indication of the greater amount and good quality of most of the water produced from the alluvium.

1-9 Previous Studies

There has been no published study on the hydrology of Pueblo Colorado Wash Aquifer, although several comprehensive studies have been completed on important aquifers in the region, such as aquifers underlying Black Mesa by Lopes and Hoffman (1997) and HISGeoTrans Inc. (1993).

Navajo Tribal Utility periodically tests the quality of water produced from the Pueblo Colorado Wash by sampling water supplied to the comminities. In addition, a reconnaissance water sampling study was conducted by the U.S. Geological Survey in the Pueblo Colorado Wash area in 2000-2004. In addition, the results of water testing of wells from 1950's were compiled by Kister and Hatchett (1963).

In the Navajo and Hopi reservations, several studies have been conducted on different aquifers, mostly on Black Mesa.

Previous investigations include:

Boner et al. (1992), Boner et al. (1988), Boner et al. (1991), Brown and Eychaner (1988), Cooley et al. (1969), Davis et al. (1963), Eychaner (1983), Fisk et al. (2003), Fisk et al. (2004), GeoTrans, Inc., (1987), Harshbarger et al. (1966), Hart, and Sottilare (1988), Hill (1985), Hill and Sottilare (1987), Hill and Whetten (1986), HSIGeoTrans, Inc., (1993), HSIGeoTrans, Inc. (1999), Kister and Hatchett

(1963), Littin (1992), Littin et al. (1999), Littin and Monroe (1995)a, Lopes and Hoffmann (1997), McCormack et al. (2002), McCormack et al. (2003), Smith et al. (1995), Sottilare (1992), Tadayon et al. (1999), Thomas and Truini (2000), Thomas (2002)a, Truini, and Longsworth, (2003), Truini and Thomas (2004), Truini et al. (2005), Wilson and Garrett (1988), Zhu et al. (1998), Zhu (2000).

1-10 Geologic Setting

The position of the Pueblo Colorado Wash is affected by the Defiance Plateau as well as faults and landslides. The Defiance Plateau uplifted from late Mesozoic through mid-Miocene time (Bump and Davis 2003) and consists of Mesozoic and Tertiary rocks (Cooley et al. 1969). The exposed bedrock on the east side of Pueblo Colorado Wash is horizontal; however, in several locations on the west side of the wash, it is folded and faulted. On the eastern and western boundaries of the wash, especially the western boundary near Greasewood, landslides are important structural factors in determining the shape of the transitional zone from alluvium to bedrock.

The geologic units exposed at the surface in the study area, from the oldest to the youngest are Cutler Formation (De Chelly Sandstone), Chinle Formation, Wingate Formation, Bidahochi Formation and Quaternary deposits (Ulrich et al. 1984).

1- De Chelly Sandstone is the oldest rock unit found in the study area. Exposures reveal crossbedded and well layered sandstones near Kinlichee spring. De Chelly Sandstone (Coconino Sandstone equivalent) is an early Permian member of Cutler Formation and interfingers with the Supai Formation in area of Defiance Plateau (Cooley 1969).

2- Chinle Formation: In the Flagstaff Quadrangle (1984), this formation is divided into three members with a maximum thickness of 491 meters. The three members are:

-Shinarump Member: this member is exposed mostly in the northern part of the Pueblo Colorado Wash near Kinlichee and in the northern part of the Steamboat Wash. It is composed of weakly cemented yellowish-gray conglomeratic sandstones and conglomerate, which contains lenses and pellets of mudstone probably derived from the underlying Moenkopi Formation. The sandstone consists of poorly sorted subrounded to subangular, med to coarse quartz grains. The conglomerate, occurring as stringers or lenses, is composed of quartz, quartzite, jasper pebbles and petrified wood fragments embedded in a sandstone matrix. In most places, the Shinarump Member displays low- to high-angle, medium- to large-scale trough cross beds. Ripple marks, mud cracks, and current lineations indicate that the Shinarump Member is a fluvial deposit (Irwin et al., 1962). In the study area, the thickness of the Shinarump Member is 0-21 meters (Ulrich et al 1984).

-Petrified Forest member: The member crops out in the southern parts of the study area, along both the Pueblo Colorado Wash flood plain. It is probably present under the course of the wash, mostly covered by the Owl Rock Member and Quaternary deposits. The member consists of thick and very thick bedded series of weakly cemented lenticular beds of marl, claystone, mudstone, siltstone, minor units of fine to coarse grained sandstone, and conglomerate. Many beds appear and disappear within a few feet of each other, but a few layers trace more than one mile. The sandstone and siltstone units, where clearly exposed, have large-scale, low-angle trough crossbeds. It is common for one set of crossbeds to be truncated by those of another set, suggesting sedimentation by meandering streams (Irwin et al. 1962). The thickness of this member in the study area is 0-280 meters (Ulrich et al 1984).

- Owl Rock Member: This member is exposed in the flood plain walls along the wash. It is composed of mottled light –gray and grayish-pink interbedded limestone and calcareous siltstone. The thickness varies from around 100 meters near Little Colorado River to 190 meters near Black Mesa.

3- Wingate Formation: The base of the Wingate Formation is an unconformity that overlies the Triassic rocks. This formation comprises chiefly eolian deposits and fluvial deposits from ephemeral streams. The eolian deposits are intrerbedded with fluvial and marine deposits (Blakey, 1996). The Wingate formation is exposed in the northern parts of the study area and mainly consists of reddish-brown, fine-grained stratified sandstones.

4- Bidahochi Formation: This Upper Tertiary formation is exposed over most of the study area Based on the Repenning and Irwin (1954) subdivisions, this formation is subdivided into three members:

-Lower Member: composed of white, pink, red calcareous thick bedded to structureless claystone, siltstone, and sandstone with intrabeds of white-gray vitric rhyolitic volcanic ash. This member crops out in southern and southwestern parts of study area.

-Middle Member: This member is mostly made of volcanic material including brown to greenish-brown interbedded nephelinitic to lamprophyre fall, surge, and reworked pyrocasts with epiclastic sediments. Thick 0-20 meter black nephelinitic to lamprophyric mafic lava flows occur in this member. This member is exposed in the southern and southwestern parts of the study area.

Upper Member: This member consists of tannish-white, fine to coarse grained, weakly calcareous, cross-bedded eolian sandstone. There are thin layers of nephenilitic-lamprophyric tuff in this member. Moreover thin layers of rhyolitic ash occur with this member. The upper member crops out mainly in the northern parts of the study area from Cornfield to Ganado.

5- Quaternary deposits: Pueblo Colorado Wash alluvium is an alluvial aquifer that was deposited in an incised channel cut into lithified sedimentary rocks ranging from Tertiary to Permian age, some of which are also aquifers. The older formations are important as a source of detritus that forms the alluvium and they may presently be sources of water that discharge into the alluvium. The Quaternary deposits in the study area consist of terraces, alluvial deposits, and eolian deposits.

-Terrace Deposits: several terrace deposits are located along the banks of the wash. They are generally made of fine-grained heterogeneous sediments interbedded with lenses composed of gravels and coarser sediments.

- Alluvial Deposits: Much of the course of Pueblo Colorado Wash and the body of the aquifer are made of alluvial deposits. Observations made on exposures along erosional channel cuts during this study and well logs indicate that the wash and the alluvium consist of heterogeneous fine-grained deposits—silt and sand—with lenses of gravel and sand at different depths (figure1-1). The thickness of alluvium is not uniform along the wash and varies from about 20 meters (south of Greasewood) to more than 70 meters (south of Cornfield) (table 1-2). The fine-grained deposits are generally thicker and more common than the gravelly-sandy lenses. The data from well logs show that the thickness of gravelly-sandy lenses varies from 3 to 20 meters. Additionally, in some wells the alluvium becomes coarser in the deeper parts—at the bedrock boundaries—and pebble-sized particles and quartz grains are the dominant constituents of the alluvium. The thickness of alluvium pinches out after Twin Buttes and disappears (Cooley 1969).

- Eolian Deposits: Along both banks of Pueblo Colorado Wash, the flood plain is partly covered by dunes and, in places, by a thin mantle of wind-blown sand. These deposits are well sorted and lighter in color than the alluvium. The quartz and feldspar grains are identifiable in these deposits and clay particles are less abundant than in the alluvium deposits. The dunes are composed of more homogenous sediments than the alluvium. The texture of eolian deposits makes them more permeable than the alluvial deposits.

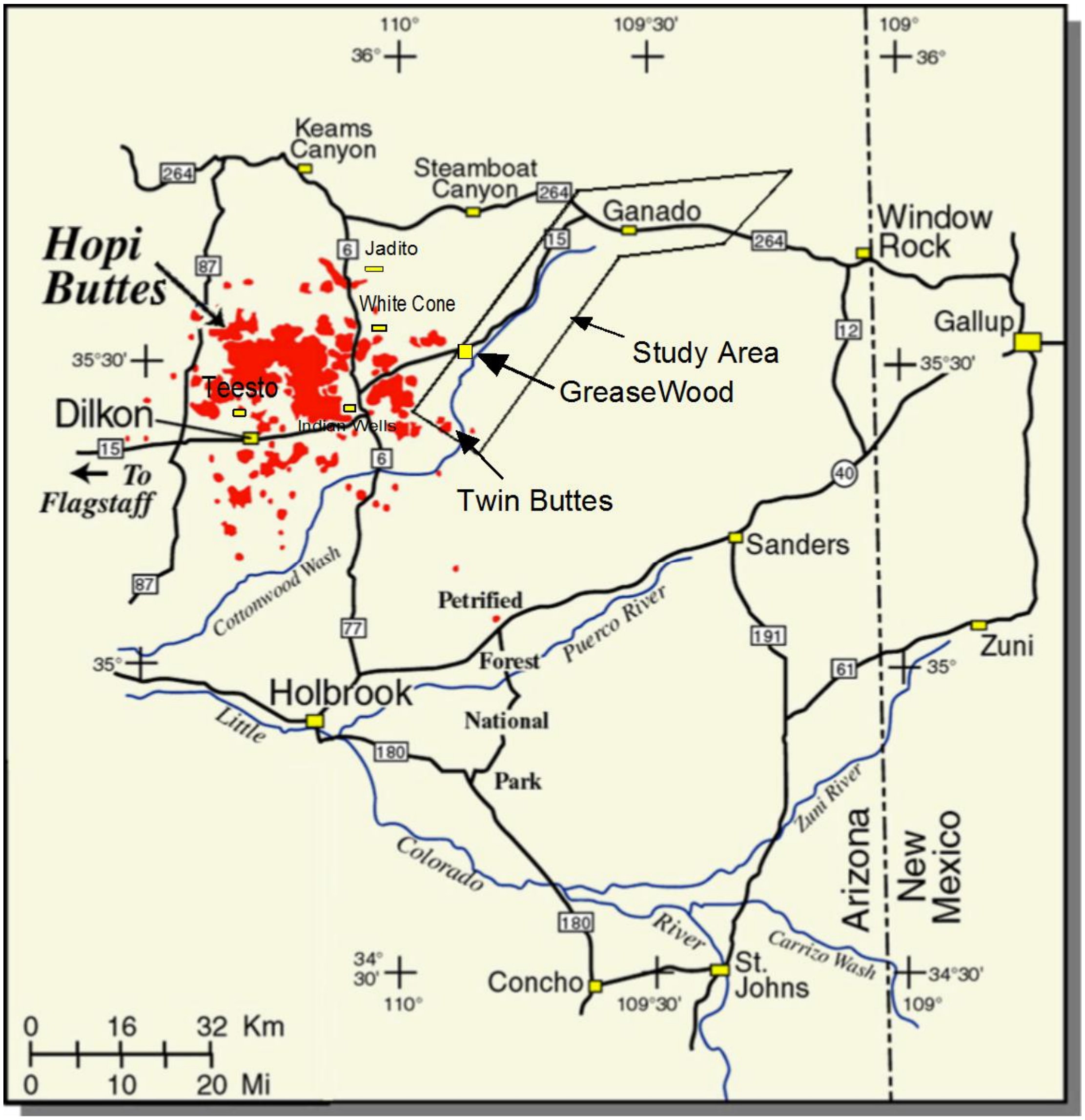


Figure 1-1: The study area, access roads, and Indian communities using water from Pueblo Colorado Wash Aquifer. The red areas indicate exposed volcanic rocks including diatremes (modified from www.esp.cr.usgs.gov)

Figure: 1-2: A gravel-sand lens surrounded by fine-grained sediments (fine sand and silt) located near Kinlichee spring.

Chapter 2

Field Work, Lab Analyses and Analytical Results

In this chapter the methods used for sampling and analyses of sediments and water, are presented along with the analytical results.

2-1 Sediment Sampling and Analyses

To examine the clay mineralogy of alluvium, seven samples were taken from the wash and alluvial sediment for XRD analysis. The sample locations were chosen randomly but with the intent of obtaining representative samples along the length of the study area. Samples were collected, using a plastic spoon, from the surficial sediments and preserved in plastic zip-lock bags to avoid any loss of water. The samples were carried to the lab and refrigerated on the same day at 4ºC.

A Siemens D-500 powder X-ray Diffractometer (XRD) with a 2000W Copper X-ray tube and graphite monochrometer was used to identify the clay minerals in the samples. The D-500 is interfaced with a PC running PC-AT software through a Daco MP microprocessor. X-ray tube settings were adjusted to 43 kilovolts and 38 mega amperes using nickel filtered CuKα Radiation. Distilled-deionized water with sodium tripolyphosphate were added to each sample and then sonified at 200 W for 5 minutes to disperse the clay minerals. Each sample was fractionated for particles <2 µm in diameter by centrifugation on an IEC Centra-7 centrifuge. The resultant supernatant was filtered through 0.45 µm pore size membrane filters attached to a vacuum filtration apparatus. The sediment on the filter was then transferred onto a glass slide to prepare an oriented mount. Three main treatments were used to analyze the samples: 1)air-dried, 2) ethylene glycol saturated, and 3) heat treated at 370 °C and 550°C. Untreated, oriented slides were analyzed from 2-35º 2θ. The ethylene glycol saturated and heat-treated oriented samples were analyzed from 2-22° 2θ. The scan condition used 0.02° 2 θ steps counted for 2 seconds per step.

The results of XRD analyses revealed that smectite, illite-smectite, kaolinite, chlorite, calcite, and quartz are present in all samples but with different abundances. Smectite is the most abundant clay mineral in all samples.

2-2 Water Sample Sites

The study area is subdivided into different aquifers based on field observations and topographic maps. Table 2-1 shows the subdivision of the possible aquifers around the Pueblo Colorado Wash aquifer. The study area ends at the topographic divide separating Pueblo Colorado Wash and the Snake Flat area in the north and Steamboat Wash alluvium to the west. One sample was taken from the Snake Flat area and the three samples were taken from Steamboat Wash alluvium. In the south, the study area ends at Twin Buttes. In the east, the study area neighbors the edge of the Defiance Plateau. Two samples, located along State Route 191 between Ganado and Klagetoh, were taken from this eastern edge.

Water samples were collected from all available sites along the PCW within the study area, which included hand pump wells, windmills, electric pumps and surface water. Samples were also collected from a few windmills and hand pump wells in the area surrounding the PCW for comparison (see tables 2-1 and 2-2).

a) Hand pumps, less than 10 meters deep, are distributed throughout the Pueblo Colorado Wash. They produce water that is collected in subsurface concrete vaults that are as much as 10 m deep. These vaults installed 40 to 50 years earlier and are designed to collect and store water from unconsolidated units. Many of these wells were dry at the time of sampling; a change reported to be recent by residents, and is attributed to lowering of the ground water level.

b) Windmills extract water from wells installed to depths as great as 60 m in the alluvium and deeper in some bedrock units. Water produced from these wells is stored in proximal tanks and is used largely for livestock. These sites typically have one or more troughs for the livestock so animal wastes commonly litter the ground surface.

c) Water is produced from NTUA wells, and wells associated with the Greasewood boarding school, using electric pumps. These wells withdraw the greatest amount of water from the alluvium. During 2002, 93 million gallons was extracted from the three NTUA wells located 1 to 2 miles northeast of Greasewood

Samples of surface water were collected from a spring near Kinlichee, Ganado Lake, and the Ganado sewage discharge.

2-2-a Sample Collection and Preservation

Water samples were collected in June, and August of 2004. To have samples representative of the groundwater the following methods were used:

a) At the hand pumps, water was pumped for 3-5 minutes to purge the pump. Temperature and pH were measured during subsequent pumping until constant pH and temperature. Depending on use and local hydrologic conditions at the time of sampling, the sampled water may be modified by evaporation during storage.

b) At windmills, water was sampled as the well was pumping, from the well shafts that conduct water from the wells to the storage tanks. At these sites, samples were taken 10-15 minutes after the windmills produced water. Nalgene polyethylene hose was used to carry the water from the well shaft to a Teflon beaker or field measurement kit container for analysis.

c) At the electric pump sites located near the Greasewood Boarding School, water was sampled from valves installed directly above the well pump and before the water was transferred to the chlorination tank. Water was allowed to run out of the valve for 5 minutes to have samples representative of the groundwater

d) At the electric pump sites managed by NTUA, water was allowed to run for five minutes before sampling to obtain constant pH and temperature, and to ensure samples are representative of the groundwater at those sites.

Once stable pH and temperature were obtained, samples were collected. For each site a total of four separate subsamples were collected for 1) anion analyses, 2) cation analyses, 3) stable isotope analyses, and 4) alkalinity. At some sites, a fifth sample was collected for analyses of $\delta^{13}C$ of dissolved inorganic carbon (DIC). Bottles used to store the samples were prepared as follows:

-The polyethylene bottles, used for storage of water for cation analyses, were first rinsed with deionized water, soaked in 3N nitric acid overnight, then rinsed three times with deionized water, and then soaked in eighteen megaohm deionized water overnight. The water was then poured off and the bottles transported to the field.

-The water bottles for anion analysis were rinsed two times with deionized water, soaked with deionized water overnight, water poured off and the bottles then transported to the field.

-Samples for isotope and alkalinity analyses were stored in glass bottles used directly as supplied. Glass bottles used for the carbon isotope analyses were prepared using the same method of preparation as applied to the cation bottles.

-Samples for cation and trace element, anion and $\delta^{13}C_{DIC}$ analyses were filtered to less than 0.2 μm using syringe filters; other samples were unfiltered. During collection of all samples, each bottle was rinsed twice with 10 milliliters of filtered or unfiltered sample water as appropriate. Samples for the base cations and trace element analysis were acidified with concentrated Ultrex II nitric acid to lower pH to less than 2. Blank samples for cations and anions were collected in the field using distilled water to verify the suitability of sample collection and storage methods.

-A sample of runoff was collected for deuterium and ^{18}O analyses from water flowing about 1 meter from the bank of Pueblo Colorado Wash by sinking two glass bottles into the runoff. The open bottles were kept under the water for about 5 minutes so that the bottles were thoroughly rinsed, all air was flushed, and the samples represent the runoff.

All bottles were sealed with electrical tape to avoid loosening and leakage. They were then kept in plastic zip-lock bags, temporarily stored cool with ice in a cooler during transportation, and then placed in a refrigerator at 4°C upon arrival at the laboratory.

2-2-b Field Measurements

The following parameters were measured in the field:

-*pH*: to measure pH, an Orion portable pH meter, model SA 250, with a Ross/Orion combination electrode, was used. The meter was calibrated with pH 4.0, 7.0 and 10.0 Baker Analyzed buffer solutions before each measurement.

- *Specific Conductance*: A YSI S-C-T field meter was used to measure specific conductance. The conductance meter was calibrated against a potassium chloride solution. All measurements were recorded in µ S/cm.

- *Temperature*: measured in degree Celsius and was reported by the conductance meter simultaneously with reading the specific conductance. The measured values were consistent with temperatures reported by the pH meter during pH measurements.

-*Dissolved Oxygen* (O_2): field kits were used to measure the dissolved oxygen in the samples. The measurements were conducted immediately after sampling to avoid contamination and approaching saturation with atmospheric oxygen or depletion caused by biological activities. Although the analyses were conducted promptly, handpumps typically produce water from subsurface vaults that are open to air and the mechanism of pumping; both windmills and electric pumps can entrain air. Two different field kits, with two ranges of sensitivity, were used:

a- CHEMets Kit, K-7512, with a range of 1-12 mg/l of dissolved oxygen. This kit uses reagent ampoules and it is based on colorimetric analysis. The test employs the indigo carmine method (ASTM D 888-87, Dissolved Oxygen in Water, Test Method A), and (Gilbert et al 1982). In an acidic solution, oxygen oxidizes the yellow-green colored leuco of indigo carmine to form a highly colored blue dye. The resulting blue color is proportional to the dissolved oxygen concentration in the sample.

b- CHEMets Kit, K-7501, with a range of 0 to 1 mg/l of dissolved oxygen. This kit uses reagent ampoules and it is based on colorimetric analysis. The test employs the Rhodazine D^{TM} Method—ASTM D 5543-94 (1999), Low Level Dissolved Oxygen in Water, Test Method A, and ASTM Power Plant Manual (1984). Dissolved oxygen reacts with the pale yellow-colored leuco form of Rhodazine D to produce a deep rose color. The resulting color is proportional to the dissolved oxygen concentration in the sample.

- *Dissolved Hydrogen Sulfide (H_2S)*: field kit—CHEMets Kit, K-9510--used to measure the dissolved hydrogen sulfide in the samples. The kit is able to measure the sulfide in two different ranges, 0-1 mg/l and 1-10 mg/l. This kit uses reagent ampoules for determination of sulfide in water. The test method employs the methylene blue chemistry—APHA Standard Methods, method 4500-S^2-D (1992) and EPA Methods for Chemical Analysis of Water and Wastes, method 376.2 (1979). In acidic solution, sulfide reacts with N, N-dimethyl-p-phenylenediamine and ferric chloride to produce methylene blue. The resulting blue color is directly proportional to the sulfide concentration. As sulfide is very volatile, especially when a sample is acidified, the samples were tested and analyzed for sulfide contents immediately.

-*<u>Dissolved Ammonia (NH_3)</u>*: field kit—CHEMets Kit, K-1410—used to measure the dissolved ammonia in the samples. The kit is able to measure the dissolved ammonia in two different scales, 0-1 mg/l and 1-10 mg/l. This kit uses a catalyst solution, an activator solution, and reagent ampoules for determining monochloramine and free ammonia concentration in water. The test employs the Salicylate chemistry—Krom, Michael D. (1980) Spectrophotometric determination of Ammonia, and Methods for the Chemical Analysis of Water and Wastes (1979). Free ammonia reacts with hypochlorite to form monochloramine. Monochloramine reacts with salicylate, in the presence of sodium nitro-ferricyanide, to form 5-aminosalicylate, a green-colored complex. This test method measures free ammonia and monochloramine and the results are expressed in mg/l of ammonianitrogen (NH_3-N).

-*<u>Dissolved Ferrous Iron (Fe^{2+})</u>*: field kit—CHEMtes Kit, K-6210—used to measure dissolved ferrous iron in the samples. The kit is able to measure dissolved ferrous iron in two ranges, 0-10 mg/l and 1-10 mg/l. This kit uses reagent ampoules to determine the dissolved ferrous iron and is based on colorimetric analysis. The test employs the phenanthroline chemistry—APHA Standard Methods, method 3500-Fe D (1992) and ASTM D 1068-88, Iron in Water, Test Method A. Ferrous iron reacts with 1, 10-phenanthroline to an orange-colored complex in direct proportion to ferrous iron concentration.

The results of the field measurements are shown in the table 2-3. Concentrations of all colorimetric methods were determined visually by comparison with the standards provided with the test kits.

- Location of sample sites: to provide a GPS-based map and having the exact location of the samples, all site locations were located a Magellan GPS 4000 XL. The coordination system—Datum—used by the GPS is NAD 27 (table 2-2).

2-3 Laboratory Analyses and Methods

The laboratory analyses were done in different analytical labs:

Alkalinity

Alkalinity titrations were performed in the Analytical Chemistry Lab, Chemistry Department, at Northern Arizona University. An auto-titration apparatus was set up with an Orion Research model 701A digital/ Ionalyzer pH meter and a Ross combination electrode. Standardized hydrochloric acid was transferred with a Technicon proportioning pump delivering 1.78 ml/min. For each titration, 25 milliliters of sample were used and acid was added to reach the endpoint of pH 4.3. The total alkalinity results were reported as mg/l of bicarbonate (see tables 2-4 and 2-5).

Base Cation Analyses

Concentrations of sodium, potassium, magnesium, and calcium were determined by flame atomic absorption in the Analytical Chemistry Lab, Chemistry Department, at the Northern Arizona University, using a Perkin-Elmer model 500 atomic absorption spectrophotometer and hollow cathode lamps. Different standard solutions were made for different cations—sodium 1mg/l, 2.5 mg/l, 5 mg/l, potassium 1mg/l, 2.5mg/l, 5mg/l, magnesium 0.2mg/l, 0.5mg/l, 1 mg/l, 2mg/l and calcium 2.5mg/l, 5mg/l, 10mg/l. Each sample was pretreated with a solution of 10000 mg/l of cesium and lanthanum to ensure that all atoms to be analyzed were in ground state and phosphate complexes would not occur. Most samples were diluted so that concentrations fell within the linear working range of the instrument for sodium, calcium, and magnesium. Some samples were analyzed for potassium without dilution and the only diluting factor was the addition of the cesium and lanthanum solution. Standard curves were constructed for each run, and frequently calibration checks were made between every 8 samples. To ensure precision, some samples were diluted, pretreated, and analyzed repeatedly between other samples to check the outputs. Replicate samples also were analyzed at the USGS analytical lab, Denver Colorado. The calculations of the concentrations were made by considering the dilution factors and the standard curves (see tables 2-4 and 2-5).

Anion Analyses

The anion concentrations were determined by Ion Chromatography (I.C.) at the USGS Mineral Team Analytical Laboratories, located at the Denver Federal Center, Lakewood, Colorado. The methods for I.C., described below, are based on Taggart et al. (2002).

The following methods and instruments were used to determine the fluoride, chloride nitrate, bromide, sulfate, and phosphate concentrations:

-Ion Chromatograph (Dionex Model DX-120)

-Guard Column (Dionex AG-14)

- Analytical Column (Dionex AS-14)

-Anion Self-Regenerating Suppressing 9Dionex ASRS-II)

-Conductivity Detector (Dionex DS4 Detection Stablizer)

-Automated Sampler (AS40)

-PeakNet Workstation Software that controls the instrumentation; automatically collects, processes, and reports data; and provides utilities that interpret analytical results.

-Reagents are:

a) Deionized water with a resistivity of 17.8 mega-ohms or greater

b) Sodium carbonate, Na_2CO_3 ACS reagent grade

c) Sodium bicarbonate, $NaHCO_3$ ACS reagent grade

d) Eluent: 3.5 mM Na_2CO_3, 1.0 mM $NaHCO_3$.

With these operating conditions, fluoride is linear from 0.8 to 4 mg/l, chloride from 0.08 to 4 mg/l, nitrate from 0.08 to 4 mg/l, and sulfate from 1.2 to 80 mg/l. Solutions with higher concentrations were diluted to the operating range. Calibration was accomplished by injection of multi-element anion standards containing the anions of interest. A calibration curve for each component is determined from the data acquired for each different calibration level. A correlation coefficient or “r” value of 0.995 or better should be obtained, using either a linear, cubic, or point to point interpolation. A linear fit is used most often in this method and is determined by a least-squares calculation to fit a line through the calibration points. When the analyte concentration for a specific component approaches the limit of the calibration range, the detector response flattens out toward one extreme or the other. In this case, a quadratic fitting may be used (see table 2-4 and 2-5).

Trace Elements, Iron and Silica Analyses

The trace elements (Ag, Al, As, Ba, Be, Bi, Cd, Ce, Co, Cr, Cs, Cu, Dy, Er, Eu, Ga, Gd, Ge, Ho, La, Li, Lu, Mn, Mo, Nb, Nd, Ni, P, Pb, Pr, Rb, Sb, Sc, Se, Sm, Sr, Ta, Tb, Th, Ti, Tl, Tm, U, V, W, Y, Tb, Zn, Zr), as well as iron and silica concentrations were determined by Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) at the USGS Mineral Team Analytical Laboratories, located at the Denver Federal Center, Lakewood, Colorado (tables 2-6, 2-7 and 2-8). The methods for ICP-MS, described below, are based on Taggart (2002).

The following methods and instrument were employed:

- Inductively Coupled Plasma Mass Spectrometer, Perkins-Elmer Elan 600
- Reagents: a) deionized water

  b) Nitric acid, ULTREX grade (70% concentration

  c) 1% HNO_3: Dilute 10 ml concentrated HNO_3 to 1000 ml with DI water

- Internal standard, which is a solution of 500 µg/l Li, 20 µg/l Rd, and 10 µg/l Ir by performing serial dilution of commercial aqueous standards using 1% HNO_3
- Calibration standards used are the following:
  - a) Standard 1 contains 0.200 mg/l of the following elements in 1% $HNO_{3:}$ Ag, Al, As, Ba, Be, Ca, Cd, Cr, Cs, Cu, Fe, Ga, K, Li, Mg, Mn, Na, Ni, Pb, Rb, Se, Sr, Tl, U, V, and Zn.
  - b) Standard 2 contains 0.010 mg/l of the following elements in 1% HNO_3: Ge, Mo, Nb, P, S, Si, Ta, Ti, W, Zr.
  - c) Standard 3 contains 0.010 mg/l of the following elements in 1% HNO_3: Ce,

La, Nd, Sc, Y.

d) Standard 4 contains 1.00 mg/l of Fe, Al, and Si in 1% HNO_3.

e) Standard 5 is USGS WRD standard reference water sample T-134.

f) Standard 6 contains 142 mg/l SO_4^{2-}.

Prior to analyzing samples, a dual detector calibration and auto-lens adjustment are performed according to manufacturer recommendations. The instrument is then calibrated using the calibration solutions listed above.

Deuterium, ^{18}O, and ^{13}C Analyses

δD, $\delta^{18}O$ and $\delta^{13}C$ were performed at the University of Arizona Department of Geosciences in Tucson, Arizona, with the following methods and instruments:

δ D and $\delta^{18}O$ were measured on a gas-source isotope ratio mass spectrometer (Finnigan Delta S). For hydrogen, samples were reacted at 750°C with Cr metal using a Finnigan H/Device coupled to the mass spectrometer. For oxygen, samples were equilibrated with CO_2 gas at approximately 15°C in an automated equilibration device coupled to the mass spectrometer. Standardization is based on international reference materials VSMOW and SLAP. Precision is 0.9 per mil or better for δD and 0.08 per mil or better for $\delta^{18}O$ on the basis of repeated internal standards. $\delta^{18}O$ and $\delta^{13}C_{DIC}$ were measured using an automated carbonate preparation device (KIEL-III) coupled to a gas-ratio mass spectrometer (Finnigan MAT 252). Powdered samples were reacted with dehydrated phosphoric acid under vacuum at 70°C. The isotope ratio measurement is calibrated based on repeated measurements of NBS-19 and NBS-18 and precision is ± 0.1 ‰ for $\delta^{18}O$ and ±0.06‰ for $\delta^{13}C$ (1δ). Tables 2-8, 2-9, and 2-10 show the results of isotopic analyses.

Field Number	Description of the Host Sediments	Navajo Reservation Number	Water Source	Date of Collection	Depth	Aquifer
04PSD1	Next to the PCW Eolian Sand	Unknown	Hand Pump	July/2004	S-W	PCW
04PWW2	Alluvium	Unknown	Windmill	July/2004	D-W	PCW
04PWW3	Alluvium	17M91A	Windmill	July/2004	D-W	PCW
04PWW5	Alluvium	17K367	Windmill	July/2004	D-W	PCW
04PWW6	Alluvium	17K338	Windmill	July/2004	D-W	PCW
04PWW7	Alluvium	Unknown	Windmill	July/2004	D-W	PCW
04PF11	Alluvium	Boarding School Well#7-Room#705	Electric Pump	July/2004	D-W	PCW
04PF13	Alluvium	Boarding School Well#2-Room#503	Electric Pump	July/2004	D-W	PCW
04PF14	Alluvium	Boarding School Well#1-Room#408	Electric Pump	July/2004	D-W	PCW
04PF15	Alluvium	Boarding School Well#3-Room#505	Electric Pump	July/2004	D-W	PCW
04PF16	Alluvium	Boarding School Well#5-Room#507	Electric Pump	July/2004	D-W	PCW
04PWW17	Alluvium	17M340	Windmill	Aug/2004	D-W	PCW
04PS18	Alluvium	Unknown	Hand Pump	Aug/2004	S-W	PCW
04PWW19	Bed Rock	17T568	Windmill	Aug/2004	D-W	PCW
04PWN20	Alluvium	NTUA Well#1	Electric Pump	Aug/2004	D-W	PCW
04PWN21	Alluvium	NTUA Well#2	Electric Pump	Aug/2004	D-W	PCW
04PWN22	Alluvium	NTUA Well#3	Electric Pump	Aug/2004	D-W	PCW
04PC23	Alluvium	# 17-5-4	Hand Pump	Aug/2004	S-W	PCW
04PS24	Alluvium	# 17-3-5	Hand Pump	Aug/2004	S-W	PCW
04PS25	Alluvium	# 17-5-7	Hand Pump	Aug/2004	S-W	PCW
04PS26	Alluvium	# 17-7-2	Hand Pump	Aug/2004	S-W	PCW
04PCS29	Alluvium	# 17-3-3	Hand Pump	Aug/2004	S-W	PCW
04KW01	De Chelly sandstone	Spring	Spring	Aug/2004	S-W	PCW
04PGW27	Bed Rock	17K2	Windmill	Aug/2004	D-W	Defiance
04PGW30	Bed Rock	Unknown	Windmill	Aug/2004	D-W	Defiance
04PGS28	Bed Rock	17-4-27	Windmill	Aug/2004	S-W	Snake Flat
TSN03	Alluvium	17K306	Windmill	July/2001	D-W	PCW
TSN04	Alluvium	17M-203	Windmill	July/2001	D-W	S-B
TSN09	Alluvium/Bed Rock	17T-559	Windmill	July/2001	D-W	S-B
TSN37	Bed Rock	17T-518	Windmill	Sep/2001	D-W	S-B
TSN11CD	Bed Rock	17T-540	Windmill	N/A	D-W	S-B
TSN33SWE	Bed Rock	17M-246	Windmill	N/A	D-W	S-B
TSN34HA	Bed Rock	17T-517	Windmill	N/A	D-W	S-B
TSN37TH	Bed Rock	17T-518	Windmill	N/A	D-W	S-B
TSN39CS	Bed Rock	17T-523	Windmill	N/A	D-W	Defiance
TSN48JW	Bed Rock	17T-522	Windmill	N/A	D-W	S-B
TSN49TC	Bed Rock	17M-187	Windmill	N/A	D-W	Defiance
TSN66JS	Alluvium	Unknown	Hand Pump	N/A	S-W	S-B
TSN69PJW	Bed Rock	Unknown	Windmill	N/A	D-W	Defiance
TSN109GL	--------	-------	Lake	N/A	----	-----
TSN110GSD	--------	-------	Sewage	-----	----	----

Table 2-1: The general characteristics of water sample collection sites. Deep water (D-W; >10m) and shallow water (S-W; <10 m) were differentiated by the depth of the well. The green boxes are data from USGS unpublished data. PCW= Pueblo Colorado Wash S-B= Steamboat Wash
N/A = Not Available

Field Number	Longitude-NAD27	Latitude- NAD27
04PSD1	109 36.844	35 41.141
04PWW2	109 39.377	35 41.821
04PWW3	109 40.998	35 38.945
04PWW5	109 44.599	35 36.265
04PWW6	109 45.945	35 35.047
04PWW7	109 51.350	35 30.609
04PF11	109 51.313	35 31.097
04PF13	109 51.265	35 31.227
04PF14	109 51.197	35 31.273
04PF15	109 51.044	35 31.423
04PF16	109 50.794	35 31.641
04PWW17	109 52.164	35 29.379
04PS18	109 53.904	35 26.647
04PWW19	109 49.757	35 31.100
04PWN20	109 49.863	35 32.287
04PWN21	109 49.668	35 32.690
04PWN22	109 49.387	35 32.972
04PC23	109 42.559	35 38.683
04PS24	109 48.909	35 34.048
04PS25	109 47.865	35 34.181
04PS26	109 49.195	35 32.809
04PCS29	109 43.321	35 37.600
04KW01	109 25.479	35 45.129
04PGW27	109 30.637	35 41.107
04PGW30	109 32.403	35 37.282
04PGS28	109 36.809	35 45.585
TSN03	W 109.8885	N 35.40767
TSN04	W -109.92115	N 35.54948
TSN09	W -109.8525	N 35.46533
TSN37	W -109.96203	N 35.60763
TSN11CD	W -109.9615	N 35.53100
TSN33SWE	W -109.8315	N 35.64716
TSN34HA	W -109.84717	N 35.61317
TSN37TH	W -109.96203	N 35.60763
TSN39CS	W -109.64055	N 35.58389
TSN48JW	W -109.79350	N 35.61917
TSN49TC	W -109.75417	N 35.46667
TSN66JS	W -109.77039	N 35.67960
TSN69PJW	W -109.64605	N 35.41735
TSN109GL	W-109.52007	N 35.73143
TSN110GSD	W-109.56518	N 35.70932

Table 2-2: Locations of the sampled sites. The green boxes are from USGS unpublished data.

Field Number	**Conductivity (μ S/cm)**	**pH**	**Temp. (°C)**	**Dissolved O_2 (mg/l)**	**Dissolved Fe^{2+} (mg/l)**	**Ammonia (mg/l)**	**H_2S (mg/l)**
04PSD1	1318	8.54	15.8	2.5	< 0.1	0	0
04PWW2	857	8.26	15.1	3	0	0.1	0
04PWW3	1425	7.41	14.1	< 1	0.2	0.2	0
04PWW5	2350	7.59	17.5	< 1	3	0	< 0.1
04PWW6	625	7.47	15.6	< 1	<0.1	0.1	0
04PWW7	739	8.31	19.5	5.5	<0.1	0	0
04PF11	981	7.78	14.6	2	<0.1	0	0
04PF13	1113	7.84	16	1	0.1	0	0
04PF14	888	7.82	17.6	4	<0.1	0	0
04PF15	841	7.82	15	1	1	0.1	0
04PF16	763	7.85	15.5	1	0.8	0	0
04PWW17	1391	7.83	16.4	3	0.2	0.1	0
04PS18	1288	8.93	25	5	<0.1	0	0
04PWW19	561	9.48	18.2	1.5	<0.1	0	0
04PWN20	677	7.82	15.6	1	1	0	0
04PWN21	818	7.6	15.9	1	0.8	0	0
04PWN22	737	7.71	16.4	1	1	0.1	0
04PC23	1057	7.66	18.2	2	0.2	0	0
04PS24	732	7.98	14.6	3.5	<0.1	0	0
04PS25	505	8.18	16.5	4	<0.1	0	0
04PS26	669	7.92	18.5	2	<0.1	0	0
04PCS29	1280	7.87	15.9	4	<0.1	0	0
04KW01	394	7.74	22.6	N/D	N/D	N/D	N/D
04PGW27	381	7.62	14	2	0.1	N/D	0
04PGW30	447	7.59	15.9	2	N/D	N/D	0
04PGS28	2110	8.44	18.8	< 1	<0.1	0	0
TSN03	26600	7.94	22	N/D	N/D	N/D	N/D
TSN04	4970	7.65	19.5	6	0.4	N/A	N/A
TSN09	1760	7.92	17.8	2	0.1	N/A	N/A
TSN37	1290	9.82	15	<0.1	0.1	N/A	N/A
TSN11CD	795	9.21	N/A	N/A	N/A	N/A	N/A
TSN33SWE	347	8.22	N/A	N/A	N/A	N/A	N/A
TSN34HA	708	9.48	N/A	N/A	N/A	N/A	N/A
TSN37TH	664	9.82	N/A	N/A	N/A	N/A	N/A
TSN39CS	356	7.99	N/A	N/A	N/A	N/A	N/A
TSN48JW	520	8.52	N/A	N/A	N/A	N/A	N/A
TSN49TC	502	9.00	N/A	N/A	N/A	N/A	N/A
TSN66JS	598	7.71	N/A	N/A	N/A	N/A	N/A
TSN69PJW	287	7.89	N/A	N/A	N/A	N/A	N/A
TSN109GL	N/A	9.1	N/A	N/A	N/A	N/A	N/A
TSN110GSD	N/A	7.50	N/A	N/A	N/A	N/A	N/A

Table 2-3: Results of the field analyses of water samples. The green boxes are data from USGS unpublished data. N/D = Not Determined N/A = Not Available

Sample	**F^-**	**Cl^-**	**Br^-**	**NO_3^-**	**$H_2PO_4^-$**	**SO_4^{--}**	**HCO_3^-**	**K^+**	**Na^+**	**Ca^{++}**	**Mg^{++}**	**Charge Balance**
04PSD1	3.3	122	.63	27	<0.1	149	410	1.01	284	9.95	6.67	-3.34
04PS18	2.7	48.4	0.46	6.1	0.16	208	453.9	5.4	265.6	10.86	3.07	-7.08
04PC23	.85	70	0.7	<0.1	<0.1	52.3	543.1	1.6	183.3	61.25	16.7	3.6
04PS24	1.6	49.1	0.48	<0.1	<0.1	44.3	366.2	8.06	34.2	40.44	55.25	1.7
04PS25	1	32.7	0.46	32.2	<0.1	27.3	215.8	5.03	25.8	59.45	13.54	-5
04PS26	1.6	41.6	0.37	0.7	0.13	19.8	352	14.67	46.2	41.69	41.2	5.4
04PGS28	1.55	59	0.26	3.7	<0.1	630	421.8	4.13	332.8	10.52	5.9	-34
04PCS29	1	169	1.48	2.3	<0.1	19.3	530.7	6.25	199	59.5	15.36	-6.8
04KW01	0.2	14.1	0.1	<0.1	<0.1	11	181	3.19	10.35	42.3	9.5	-5.3

Table 2-4: The concentrations of major cations and charge balance of the shallow water in Pueblo Colorado Wash Aquifer (all units are in mg/l).

Sample	F^-	Cl^-	Br^-	NO_3^-	$H_2PO_4^-$	SO_4^{--}	HCO_3^-	K^+	Na^+	Ca^{++}	Mg^{++}	Charge Balance
04PWW2	0.52	411	1.3	188	<0.1	1390	231.2	3.32	914.7	39.9	24.35	-8.1
04PWW3	0.46	39.5	0.2	<0.1	<0.1	10.3	413.9	2.07	92.1	43.9	21.13	-1.8
04WW5	0.9	480	2.4	<0.1	<0.1	9	506.8	4.38	303	99.2	32.94	-5.32
04WW6	.75	49.6	.26	<0.1	<0.1	20.3	313.5	1.13	40.4	70.75	16.44	-4.96
04WW7	2.1	63	.38	<0.1	<0.1	23	330.8	3.77	125.4	18.05	20.93	4.63
04PF11	1.4	121	0.78	0.3	<0.1	12	405.1	5.59	143.4	29.63	24.75	-4.86
04PF13	1	164	0.96	<0.1	<0.1	14.8	410.4	8.07	185.8	28.2	18.75	-4.19
04PF14	1.2	98.3	0.6	0.6	<0.1	17.6	410.4	1.97	114	38.1	25.38	-7.44
04PF15	1.3	95.4	0.6	<0.1	<0.1	2	385.6	4.88	87.6	42.1	36.63	-1.09
04PF16	1.3	85.2	0.52	<0.1	<0.1	18.5	357.3	4.28	73	44.4	35.99	-3
04PWW17	2	215	1.1	2.8	<0.1	83	414.8	6.82	200.9	47.6	30.7	-6.69
04PWW19	1.55	106	<0.05	1.5	<0.1	19.5	265.35	2.17	174.8	1.27	0.26	-1.4
04PN20	0.93	59	0.45	<0.1	<0.1	31.5	322.1	4.4	73.8	47.4	26.4	2.8
04PN21	1.1	86.9	0.68	<0.1	<0.1	0..2	389.2	4.65	81.1	58.85	27.75	-0.29
04PN22	0.94	71.1	0.42	<0.1	<0.1	1.1	365.6	4.41	58.6	59.62	27.55	-2.12
04PGW27	0.26	15	0.14	4.5	<0.1	8.6	219.1	1.61	7	62.5	7.31	-5.2
04PGW30	.25	30.2	0.16	4.7	<0.1	12.1	231.2	1.76	15.3	73.16	4.7	-4.9
TSN03	<0.8	15000	N/D	<1.8	N/D	1400	188	31	7000	1000	860	-6.4
TSN04	2	670	N/D	<1.8	N/D	1400	376	18	910	120	56	-7.7
TSN09	1.6	110	N/D	47	N/D	390	376	2.9	280	49	24	-9.2
TSN37	0.8	11	N/D	<1.8	N/D	18	342	1.4	137	0.66	0.11	-4.4

Table 2-5: The concentrations of major cations, anions, and charge balance of the deep water in Pueblo Colorado Wash Aquifer (all units are in mg/l). N/D= not determined

Sample	Ag (µ g/l)	Al (µ g/l)	As (µ g/l)	Ba (µ g/l)	Be (µ g/l)	Bi (µ g/l)	Ca (m g/l)	Cd (µ g/l)	Ce (µ g/l)	Co (µ g/l)	Cr (µ g/l)
04PSD1	<3	3	13	52.4	<0.05	< 0.2	9.25	0.03	< 0.01	0.12	<1
04PS18	<3	23	26	26	<0.05	< 0.2	12	0.03	0.02	0.05	1.1
04PC23	<3	<2	5.8	197	<0.05	< 0.2	62.4	0.07	0.01	0.34	<1
04PS24	<3	2	21.9	12.2	<0.05	< 0.2	43.6	0.04	< 0.01	0.03	<1
04PS25	<3	<2	4.2	110	<0.05	< 0.2	59.7	0.04	0.02	0.04	<1
04PS26	<3	<2	15.3	76.7	<0.05	< 0.2	43	<0.02	< 0.01	0.06	<1
04PGS28	<3	4.2	8.2	22.3	<0.05	< 0.2	11.7	0.04	0.02	0.05	<1
04PCS29	<3	<2	5.6	303	<0.05	< 0.2	62.6	0.05	< 0.01	0.1	<1
04KW01	<3	<2	2	411	<0.05	< 0.2	53.9	<0.02	0.02	0.17	<1

Table 2-6: The concentrations of minor and trace elements in the shallow water of Pueblo Colorado Wash Aquifer.

Sample	**Cs (µg/l)**	**Cu (µg/l)**	**Dy (µg/l)**	**Er(µ g/l)**	**Eu(µ g/l)**	**Fe(µ g/l)**	**Ga(µ g/l)**	**Gd(µ g/l)**	**Ge(µ g/l)**	**Ho(µ g/l)**	**K(m g/l)**
04PSD1	0.04	4.3	< 0.005	< 0.005	0.006	<50	< 0.05	< 0.005	< 0.05	< 0.005	0.95
04PS18	< 0.02	6.5	< 0.005	< 0.005	< 0.005	<50	< 0.05	< 0.005	0.06	< 0.005	5.56
04PC23	5.8	0.56	< 0.005	< 0.005	0.02	92	< 0.05	< 0.005	< 0.05	< 0.005	1.74
04PS24	1.52	4.4	< 0.005	< 0.005	< 0.005	<50	< 0.05	< 0.005	< 0.05	< 0.005	8.07
04PS25	0.02	0.76	< 0.005	< 0.005	0.01	<50	< 0.05	< 0.005	< 0.05	< 0.005	4.88
04PS26	< 0.02	<0.5	< 0.005	< 0.005	0.01	<50	< 0.05	< 0.005	< 0.05	< 0.005	14.2
04PGS28	6.33	1.2	< 0.005	< 0.005	< 0.005	<50	< 0.05	< 0.005	0.1	< 0.005	3.94
04PCS29	< 0.02	5.1	< 0.005	< 0.005	0.04	<50	< 0.05	< 0.005	< 0.05	< 0.005	6.73
04KW01	< 0.02	0.8	< 0.005	< 0.005	0.056	<50	< 0.05	0.01	< 0.05	< 0.005	3.19

Table 2-6 (continued)

Sample	La (µ g/l)	Li (µ g/l)	Lu (µ g/l)	Mg(mg/l)	Mn (µg/l)	Mo (µg/l)	Na(mg/l)	Nb (µg/l)	Nd (µg/l)	Ni (µ g/l)	P(µ g/l)
04PSD1	0.02	145	< 0.1	6.99	14	17.3	nr	0.32	< 0.01	1.2	0.02
04PS18	0.04	61.1	< 0.1	2.75	0.6	15.6	nr	0.2	< 0.01	0.5	0.07
04PC23	0.01	172	< 0.1	15.2	427	34.9	nr	< 0.2	< 0.01	1.8	0.04
04PS24	0.01	148	< 0.1	51.4	31.6	19.9	45.4	< 0.2	< 0.01	0.9	< 0.01
04PS25	0.04	64.7	< 0.1	12.6	0.6	11.9	29.2	< 0.2	< 0.01	1.5	0.04
04PS26	0.02	130	< 0.1	41.2	125	4.4	50.3	< 0.2	< 0.01	1.1	0.06
04PGS28	0.03	250	< 0.1	5.24	10.5	21.4	nr	< 0.2	< 0.01	0.4	0.02
04PCS29	< 0.01	84.4	< 0.1	14.7	71.6	19.1	nr	< 0.2	< 0.01	2	0.02
04KW01	0.01	8.3	< 0.1	11	13	< 2	12	< 0.2	0.03	1.2	< 0.01

Table 2-6 (continued)

Sample	Pb(μ g/l)	Pr(μ g/l)	Rb(μ g/l)	Sb(μ g/l)	Sc(μ g/l)	Se(μ g/l)	SiO_2(mg/l)	Sm(μ g/l)	SO_4(m g/l)	Sr(μ g/l)	Ta(μ g/l)
04PSD1	0.3	< 0.01	0.46	<0.3	1.2	6.7	9.8	< 0.01	139	1710	0.38
04PS18	0.4	< 0.01	5.14	<0.3	2.4	21	19.7	< 0.01	201	595	0.24
04PC23	<0.05	< 0.01	0.7	<0.3	3.3	3.7	27.1	< 0.01	46	1200	0.08
04PS24	0.3	< 0.01	1.96	<0.3	6.3	2.2	56	< 0.01	38	2290	< 0.02
04PS25	<0.05	< 0.01	1.25	<0.3	4.2	2.8	33.8	< 0.01	23	640	< 0.02
04PS26	<0.05	< 0.01	2.13	<0.3	5.8	1.5	48.7	< 0.01	18	1100	< 0.02
04PGS28	0.2	< 0.01	2.55	<0.3	1.8	4.4	14.7	< 0.01	531	1110	0.2
04PCS29	0.3	< 0.01	2.47	<0.3	3.3	6.2	26.9	< 0.01	16	1050	0.08
04KW01	<0.05	< 0.01	0.48	<0.3	< 0.6	1.1	3.7	0.01	9	384	< 0.02

Table 2-6 (continued)

Sample	**Tb(μg/l)**	**Th(μg/l)**	**Ti(μ g/l)**	**Tl(μ g/l)**	**Tm(μg/l)**	**U(μ g/l)**	**V(μ g/l)**	**W(μ g/l)**	**Y(μ g/l)**	**Yb(μg/l)**	**Zn(μg/l)**	**Zr(μg/l)**
04PSD1	< 0.005	< 0.2	2	<0.1	< 0.005	47.3	88.7	< 0.5	0.02	< 0.005	61.7	< 0.2
04PS18	< 0.005	< 0.2	3	<0.1	< 0.005	47.9	156	< 0.5	0.02	< 0.005	7.7	< 0.2
04PC23	< 0.005	< 0.2	0.7	<0.1	< 0.005	77.9	9	< 0.5	0.02	< 0.005	1	< 0.2
04PS24	< 0.005	< 0.2	0.6	<0.1	< 0.005	25.1	50.1	< 0.5	0.02	< 0.005	62.3	< 0.2
04PS25	< 0.005	< 0.2	< 0.5	<0.1	< 0.005	6.09	18	< 0.5	0.01	< 0.005	1.4	< 0.2
04PS26	< 0.005	< 0.2	< 0.5	<0.1	< 0.005	10.3	14.3	< 0.5	0.01	< 0.005	1.4	< 0.2
04PGS28	< 0.005	< 0.2	7.7	<0.1	< 0.005	46.4	139	< 0.5	0.02	< 0.005	15	< 0.2
04PCS29	< 0.005	< 0.2	< 0.5	<0.1	< 0.005	14.3	4.5	< 0.5	0.01	< 0.005	165	< 0.2
04KW01	< 0.005	< 0.2	< 0.5	<0.1	< 0.005	0.92	1.4	< 0.5	0.02	< 0.005	1	< 0.2

Table 2-6 (continued)

Sample	**Ag(μ g/l)**	**Al(μ g/l)**	**As(μ g/l)**	**Ba(μ g/l)**	**Be(μ g/l)**	**Bi(μ g/l)**	**Ca(m g/l)**	**Cd(μ g/l)**	**Ce(μ g/l)**	**Co(μ g/l)**	**Cr(μ g/l)**
04PWW2	<3	<2	8.5	7.61	<0.05	< 0.2	39.9	0.08	< 0.01	0.05	<1
04PWW3	<3	<2	2	334	<0.05	< 0.2	41.4	<0.02	< 0.01	0.04	<1
04WW5	<3	<2	3.4	3040	<0.05	< 0.2	99.2	<0.02	< 0.01	0.1	<1
04WW6	<3	<2	8.8	417	<0.05	< 0.2	73.8	<0.02	< 0.01	0.12	<1
04WW7	<3	1.9	9.4	250	<0.05	< 0.2	19.6	0.05	< 0.01	0.06	<1
04PF11	<3	2.6	4.4	303	<0.05	< 0.2	29.2	0.04	< 0.01	0.04	<1
04PF13	<3	<2	3.7	242	<0.05	< 0.2	28.8	0.04	< 0.01	0.04	<1
04PF14	<3	<2	3.6	132	<0.05	< 0.2	39.2	0.13	< 0.01	0.03	<1
04PF15	<3	<2	20.8	3500	<0.05	< 0.2	43.8	0.03	< 0.01	0.07	<1
04PF16	<3	<2	5.3	2220	<0.05	< 0.2	45.5	0.05	< 0.01	0.06	<1
04PWW17	<3	<2	24.7	227	<0.05	< 0.2	44.7	0.08	< 0.01	0.08	<1
04PWW19	<3	6.2	109	5.15	<0.05	< 0.2	1.27	0.03	0.02	<0.02	<1
04PN20	<3	<2	8	745	<0.05	< 0.2	52.4	0.04	< 0.01	0.02	<1
04PN21	<3	<2	1	1300	<0.05	< 0.2	60.2	<0.02	< 0.01	0.03	<1
04PN22	<3	<2	1	869	<0.05	< 0.2	57.5	<0.02	< 0.01	<0.02	<1
04PGW27	<3	2.4	1	338	<0.05	< 0.2	62.5	0.05	< 0.01	0.03	<1
04PGW30	<3	<2	<1	254	<0.05	< 0.2	72.6	0.02	< 0.01	0.03	<1
TSN03	0.4	<1	8	40	<0.5	< 0.1	1000	<0.2	< 0.1	<0.2	<10
TSN04	0.01	<0.1	11	10	<0.05	< 0.01	120	<0.02	< 0.01	<0.02	<1
TSN09	<0.01	20	9.5	17	<0.05	< 0.01	49	<0.02	0.07	<0.02	<1
TSN37	<0.01	2.8	110	7.7	<0.05	< 0.02	0.66	<0.02	< 0.01	<0.02	<1

Table 2-7: The concentrations of minor and trace elements in the deep water of Pueblo Colorado Wash Aquifer. N/A = Not Available N/D = Not Determined

Sample	**Cs(μ g/l)**	**Cu(μ g/l)**	**Dy(μ g/l)**	**Er(μ g/l)**	**Eu(μ g/l)**	**Fe(μ g/l)**	**Ga(μ g/l)**	**Gd(μ g/l)**	**Ge(μ g/l)**	**Ho(μ g/l)**	**K(m g/l)**
04PWW2	0.04	2.9	< 0.005	< 0.005	< 0.005	<50	< 0.05	< 0.005	0.07	< 0.005	3.49
04PWW3	< 0.02	<0.5	< 0.005	< 0.005	0.04	<50	< 0.05	< 0.005	< 0.05	< 0.005	1.98
04WW5	0.1	0.64	< 0.005	< 0.005	0.32	3100	< 0.05	< 0.005	0.1	< 0.005	4.14
04WW6	< 0.02	0.51	< 0.005	< 0.005	0.05	<50	< 0.05	< 0.005	< 0.05	< 0.005	1.18
04WW7	0.03	3.8	< 0.005	< 0.005	0.03	<50	< 0.05	< 0.005	< 0.05	< 0.005	4.16
04PF11	0.04	2.6	< 0.005	< 0.005	0.04	<50	< 0.05	< 0.005	< 0.05	< 0.005	5.84
04PF13	0.44	0.74	< 0.005	< 0.005	0.03	118	< 0.05	< 0.005	< 0.05	< 0.005	7.43
04PF14	< 0.02	1.9	< 0.005	< 0.005	0.01	<50	< 0.05	< 0.005	< 0.05	< 0.005	2.14
04PF15	< 0.02	0.67	< 0.005	< 0.005	0.42	1030	< 0.05	< 0.005	0.05	< 0.005	5.19
04PF16	< 0.02	0.69	< 0.005	< 0.005	0.24	228	< 0.05	< 0.005	< 0.05	< 0.005	3.8
04PWW17	0.1	1	< 0.005	< 0.005	0.02	<50	< 0.05	< 0.005	< 0.05	< 0.005	6.98
04PWW19	< 0.02	0.74	< 0.005	< 0.005	< 0.005	<50	0.1	< 0.005	0.07	< 0.005	2.19
04PN20	0.08	<0.5	< 0.005	< 0.005	0.089	1030	< 0.05	< 0.005	0.07	< 0.005	4.68
04PN21	< 0.02	<0.5	< 0.005	< 0.005	0.15	665	< 0.05	< 0.005	< 0.05	< 0.005	4.99
04PN22	< 0.02	<0.5	< 0.005	< 0.005	0.1	670	< 0.05	< 0.005	< 0.05	< 0.005	4.67
04PGW27	0.21	2.4	< 0.005	< 0.005	0.04	<50	< 0.05	< 0.005	0.07	< 0.005	1.63
04PGW30	0.11	2.1	< 0.005	< 0.005	0.03	<50	< 0.05	< 0.005	0.07	< 0.005	1.7
TSN03	0.2	10	< 0.05	< 0.05	< 0.05	1200	< 0.2	< 0.05	< 0.2	< 0.05	31000
TSN04	0.06	2	< 0.005	< 0.005	< 0.005	300	< 0.02	< 0.005	0.08	< 0.005	18000
TSN09	< 0.01	4	< 0.005	< 0.005	< 0.005	76	< 0.02	0.007	0.3	< 0.005	2900
TSN37	< 0.01	1.2	< 0.005	< 0.005	< 0.005	13	0.28	< 0.005	0.068	< 0.005	920

Table 2-7 (continued).

Sample	La(μ g/l)	Li(μ g/l)	Lu(μ g/l)	Mg(m g/l)	Mn(μ g/l)	Mo(μ g/l)	Na(mg/l)	Nb(μ g/l)	Nd(μ g/l)	Ni(μ g/l)	P(μ g/l)
04PWW2	0.01	387	< 0.1	25.3	0.6	38.5	Nr	< 0.2	< 0.01	0.6	< 0.01
04PWW3	0.01	94.7	< 0.1	18.6	78	4	102	< 0.2	< 0.01	0.8	0.01
04WW5	0.06	125	< 0.1	30.2	291	< 2	Nr	< 0.2	0.01	1.5	< 0.01
04WW6	0.02	45.9	< 0.1	15.8	206	4.3	46.7	< 0.2	< 0.01	1.3	0.02
04WW7	0.03	101	< 0.1	20.6	55.3	20.5	144	< 0.2	< 0.01	0.7	0.02
04PF11	0.04	133	< 0.1	25.2	24.5	23.4	Nr	< 0.2	< 0.01	0.7	0.01
04PF13	0.54	153	< 0.1	17.6	9.3	18.9	Nr	< 0.2	< 0.01	0.6	< 0.01
04PF14	< 0.01	140	< 0.1	24.1	15.7	12.9	138	< 0.2	< 0.01	0.9	< 0.01
04PF15	0.07	113	< 0.1	37.2	231	12.1	113	< 0.2	0.02	0.6	0.04
04PF16	0.02	111	< 0.1	35.3	251	12.2	89.5	< 0.2	0.01	0.8	0.03
04PWW17	0.08	191	< 0.1	31.8	82.2	52.6	Nr	< 0.2	< 0.01	1	0.03
04PWW19	0.4	39.2	< 0.1	0.2	1.7	6.9	Nr	< 0.2	< 0.01	<0.4	0.02
04PN20	0.11	87.7	< 0.1	27.9	264	16.6	63.3	< 0.2	< 0.01	0.7	0.04
04PN21	0.02	79.9	< 0.1	27.3	314	4.4	103	< 0.2	< 0.01	0.7	0.08
04PN22	0.01	77.6	< 0.1	27.6	192	4.2	73.6	< 0.2	< 0.01	0.7	0.04
04PGW27	0.02	23.6	< 0.1	7.31	2.4	< 2	7.64	< 0.2	< 0.01	1.3	< 0.01
04PGW30	< 0.01	64.1	< 0.1	5.31	4	< 2	17.1	< 0.2	< 0.01	1.2	< 0.01
TSN03	< 0.1	2400	N/A	860	500	99	7000	< 0.1	N/A	<1	< 10
TSN04	< 0.01	390	N/A	56	230	820	910	< 0.01	N/A	<0.1	8
TSN09	0.03	160	N/A	24	8.5	99	280	0.03	N/A	<0.1	25
TSN37	< 0.01	16	N/A	0.11	0.99	4.5	>100	< 0.01	N/A	<0.1	340

Table 2-7 (continued).

Sample	**Pb(μ g/l)**	**Pr(μ g/l)**	**Rb(μ g/l)**	**Sb(μ g/l)**	**Sc(μ g/l)**	**Se(μ g/l)**	**SiO$_2$(mg/l)**	**Sm(μ g/l)**	**SO$_4$(m g/l)**	**Sr(μ g/l)**	**Ta(μ g/l)**
04PWW2	0.06	< 0.01	1.15	<0.3	1.2	92.5	10	< 0.01	1380	9430	< 0.02
04PWW3	<0.05	< 0.01	0.35	<0.3	2	1.3	16	< 0.01	7	2300	< 0.02
04WW5	<0.05	< 0.01	2.56	<0.3	3	13.8	22.5	< 0.01	4	3680	< 0.02
04WW6	0.07	< 0.01	0.48	<0.3	4.2	1.6	35.8	< 0.01	17	1140	< 0.02
04WW7	<0.05	< 0.01	0.59	<0.3	2.7	2.2	24.3	< 0.01	21	959	< 0.02
04PF11	0.5	< 0.01	2.5	<0.3	3.2	5.1	27.6	< 0.01	10	1110	< 0.02
04PF13	0.2	< 0.01	2.64	<0.3	3.4	7	28.3	< 0.01	12	905	0.07
04PF14	0.3	< 0.01	0.73	<0.3	2.8	6.5	25	< 0.01	15	1080	< 0.02
04PF15	<0.05	< 0.01	1.75	<0.3	3.7	3.6	32.6	0.01	< 2	1930	< 0.02
04PF16	<0.05	< 0.01	1.08	<0.3	4.2	3.7	36.5	< 0.01	16	1690	< 0.02
04PWW17	0.06	< 0.01	1.82	<0.3	4.8	8.8	41.1	< 0.01	65	1970	0.1
04PWW19	<0.05	< 0.01	0.68	<0.3	1.4	9.8	12.4	< 0.01	17	39.2	< 0.02
04PN20	<0.05	< 0.01	1.44	<0.3	4.9	2.2	41.1	< 0.01	29	1530	< 0.02
04PN21	<0.05	< 0.01	1.72	<0.3	4.4	3	40.2	< 0.01	< 2	1630	< 0.02
04PN22	<0.05	< 0.01	1.3	<0.3	4.2	2.3	35.3	< 0.01	< 2	1410	< 0.02
04PGW27	0.3	< 0.01	1.49	<0.3	2.3	2.4	17.7	< 0.01	6	323	< 0.02
04PGW30	<0.05	< 0.01	1.27	<0.3	2.6	2.6	20.8	< 0.01	10	271	< 0.02
TSN03	<0.5	< 0.1	11	<0.2	N/A	10	20	< 0.1	1500	65000	N/A
TSN04	<0.05	< 0.01	4.6	0.02	N/A	4	23	< 0.01	1600	4700	N/A
TSN09	0.07	< 0.01	0.8	0.1	N/A	32	18	< 0.01	450	2000	N/A
TSN37	<0.05	< 0.01	0.4	<0.02	N/A	< 0.2	12	< 0.01	26	24	N/A

Table 2-7 (continued).

Sample	Tb(μ g/l)	Th(μ g/l)	Ti(μ g/l)	Tl(μ g/l)	Tm(μ g/l)	U(μ g/l)	V(μ g/l)	W(μ g/l)	Y(μ g/l)	Yb(μ g/l)	Zn(μ g/l)	Zr(μ g/l)
04PWW2	< 0.005	< 0.2	17.2	<0.1	< 0.005	28.9	27.5	< 0.5	0.05	< 0.005	207	0.2
04PWW3	< 0.005	< 0.2	< 0.5	<0.1	< 0.005	7.54	7.1	< 0.5	0.03	< 0.005	13.8	< 0.2
04WW5	< 0.005	< 0.2	< 0.5	<0.1	< 0.005	0.42	<0.5	< 0.5	0.04	< 0.005	3.5	< 0.2
04WW6	< 0.005	< 0.2	< 0.5	<0.1	< 0.005	4.94	26.1	< 0.5	0.02	< 0.005	1020	< 0.2
04WW7	< 0.005	< 0.2	< 0.5	<0.1	< 0.005	2.35	<0.5	< 0.5	0.01	< 0.005	141	< 0.2
04PF11	< 0.005	< 0.2	< 0.5	<0.1	< 0.005	11.8	13.3	< 0.5	0.01	< 0.005	6.6	< 0.2
04PF13	< 0.005	< 0.2	< 0.5	<0.1	< 0.005	30.5	8.3	< 0.5	0.02	< 0.005	3960	< 0.2
04PF14	< 0.005	< 0.2	< 0.5	<0.1	< 0.005	7.48	10.6	< 0.5	0.01	< 0.005	40.7	< 0.2
04PF15	< 0.005	< 0.2	< 0.5	<0.1	< 0.005	0.26	<0.5	< 0.5	0.05	< 0.005	20.4	< 0.2
04PF16	< 0.005	< 0.2	< 0.5	<0.1	< 0.005	1.69	1.1	< 0.5	0.03	< 0.005	16.4	< 0.2
04PWW17	< 0.005	< 0.2	1.1	<0.1	< 0.005	42.5	42.6	< 0.5	0.02	< 0.005	38.1	< 0.2
04PWW19	< 0.005	< 0.2	< 0.5	<0.1	< 0.005	24.1	293	1.3	< 0.01	< 0.005	28.5	< 0.2
04PN20	< 0.005	< 0.2	0.6	<0.1	< 0.005	< 0.1	<0.5	< 0.5	0.02	< 0.005	2.4	< 0.2
04PN21	< 0.005	< 0.2	< 0.5	<0.1	< 0.005	< 0.1	<0.5	< 0.5	0.03	< 0.005	7.3	< 0.2
04PN22	< 0.005	< 0.2	< 0.5	<0.1	< 0.005	< 0.1	<0.5	< 0.5	0.02	< 0.005	4.9	< 0.2
04PGW2	< 0.005	< 0.2	< 0.5	<0.1	< 0.005	1.69	3.8	< 0.5	< 0.01	< 0.005	959	< 0.2
04PGW3	< 0.005	< 0.2	< 0.5	<0.1	< 0.005	1.8	2.1	< 0.5	< 0.01	< 0.005	880	< 0.2
TSN03	< 0.05	< 0.2	N/A	<0.5	< 0.05	27	<1	< 0.2	0.6	< 0.1	1400	N/A
TSN04	< 0.005	< 0.02	N/A	<0.05	< 0.005	9.9	0.2	0.1	0.07	< 0.01	310	N/A
TSN09	< 0.005	< 0.02	N/A	<0.05	< 0.005	39	23	0.1	0.06	< 0.01	170	N/A
TSN37	< 0.005	< 0.02	N/A	<0.05	< 0.005	5.9	79	0.39	< 0.01	< 0.01	11	N/A

Table 2-7 (continued)

Sample	**Cl^- (mg/L)**	**F^- (mg./l)**	**NO_3^- $^($mg/l)**	**SO_4^{--} (mg/l)**	**HCO_3^- (mg/l)**	**Ca^{++} (mg/l)**	**K^+ (mg/l)**	**Mg^{++} (mg/l)**	**Na^+ (mg/l)**	**$\delta^{18}O$**	**δD**
TSN04SB	670	2	<1.8	1400	376	120	20	54	710	-12.20	-93.00
TSN09GSW	110	1.6	47	390	376	54	3.2	25	320	-8.20	-63.00
TSN11CD	9.3	1.2	1.7	110	314	1	3.8	0.12	180	-11	-84
TSN33SWE	13	0.50	34	12	143	24	4.5	10.1	27	-12.2	-109
TSN34HA	46	1.60	3	51	231	1.1	2.3	0.19	139	-14.8	-109
TSN37TH	150	2.2	<1	78	312	0.7	1.4	0.11	137	-15	-111
TSN39CS	13	0.15	29	7.9	149	43	2.2	6	20	-10.9	-79
TSN48JW	32	0.7	5.9	39	209	10	3.3	3.4	94	-15.1	-112
TSN49TC	30	2.6	<1	26	190	2.7	2.4	0.73	100	-14.6	-108
TSN66JS	66	0.2	56	29	143	55.5	1.5	6.6	29.5	-11.1	-84
TSN69PJW	4.3	0.4	16	6.6	147	24.3	2.4	5.3	18.8	-10.2	-76
TSN109GL	35	<0.1	2.2	11	170	24.7	5.5	14.5	29.5	0.8	-22
TSN110GSD	91	<0.1	<1	34	241	76.5	8.6	9.9	64.8	-8.2	-72

Table 2-8: The isotopic data, major cation and anions from the Defiance Plateau and Steamboat-Joseph Spring Wash (data from USGS Denver).

Sample	**δO^{18}**	**δD**	**δC^{13}**	**Sample**	**δO^{18}**	**δD**	**δC^{13}**
04PWW2	-9.9	-82	-4.1	04PWW19	-13.9	-107	-4.9
04PWW3	-12.3	-92	-10.5	04PN20	-11.8	-91	-7.6
04WW5	-11.4	-87	-11.7	04PN21	-11.5	-88	-7.6
04WW6	-11.0	-82	-83	04PN22	-11.4	-87	-8.9
04WW7	-11.0	-82	-7.9	04PGW27	-11.6	-88	N/D
04PF11	-11.7	-89	-9.5	04PGW30	-11.7	-88	N/D
04PF13	-11.7	-89	-6.6	TSNO3	-10.7	-83	N/D
04PF14	-11.6	-88	N/D	TSNO4	-12.2	-93	N/D
04PF15	-11.5	-88	-7.1	TSNO9	-8.2	-63	N/D
04PF16	-11.3	-85	-8.4	TSNO37	-15	-111	N/D
04PWW17	-11.2	-87	-7.9				

Table 2-9: The isotopic composition of deep water in Pueblo Colorado Wash Aquifer.
N/D = Not Determined

Sample	**δO^{18}**	**δD**	**δC^{13}**
04PSD1	-8.6	-69	-5.9
04PS18	-7.2	-69	-3.2
04PC23	-10.2	-76	-9.1
04PS24	-10.7	-81	-7.4
04PS25	-11.6	-89	N/A
04PS26	-11.0	-83	N/A
04PGS28	-7.9	-76	N/A
04PCS29	-11.9	-89	-6.6
04KW01	-8.8	-77	N/A

Table 2-10: The isotopic composition of the shallow water in Pueblo Colorado Wash Aquifer.
N/A = Not Available

Chapter 3

3-1 Water Chemistry of Pueblo Colorado Wash

The chemical and isotopic composition of water samples is commonly the basis for understanding the geochemical processes active within aquifers including the contribution of bacterial activity and water-sediment interactions. To assess the likely sources of cations and anions in ground water in the Pueblo Colorado Wash, a systematic evaluation of the variation in major ion composition in water from the alluvium was conducted. Additionally, the concentrations of some dissolved constituents in excess of recommended levels of the USEPA for drinking water are found in some wells. The high levels were evaluated to determine possible sources including human activities or natural geochemical reactions. To complete the analysis of compositional changes to ground water in the PCW alluvium, water analyses from wells in adjacent areas were made available by the USGS and included in the interpretation. Comparison of the composition of water in the PCW with that in adjacent areas was used primarily to evaluate sources of recharge.

3-2 Identification of Subpopulations

The water samples included in this study are subdivided into shallow alluvial wells, deep alluvial wells and bedrock wells, based on the source and depths of sampled water. Shallow water from the alluvium refers to wells with depths of less than 10 meters and the surface water samples. One sample included in this group was collected from runoff after a thunderstorm in July 2004. Table 2-4 lists the concentrations of major cations and major anions in the shallow water. Deep water refers to water from windmills and electric-pumped wells that are located in alluvium and draw water from depths greater than 10 meters. Table 2-5 provides the concentrations of the major cations and major anions in the deep water samples. Ground water from bedrock was collected from 3 wells in sedimentary rock on the Defiance uplift and one well adjacent to the PCW near Greasewood (04PWW19). Additional bedrock and alluvial wells were included in the USGS sample set (table 2-8).

3-3 Analyses of Chemical Parameters

In all samples, the concentrations of common cations and anions account for more than 99% of the concentrations of all dissolved inorganic species. Tables 2-4 and 2-5 show the concentrations of major cations, major anions, and charge balance in deep water and shallow water respectively. Tables 2-6 and 2-7 show the concentrations of minor and trace ions in deep alluvial water and shallow alluvial water from the Pueblo Colorado Wash. Measured pH values vary from 7.41 to 8.93 and the dissolved oxygen values are in the range of < 1 to >5 mg/l (table 2-3), which are the detection limits of oxygen field measurement kits. The values for the specific conductance vary from 505 to more than 26000 µS/cm (table 2-3).

3-4 Charge Balance and Quality Assurance of Data

The WATEQ4F (Ball and Nordstrom, 2001) program version 2.63 was used to evaluate the accuracy of the compositional data and evaluate the level of saturation with common mineral phases. WATEQ4F is an equilibrium speciation model commonly applied to investigate the interactions among solid phases and aqueous species that may control the geochemistry of multi-component systems. As a quality control measure, the charge balance error calculated by the program is used to assess the accuracy and completeness of the water analyses. In theory, all natural waters must be electrically neutral and any non-zero charge balance should reveal an analytical error. A negative charge balance indicates an apparent anion excess and a positive charge balance indicates an apparent cation excess. For analyses that are reasonably complete, the percent different between the cation and anion should be less than 5 % (Hem 1980). The following formula is used by WATEQ4F to calculate the charge balance:

$$\Delta\% = \frac{(\text{Sum of cation species} - \text{Sum of anion species})*100}{(\text{Sum of cation species} + \text{Sum of anion species})\,/2}$$

As seen, the denominator of the formula is multiplied by 1/2. Therefore, this charge balance is twice the charge balance that is normally computed. Because WATEQ4F calculates the charge balance to twice the normal methods, charge balances below 10 % are considered acceptable. Tables 2-4 and 2-5 show the calculated charge balances for water samples from the Pueblo Colorado Wash Aquifer.

All samples have charge balances within 10% except sample 04PSG28 which has a charge balance value of -34%. This large error indicates an inaccuracy in the measurement of one of the major cations or anions (excess) or there may be another cation in the sample in appreciable quantities. The samples were analyzed for minor and trace cations but none of these cations are sufficiently abundant to compensate for the percent difference between the cations and anion of this sample. Therefore, this sample is used for general interpretations but no major conclusions have been made based on the chemical composition of these samples.

Sample	Assigned #	Symbol	Sample	Assigned #	Symbol
04PSD1	1	🟥	04PS25	25	🟥
04PWW2	2	◆	04PS26	26	🟥
04PWW3	3	△	04PGW27	27	🔵
04PWW5	5	△	04GS28	28	🟥
04PWW6	6	△	04PCS29	29	🟥
04PWW7	7	△	04PGW30	30	🔵
04PF11	11	△	04KW01	31	🟥
04PF13	13	△	TSN03	32	▲
04PF14	14	△	TSN33SWE	33	🟢
04PF15	15	△	TSN34HA	34	🟢
04PF16	16	△	TSN04	35	🟢
04PWW17	17	△	TSN09	36	🔵
04PS18	18	🟥	TSN37	37	🟢
04PWW19	19	△	TSN11CD	38	🟢
04PWN20	20	△	TSN39CS	39	🔵
04PWN21	21	△	TSN48JW	48	🟢
04PWN22	22	△	TSN49TC	49	🔵
04PC23	23	🟥	TSNS66	66	🟩
04PS24	24	🟥	TSNS69PJW	69	🔵

Table 3-1: The assigned numbers and symbols for waters from Pueblo Colorado Wash (PCW) and the surrounding area. Triangles and Diamond = deep water from the PCW Squares = shallow water Blue Circles = deep water samples from east side of PCW Green Circles = deep water from west of the PCW.

Figure 3-1 shows the relative abundance of major ions among the groups of water samples. Piper diagrams were used to classify groups of wells. The hydrofacies classifications on the ion-triangle are based on the Back (1966) classifications. Back (1966) divided the ion triangles of the Piper diagrams into various fields that define water chemical facies. Each chemical facies is determined by the relative abundance of anions and cations (figure 3-2). Most water samples range from Na to Ca dominant with bicarbonate as the dominant anion. As evident on the figure there is a wide range of water compositions in the study area even within subpopulations indicated by the symbols. The spatial heterogeneity of water composition is inconsistent with a single point of recharge and transport of water down hydrologic gradient through the alluvium. The following text explores possible origins of the heterogeneity.

3-5 Hydrofacies of Shallow Water

All shallow water samples except sample 04PGS28 belong to the bicarbonate type (fig. 3-3). Sample 04PGS28 has sulfate as the dominant anion. The cation chemical facies are more scattered. Shallow water from the dug wells near Cornfield (04PC23 and 04PC29) belongs to the sodium type—similar to the deep water facies at this location. Samples 04PSD1 and 04PS18 are sodium type and have very high Na/Ca ratios. The Na:Cl (molar) is 3 and 8 and the SO_4:Ca (molar) is 6 and 9, respectively, for these samples. These ratios are not consistent with NaCl as a source of the sodium and gypsum as the source of sulfate. Sodium and sulfate instead are attributed to dissolution of sodium sulfate minerals, which occurs intermittently on local areas of the ground surface within the study area.

Samples 04PS24, 04PS25, and 04PS26 collected between Cornfield and Greasewood plot very close to each other on the Piper plot, showing that the shallow water in this area has a relatively uniform major ion composition. Sample 04PS26 belongs to the mixed-cation facies while sample 04PS24 belongs to the magnesium facies. Sample 04KW01 from Kinlichee is calcium type, and Ganado Lake is mixed-cation type.

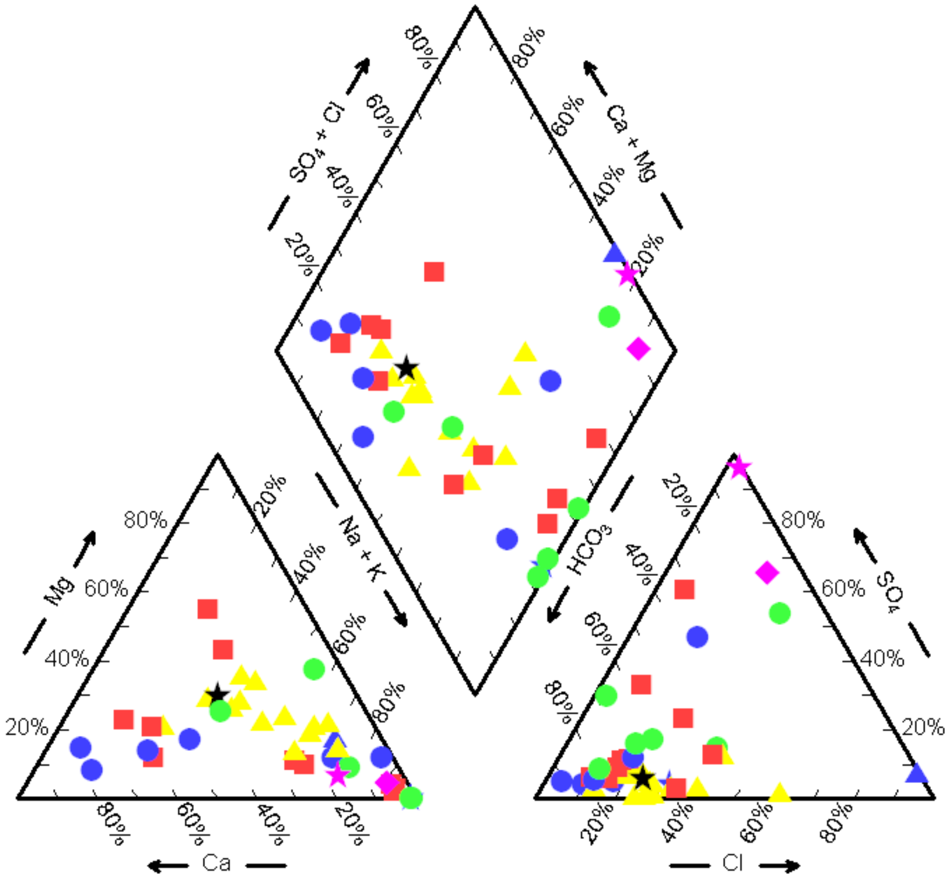


Figure 3-1: The major ion composition of water samples from the study area on the Piper diagram. The symbols are from table 3-1. Ganado Lake is shown as a black star, sample 04WW19 is shown as a blue star, and a water sample from a diatreme is shown as a pink star.

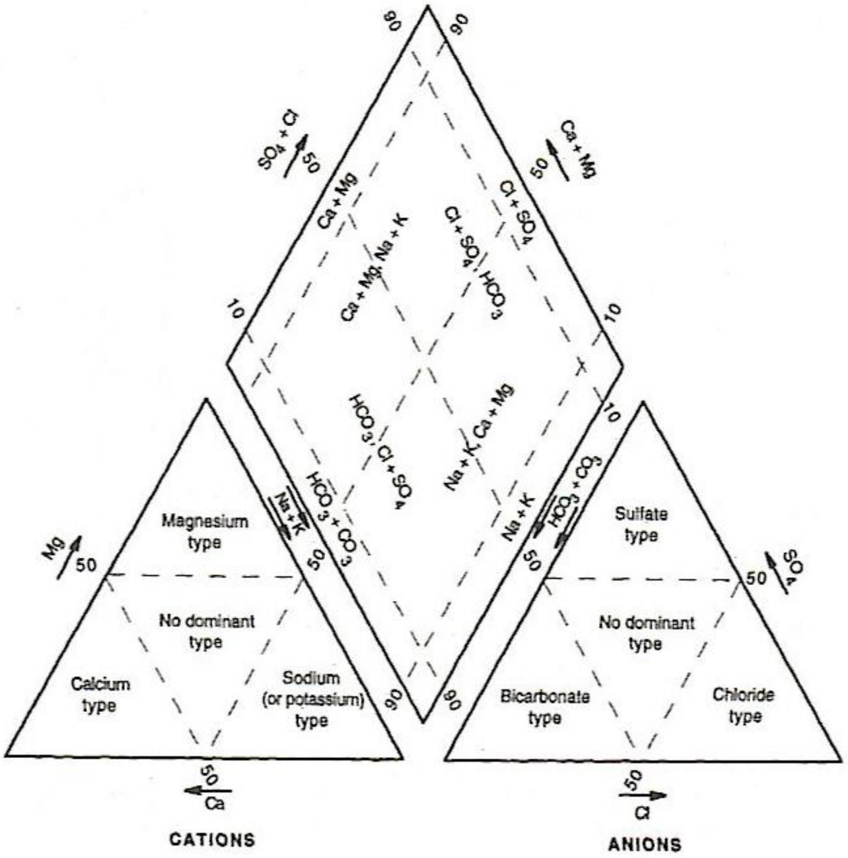


Figure 3-2: The Piper diagrams used for classification of water samples from Pueblo Colorado Wash Aquifer (after Back 1966).

The Na/Ca measured in wells near Cornfield (04PC23 and 04PCS29) is relatively high as observed in the wells described above. Considering the Na:Cl (molar) varies from 4 to 2, and Ca:SO_4 (molar) ranges from 3 to 8 for these two samples, a portion of the dissolved salts in these samples may also have originated by dissolution of sodium sulfate minerals.

3-6 Hydrofacies of Deep Water

Figure 3-4 shows the chemical facies of the deep water in the Pueblo Colorado Wash. Most deep water samples are bicarbonate type. However, samples

TSN03 and 04PWW05 are chloride type and sample 04PWW2 belongs to the sulfate facies. The cation facies are more diverse, although they systematically trend from a Na-water toward a mixed Ca-Mg water.

The overall chemical composition of the deep water is scattered and consistent trends, chemical shifts, or chemical grouping are not apparent in the diamond-shape diagram. The composition of water among the samples is spatially correlated when the aquifer is subdivided into smaller sections as discussed in the later sections of this chapter.

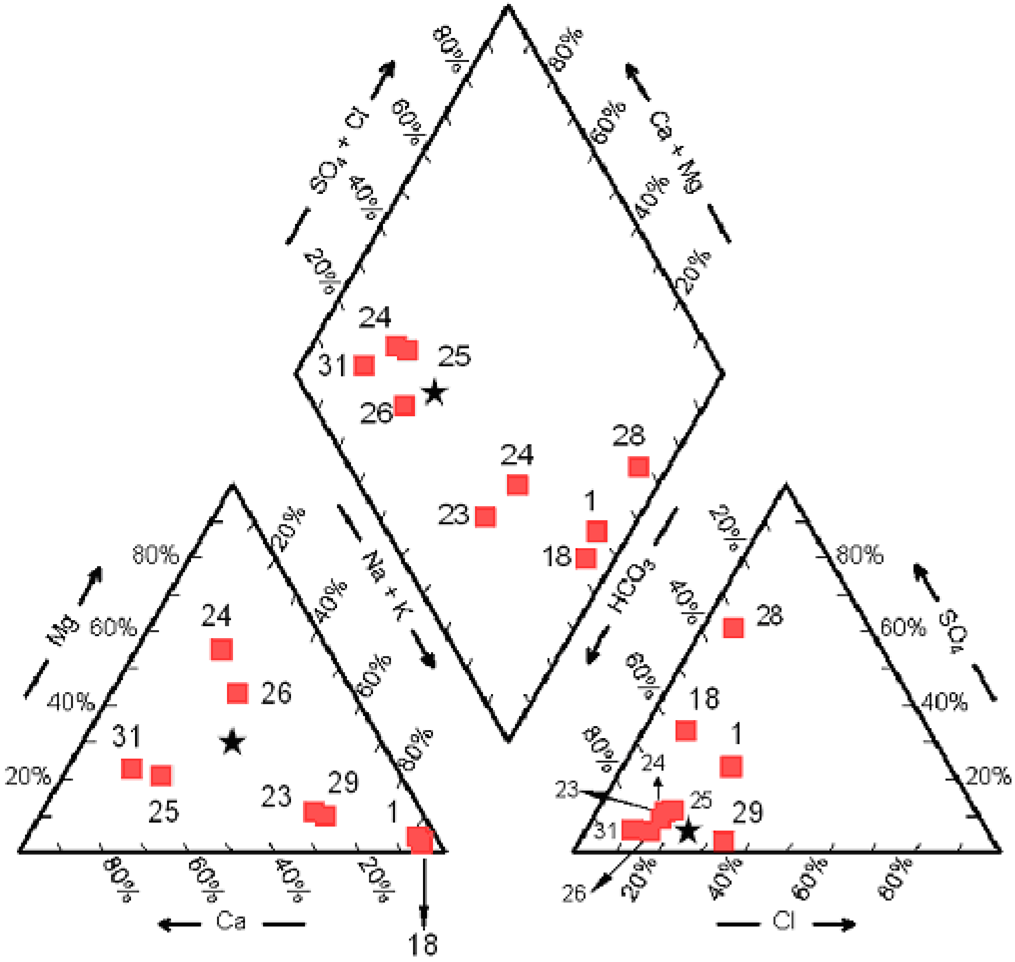


Figure 3-3: The major ion composition of shallow water samples from Pueblo Colorado Wash Aquifer. The black star is the water sample from Ganado Lake.

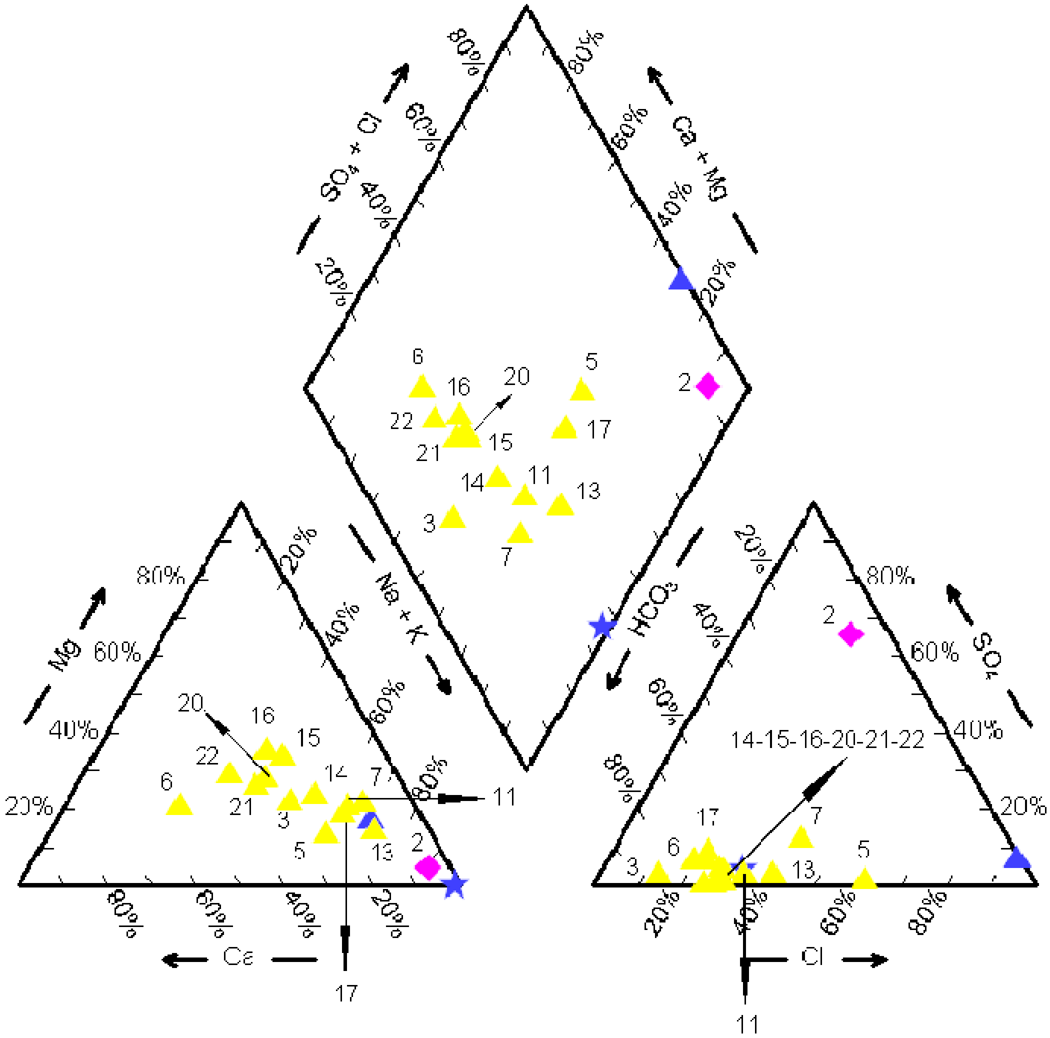


Figure 3-4: The major ion composition of deep water samples from Pueblo Colorado Wash. The blue star is sample 04PWW19.

3-7 Saturation indices

The cations and anions originate partially from precipitation as rain and snow that is modified by evaporation and interaction with the solid phases in sediments. The simple dissolution of salts, mineral dissolution and cation exchange are three important reactions that affect the groundwater chemical composition.

To test the effects of mineral dissolution/precipitation on the water composition, saturation indices were calculated for $CaCO_3$, dolomite, chalcedony, barite, and gypsum using WATEQ4f (tables 3-2 and 3-3). The saturation index for a mineral is defined by the equation:

$$\text{S.I.} = \text{LOG}\left(\frac{\text{ION ACTIVITY PRODUCT}}{\text{EQUILIBRIUM CONSTANT}}\right)$$

A saturation index with values greater than zero indicates super-saturation with respect to that mineral, less than zero indicates under-saturation, and equal to zero indicates equilibrium. However, saturation indices showing super-saturation with respect to some minerals such as albite and dolomite do not mean that these minerals are precipitating from the water. Reactions that result in precipitation of dolomite or albite are known to be kinetically slow and therefore, these phases will not from. The program calculates what is thermodynamically feasible and kinetic limitations were not evaluated. Given the experimental errors in the analytical results and uncertainty in thermodynamics values, a S.I. value 0.00 ± 0.25 is considered to indicate equilibrium.

Both deep water and shallow water are in equilibrium or close to equilibrium with respect to dolomite and aragonite (except sample 0PKW01, which is under-saturated) (tables 3-2 and 3-3). Moreover, all water samples are saturated or oversaturated with respect to chalcedony (except for sample 04KW01 and TSN37) and highly under-saturated with respect to gypsum (except for sample TSN03).

Sample	$CaCO_3$	Dolomite	Chalcedony	Barite	Gypsum
04PWW2	0.22	-0.15	-0.11	-0.06	-1.17
04PWW3	0.03	-0.05	0.10	0.13	-2.78
04PWW5	0.59	0.37	0.21	0.78	-2.67
04PWW6	0.2	-0.02	0.44	0.49	-2.28
04PWW7	0.49	0.762	0.213	0.27	-2.81
04PF11	0.20	-0.07	0.34	0.14	-2.9
04PF13	0.25	-0.03	0.33	0.09	-2.85
04PF14	0.25	0.33	0.25	-0.13	-2.65
04PF15	0.23	0.32	0.4	0.4	-3.54
04PF16	0.25	0.351	0.45	1.15	-2.55
04PWW17	0.29	0.33	0.49	0.7	-1.94
04PWW19	0.09	0.1	-0.19	-1.4	-4.13
04PN20	0.22	0.12	0.50	0.92	-2.27
04PN21	0.18	-0.03	0.49	-1.04	-4.40
04PN22	0.28	0.17	0.42	-0.48	-3.61
04PGW27	0.01	-0.42	0.15	0.14	-2.63
04PGW30	0.09	-0.50	0.20	0.11	-2.44
TSN03	0.89	2.46	-0.08	0.08	-0.42
TSN04	0.22	0.1	0.21	0.05	-0.74
TSN09	0.28	0.22	0.11	0.04	-1.36
TSN37	-0.04	-0.86	-0.27	-1.25	-4.5

Table3-2: The saturation indices for five solid phases in the deep water of Pueblo Colorado Wash Aquifer.

Both shallow and deep water show a wide range of saturation indices of barite (tables 3-2 and 3-3). Most samples are in equilibrium with barite, however, some samples such as TSN37 and 04PS24 are undersaturated and some samples such as 04PS26 and 04PN20 are oversaturated.

Sample	CaCO3	Dolomite	Chalcedony	Barite	Gypsum
04PDS1	0.26	0.30	-0.14	0.33	-2.36
04PS18	0.76	1.08	0.01	-0.04	-2.25
04PC23	0.39	0.19	0.29	0.44	-2.01
04PS24	0.33	0.70	0.64	-0.73	-2.24
04PS25	0.54	0.38	0.40	0.06	-2.20
04PS26	0.34	0.66	0.53	0.67	-2.56
04PGS28	0.11	-0.03	0.00	0.27	-1.87
04PCS29	0.54	0.43	0.31	0.25	-2.46
04KW01	-0.68	-1.9	-0.66	0.2	-2.66

Table3-3: The saturation indices for five solid phases in the shallow water of Pueblo Colorado Wash Aquifer.

3-8 Chemistry of the Deep Water and Spatial Subdivisions of Pueblo Colorado Wash Aquifer

Based on the locations of sampled wells and the corresponding water composition the aquifer can be divided into the four sections. The alluvium in the tributary between Ganado and the main course of the Pueblo Colorado Wash was not considered in defining the sections because only one ground water sample, 04KW01, was collected in this interval and it was a shallow well. The four sections were characterized as following:

-Section 1: this section consists of the north and northeastern parts of the Wash and the Defiance Plateau (see hillshade map in Appendix 1). This section begins at Kinlichee Spring and continues to the southwest and ends on the east bank of the PCW south of Cornfield and north of Greasewood (see hillshade map in Appendix 1). The water samples in this area are from bedrock and include samples 04KW01, 04PGW27 and 04PGW30, which have low conductivity (<400 µS/cm).

The water samples in this section belong to the bicarbonate and calcium facies (figure 3-5). The

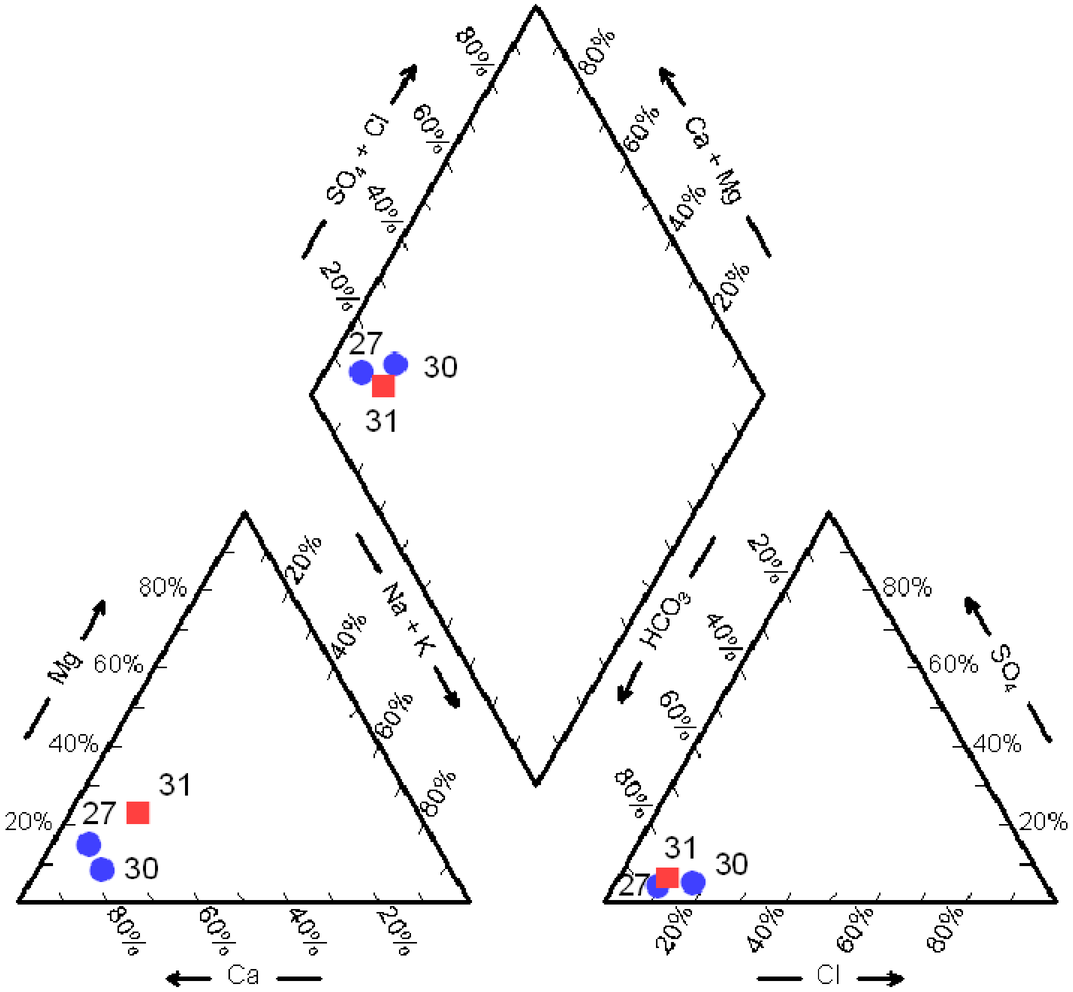


Figure 3-5: The major ion composition of water samples from section 1.

locations of the samples on the diamond-shape diagram are very close to each other, which implies the water composition in this section is uniform, although the distances between the samples are relatively long (04PKW01 is located about 3000 meters north of 04PGW27 and 04PGW30 is located about 2000 meters southwest of 04PGW27). The topographic slope of this section is from the northeast to the southwest (see hillshade map in Appendix 1). The water composition of this section is very similar to that of C-aquifer, which supplies the water drinking water for city of Ganado. The water samples from section one and the water samples from C-aquifer belong to the bicarbonate hydrofacies and calcium hydrofacies (fig 3-6).

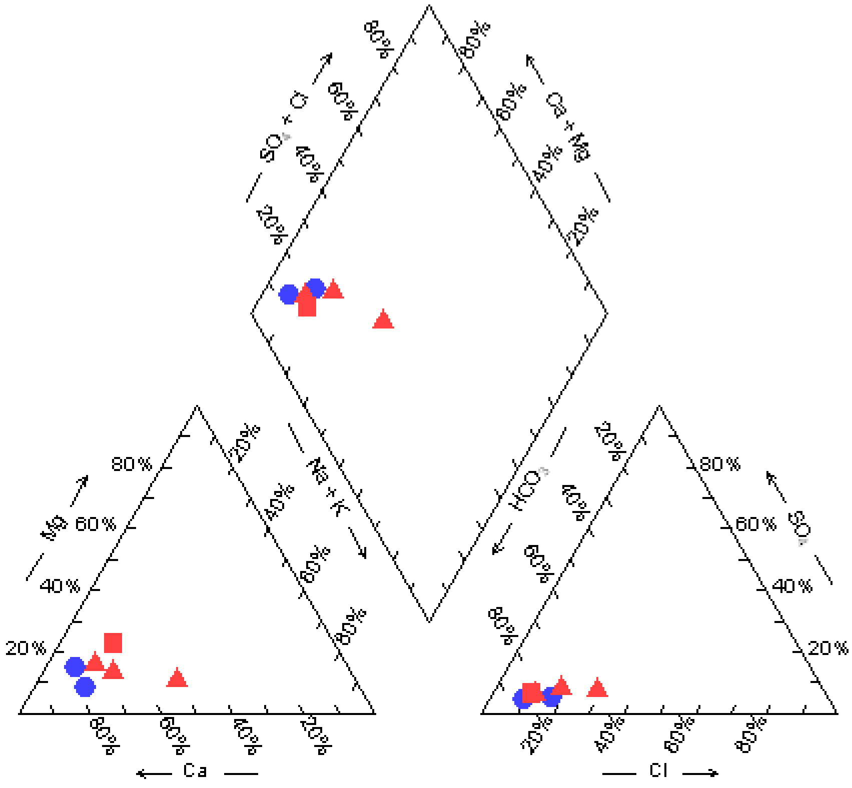


Figure 3-6: The hyrdofacies of water samples from C-aquifer and their chemical similarities to the water samples from section 1. Red triangles represent C-aquifer samples. Other symbols are from table 3-1.

-Section 2: The northern boundary of this section is road 261. The section is limited on the east by the eastern wall of the canyon, on the west by the western wall of the canyon and on the south by the Sunrise Spring (see hillshade map in Appendix 1). Samples 04PWW2, 04PWW3, and 04PWW5 belong to this section and are characterized by a wide range in water composition. Samples 04PWW2, 04PWW3 and 04PWW5 belong to sodium-dominant facies. Sample 04PWW2 belongs to the sulfate dominant facies and sample 04PWW3 belongs to bicarbonate facies. Sample 04PWW5 has chloride as the dominant anion (fig 3-7). The specific conductance values in this section are higher than those measured in samples from section 1 (table 2-3). In sample 04PWW2, the concentrations of sodium and sulfate are very high, consistent with the dissolution of sodium sulfate minerals. Sample 04PWW5 has a Na:Cl ratio of 1.5 that suggests a contribution of halite dissolution in this sample. Sample 04PWW3 can not be explained by the simple dissolution of carbonate minerals (as discussed in section 3-10). Thus, the complex composition of water in this section of PCW is interpreted to reflect the varying contribution of salt dissolution, partial dissolution of more framework minerals, and cation exchange.

-Section 3: The northern boundary of the section is Sunrise Spring. It is bounded by the canyon walls to the west and east. The southern boundary is well 04PF11 south of Greasewood (see hillshade map in Appendix 1). Eight wells are located in this section (04PWW6, 04PE11, 04PF13, 04PF14, 04PF15, 04PF16, 04PN22, 04PN21, and 04PN20). All wells have specific conductivity slightly greater than water from section 1. Wells in this section produce water with similar chemical composition although sodium increases slightly to the south. Based on the cation concentrations, three chemical facies are recognized in this section. At the northern boundary of this section, well 04PWW6, the hydrofacies is calcium dominant, from south of sample 04PWW6 to Greasewood, water is in the cation-mixed facies (wells 04PN22, 04PN21, 04PN20, 04PF15, and 04PF16) and from Greasewood to the southern boundary of section 3, sodium is the dominant cation facies (wells 04PF11, 04PF13, and 04PF14) (fig. 3-8). All water samples in this section belong to bicarbonate facies.

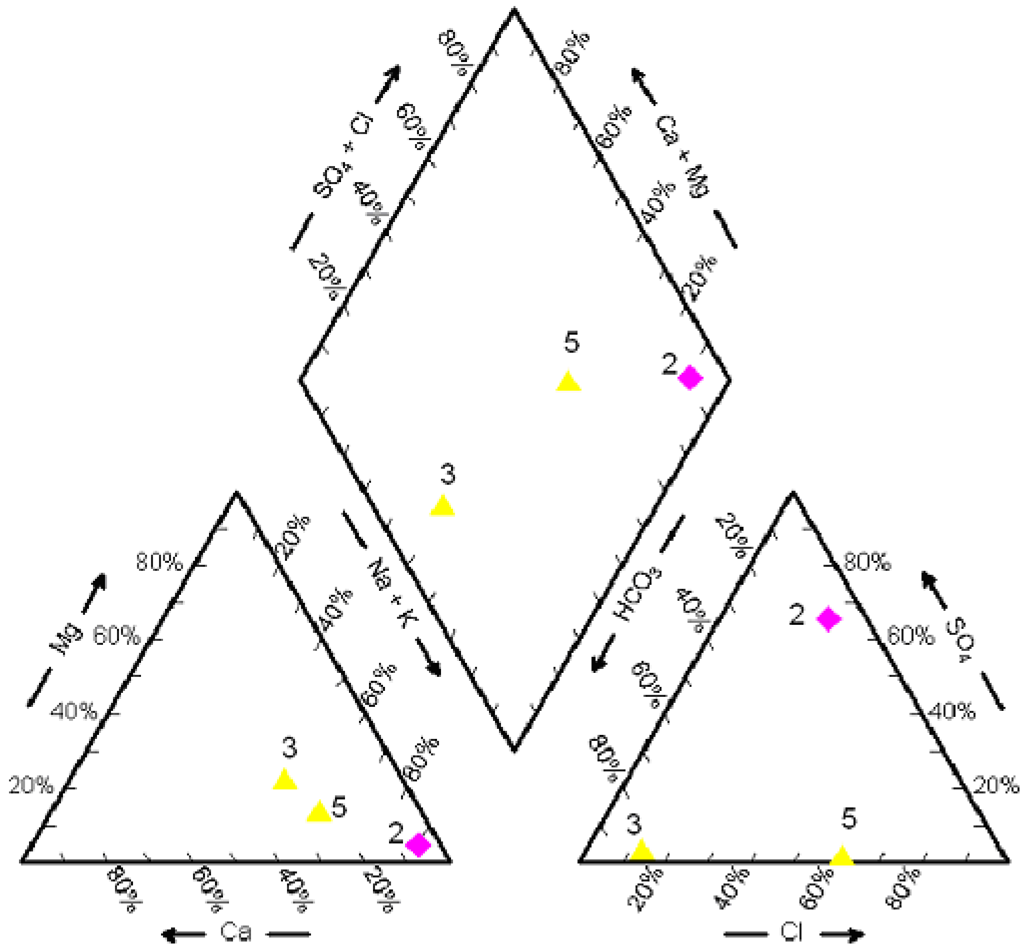


Figure 3-7: The major ion composition of water samples from section 2.

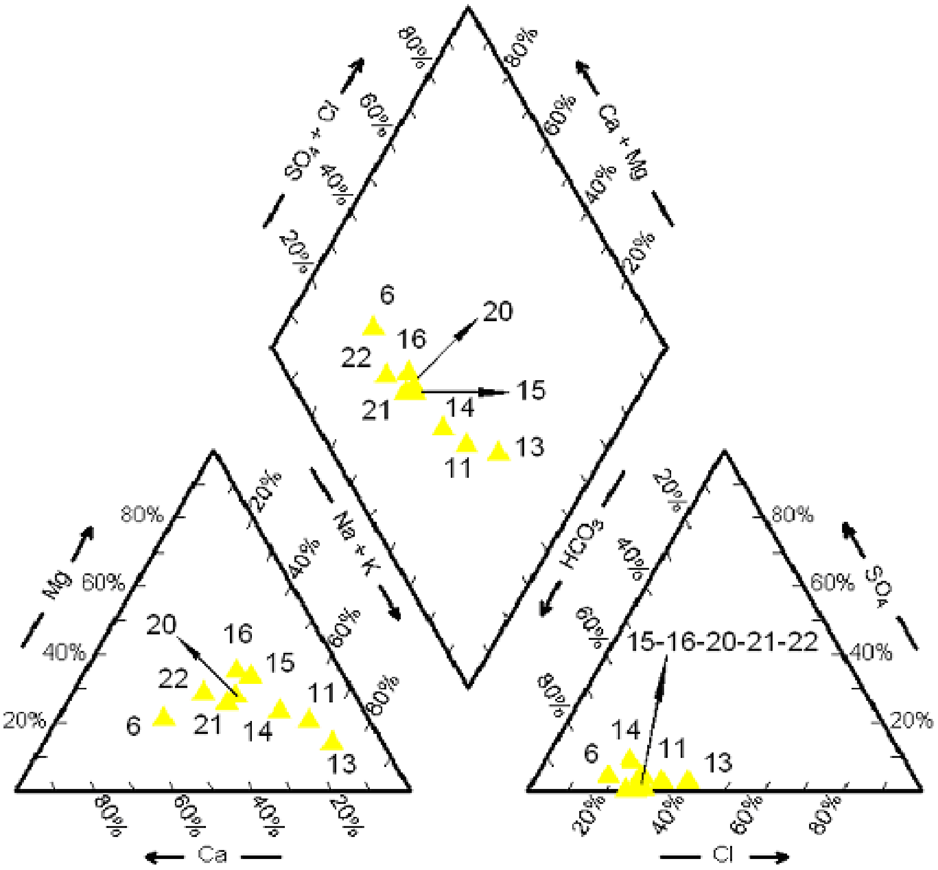


Figure 3-8: The major ion composition of water samples from section 3.

-Section 4: This section starts from well 04PWW7 to the south of Greasewood and extends south to Twin Buttes and on the east and west is limited by the bed rock exposures (see Appendix 1). Three wells are in this section, 04PWW17, 04PWW7 and TSN04. Water in this area belongs to the chloride and sodium facies (fig. 3-9). The sodium content and salinity of the water increases very rapidly from north to south so that Twin Buttes water has the highest salinity in the Pueblo Colorado Wash. This change of facies and sudden and rapid increase of chloride and sodium concentration is attributed to water mixing. The source of saline water might be either from the nearby aquifer, Steamboat alluvium, or water transported from maar-fill sediment in diatremes of the Bidahochi Formation in the surrounding area.

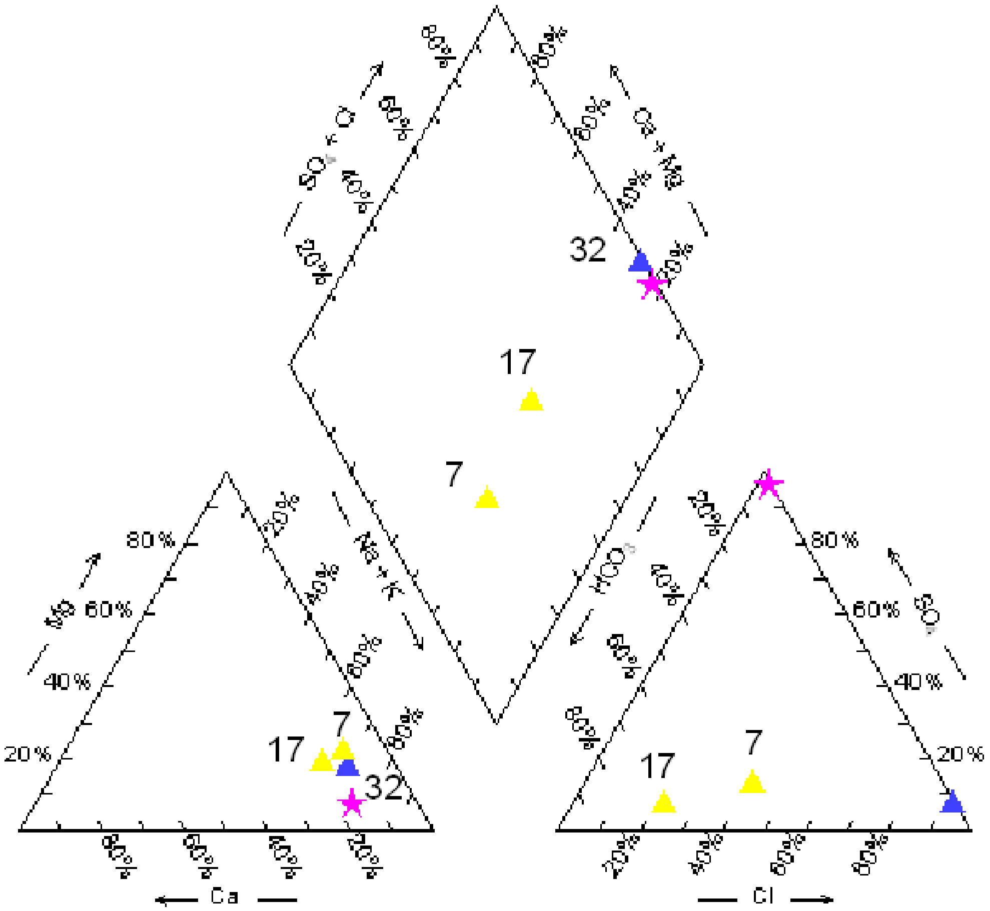


Figure 3-9: The major ion composition of water samples from section 4. The water composition from a diatreme is shown as a red star (from Akers et al. 1971). This sample does not belong to the section 4 but it is shown here to compare its chemical composition with samples from section 4.

Akers et al. (1971) noted the high dissolved salt content of water produced from some diatremes and also reported the presence of gypsum in the subsurface of the diatremes. Diatremes have been mapped south of Pueblo Colorado Wash study area, near Twin Buttes, and near the junction of Steamboat Wash with PCW.

3-9 Variation in Specific Conductance in Pueblo Colorado Wash Aquifer

Specific conductance does not vary systematically along the topographic gradient of water samples from the PCW alluvium, but intervals of progressive change are apparent (figure 3-10). Conductance increases in the deep water from north to south in the first three samples—04PWW2, 04PWW3, and 04PWW5. From sample 04PWW6, shown in pink triangles on figure 3-10, (see section 3-8) to the end of section 3, the conductance increases slightly. In section 4, the conductance increases very rapidly.

The variation in specific conductance along the topographic gradient down the PCW is attributed to the source and history of the water masses sampled. The water in section 1, which is from bedrock aquifer in Defiance Plateau (samples 04KW01, 04PGW27 and 04PWG30), has low specific conductance (table 2-3). The sudden decrease in section 3 relative to the values of section 2 is interpreted to reflect water input to the PCW alluvium from the Defiance plateau to the east. The increased salinity in the fourth section is attributed to mixing with saline water recharging from surrounding aquifers and/or dissolution of evaporite salts.

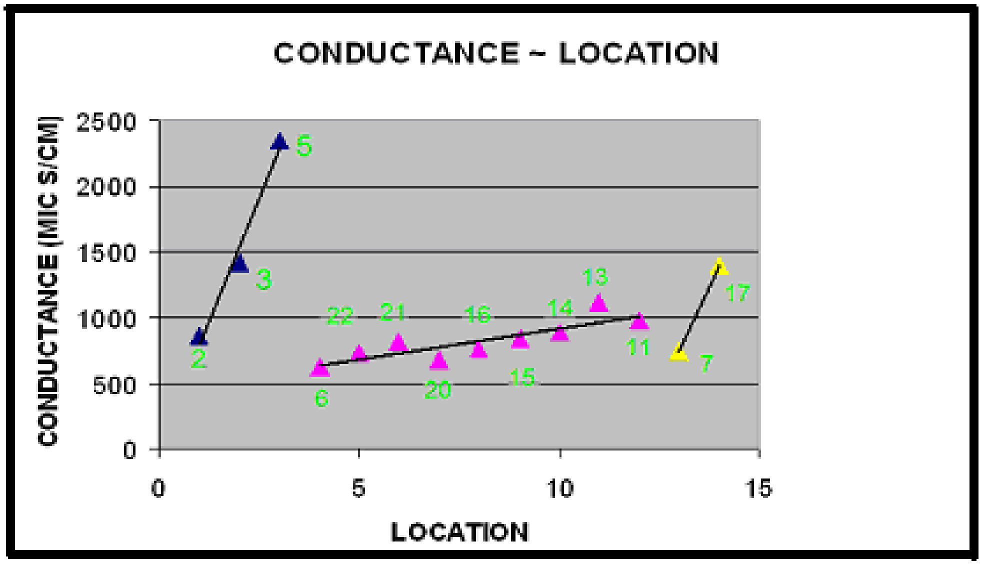


Figure 3-10: The increase of conductance from north to south (from location 1 to location 15) in the Pueblo Colorado Wash Aquifer. The X-axis indicates the sequence of the samples down gradient along PCW independent of distance. The drop in the conductance values in the middle of graph in due to recharge from Defiance Plateau. Blue triangles are samples from section 2, red triangles from section 3 and yellow triangles from section 4. The conductance of water samples from Twin Buttes is not shown on this graph since its high conductance value is out of the range of the Y axis. The assigned numbers are from table 3-1.

It is known that water-sediment interactions are a function of time (Mason and Moore 1986). Therefore, the longer the water is in contact with sediments, the greater the soluble salt content as the water approaches equilibrium with the reactive phases. Bulk samples of alluvium were analyzed by powder X-ray diffraction and determined to contain quartz, smectite, illite, feldspar, kaolinite, chlorite and calcite as major minerals (see chapter 2). These minerals can be expected to react and increase the contents of soluble components in the water. If the Pueblo Colorado Wash is considered a closed system subjected to surface recharge and slow flow, the deeper water is inferred to be older and therefore, likely to be more saline than the younger shallow water.

3-10 Origin of Dissolved Salts

The concentrations of cation and anions in ground water are not readily explained by the concentration expected by evaporation of rain, snow and snow melt. For example, to reach the measured concentrations of Ca^{++} in the ground water samples only by evaporation, the rain water needs to evaporate between one tenth and one hundredth of the initial volume (table 3-5). This would result in isotopically evolved water compositions of oxygen and hydrogen in shallow water and deep water (see tables 2-4, 2-5, 2-8, 2-9, 2-10). As will be shown evaporation is evident for most shallow water samples but is not apparent in the deep water.

Silicate and carbonate minerals are expected to be the most reactive components of the alluvium. $CaCO_3$ is weakly soluble in water—especially in shallow water in contact with atmospheric $CO_{2.}$ Letterman (1995) determined the dissolution rate of calcite about 1.92g/l per day at 25° C for pure calcite. This rate depends on the temperature, Ca/Mg in the calcite, pH and CO_2 concentration. At constant P_{CO2}, the dissolution rate varies directly with the Ca/Mg ratio and temperature. SiO_2 is expected to increase in solution in response to the weathering of feldspars and other silicate minerals as well as by dissolution of quartz (Mason and Moore 1986). As shown by the modeling results nearly all water sampled is saturated in calcite and quartz. The sample from Kinlichee (see Appendix 1) where water discharges from relatively monomineralic sandstones, is an exception. Water sampled at this site likely had inadequate time to react with the sandstone to approach saturation with quartz, and calcite may be absent.

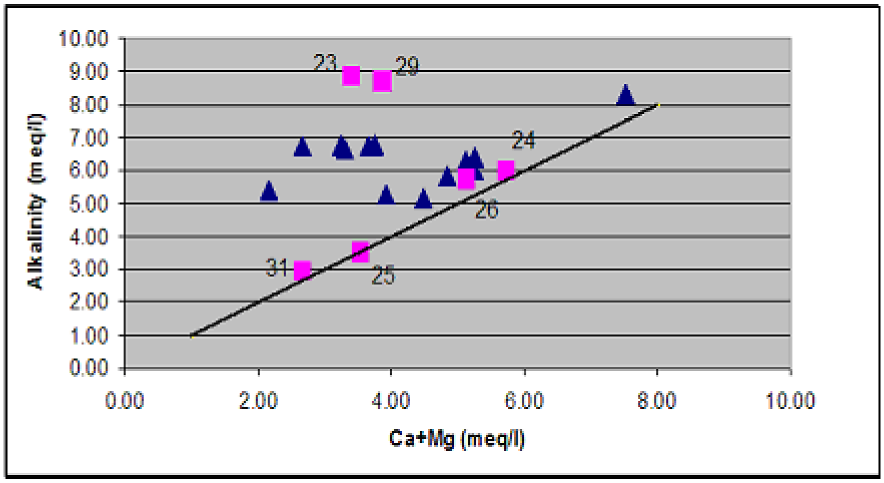


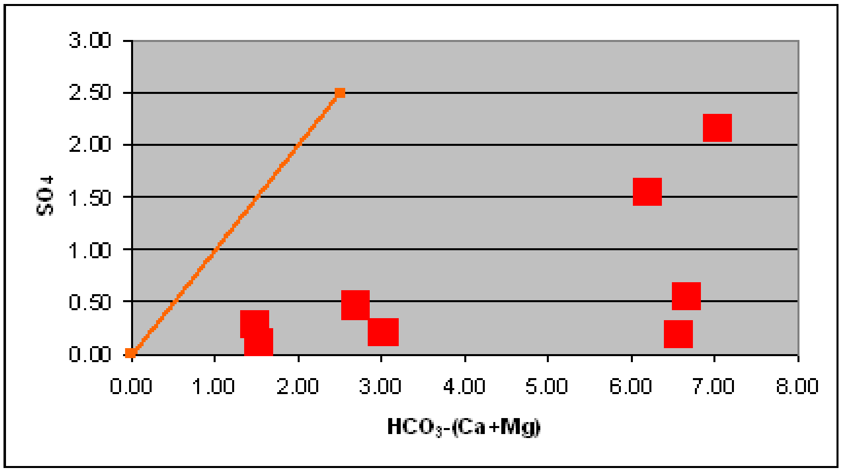
Figure 3-11: The ratio of (Ca + Mg) versus alkalinity in the deep water and shallow water of Pueblo Colorado Wash samples. Red squares represent shallow water and blue triangles represent deep water.

If simple dissolution of carbonate minerals is responsible for the concentrations of Ca^{++} and Mg^{++}, there should be a linear relation between the sum of the concentrations (in meq/l) of Mg^{++} and Ca^{++} and the water alkalinity (in meq/l). Simple dissolution of calcium-magnesium carbonate should follow 1 (HCO_3) : 1 (Ca + Mg) ratio. Figure 3-11 shows the relation between Ca^{++} + Mg^{++} versus alkalinity. To calculate this value, calcium was removed by assuming that all sulfate comes from gypsum dissolution (it will be discussed later in this section that this assumption is not true for all samples). Then the concentrations of HCO_3^- and remaining Ca + Mg were plotted. For a simple dissolution of carbonate minerals—calcite and dolomite—the water samples should be located on Y = X line which shows the 1 (HCO_3) : 1 (Ca + Mg) ratio expressed as milliequivalents per liter. All deep water samples have insufficient Ca + Mg to account for the measured bicarbonate (figure 3-11). The deficiency of Ca + Mg may have been the result of excess correction in attributing all sulfate to gypsum. As discussed previously sodium sulfates are likely an important contributor to the dissolved salts. To test the impact of the calcium in gypsum correction, the deficiency of (Ca + Mg) was plotted versus sulfate values of deep and shallow water (fig. 3-12 a and b). In both shallow and deep water, the amount of calcium that would be removed by sulfate is small relative to the overall deficiency of Ca + Mg. Therefore, another mechanism is required to produce alkalinity in excess of Ca + Mg.

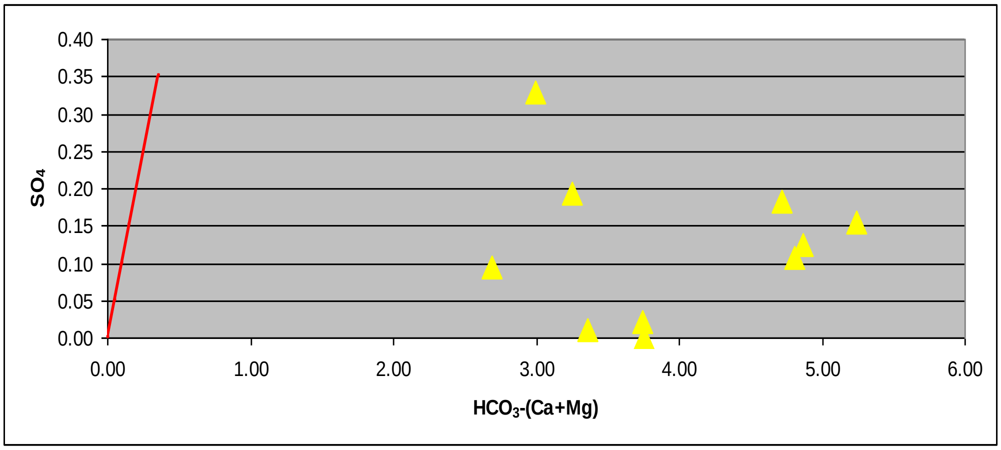
The depletion of Ca and Mg relative to bicarbonate in the deep water can be explained by cation exchange with clay minerals and the dissolution of silicate minerals. The bicarbonate in excess of the Ca + Mg content was plotted relative to sodium concentration deep water samples (fig. 3-13). The strong correlation of excess bicarbonate and sodium in both sample sets and the lack of recognized sodium carbonate salts in the study area minimizes the importance of salt dissolution as a direct sodium source. Smectite is recognized as an abundant clay mineral in the alluvium and is known to have a high cation exchange capacity. Plagioclase is also a major constituent of the alluvium and weathering could release contained sodium while raising alkalinity as shown in the following probable weathering reaction:

$$2NaAlSi_3O_8(s) + 2H_2CO_3 + H_2O \rightarrow 2Na^+ + Al_2Si_2O_5(OH)_4(s) + 4SiO_2(s) + 2\ HCO_3^-$$

The evaluation of bicarbonate and calcium-magnesium in shallow water samples define different patterns than the deep water samples. Two samples, 04PC23 and 04PCS29, show high depletion in Ca + Mg versus HCO_3^-. 04PS18 and 04PDS1 are not shown on the figure 3-6 because the concentrations of sulfate (in meq/l) are far higher than the concentrations of Ca + Mg (in meq/l) and therefore, the



a)



b)

Figure 3-12: The relative deficiency of (Ca+Mg) and bicarbonate versus sulfate for shallow water (a) and deep water (b). The lines indicate the 1:1 equivalents of calcium and sulfate required for the gypsum correction.

subtraction results are negative. These water samples require the dissolution of salts other than gypsum to account for the dissolved sulfate and therefore cannot be readily corrected.

The second mechanism of depleting Ca and Mg is through processes of cation exchange whereby a fraction of the dissolved calcium and magnesium are exchanged with sodium on labile mineral sites. Drever (2002) states that all clay minerals exhibit ion exchange behavior to some degree. Cation exchange capacity in clay minerals is a function of pH and the nature of ions occupying the exchange sites. At neutral pHs and in the presence of magnesium and calcium ions and if the exchange sites of clay minerals are occupied by sodium, calcium and magnesium are adsorbed by the clay minerals and sodium is released into solution. The presence of smectite and the results of figure 3-12 b and 3-14 support that cation exchange is an important factor to modify the chemical composition of shallow water.

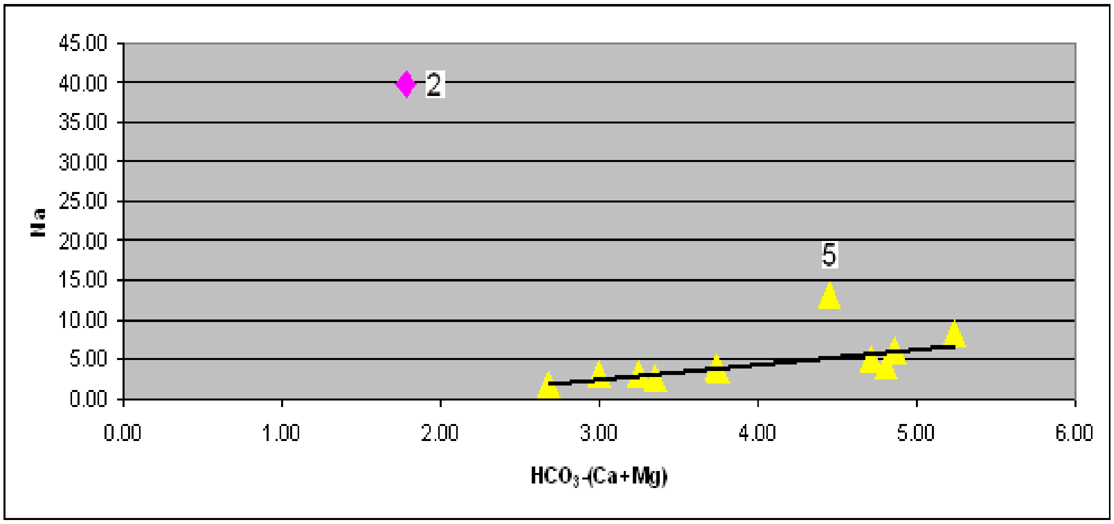


Figure 3-13: The excess of bicarbonate relative to (Ca + Mg) versus sodium in deep water samples.

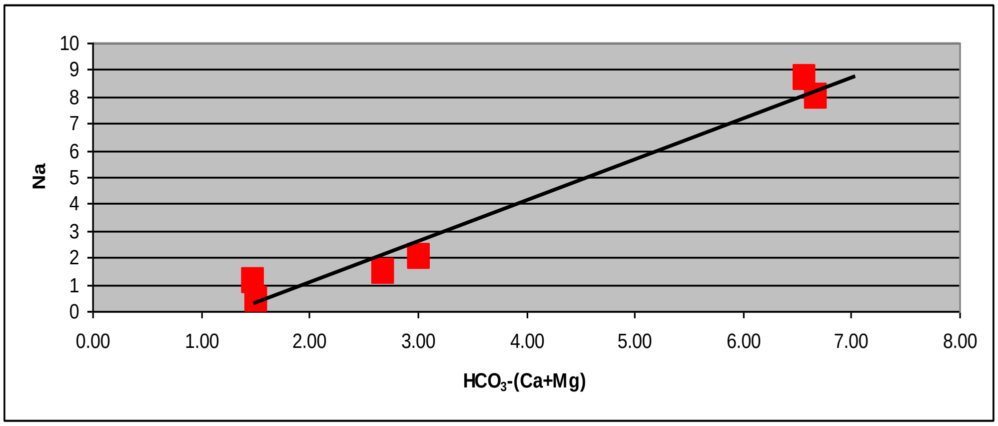


Figure 3-14: The excess of bicarbonate relative to (Ca + Mg) versus sodium in shallow water samples.

In shallow water samples, 04KW01, 04PS26, 04PS25 and 04PSC24 are located very close to the Y = X line (fig. 3-11) and therefore, in these samples, the simple dissolution of carbonate minerals can explain the concentrations of Ca and Mg. Cation exchange (observed in all samples as shown in figs 3-12, and 3-14) and the dissolution of sulfate minerals other than gypsum is necessary to explain the composition of shallow samples 04PS18, 04PDS1, 04PC23 and 04PCS29 (fig 3-11 and 3-12a).

3-11 Source of Sodium for Cation Exchange

As mentioned in the previous section, the presence of smectite and the deficiency of (Ca + Mg) relative to bicarbonate and sulfate, indicate that cation exchange is an important factor in modifying the cation composition of shallow and deep water. Clay minerals transported and deposited by flowing water to form the alluvium are initially expected to have equilibrated with water at saturation with calcite. This would result in clays with high contents of calcium in the exchange sites. For cation exchange within the alluvium to produce sodium-rich water requires a process of enriching sodium on the exchange sites. On possible mechanism would attribute sodium enrichment with progressive evaporation. Shallow water undergoes intensive evaporation and its relative sodium content increases as calcium is removed to form calcite. The residual sodium-rich shallow water would favor sodium to occupy a greater fraction of the exchange sites in the clay minerals. With progressive burial the Na-rich exchange sites would be susceptible to exhange with-Ca-rich recharge water in the aquifer below the depths of substantial evaporation.

3-12 Isotopic Composition of Groundwater in Pueblo Colorado Wash

Tables 2-9 and 2-10 present the measured isotopic composition of the deep water and shallow alluvial water samples, from the Pueblo Colorado Wash. Figure 3-15 shows the location of the water samples from the Pueblo Colorado Wash compared with the global meteoric line and Pleistocene Local Meteoric Water Line (Lopes Hoffman 1997).

Shallow water (red squares in figure 3-15) shows a wide and scattered range of hydrogen and oxygen isotopic composition. The data trend from the global meteoric line toward heavier values is consistent with evaporation of the shallow water. The equation for evaporative line for the shallow water, determined by regression, is:

$$\delta D = 4\ \delta^{18}O - 39$$

The slope of the evaporative enrichment line of the shallow water is 4, which is close to the standard slope for arid areas with humidity close to zero (Gonfiantini

1986). Two samples show the highest enrichment in the shallow water (04PSD1 and 04PS18). Both samples are next to sand dunes. Dincer et al. (1974) showed that residual water is strongly evaporated and enriched in ^{18}O and D in sand dunes of Saudi Arabia. Therefore, the higher values of shallow water in the two above mentioned samples are probably due to the mixture of newly recharged water from precipitation infiltrating through sand dunes with partially evaporated residual water in the sand dunes. Because many of the shallow water wells produce water from vaults, some evaporation may have occurred during storage in the subsurface.

The intersection of the shallow water and the global meteoric line is:

$$\delta^{18}O = -12.3\ ‰ \quad \delta D = -88\ ‰$$

These values indicate the likely composition of precipitation recharge of the shallow water from precipitation. This value is consistent with δ^{18}O and δD values of precipitation in northern Arizona (section 3-17). Deep water (yellow triangles in fig 3-15) shows a narrow range of isotopic variation if we do not consider the bedrock sample 04PWW19 (filled blue triangles). The deep water samples are located closer to the global meteoric line than the shallow water. Although the overall range of the isotopic composition of the deep water is shifted toward the right—i.e. isotopic composition of oxygen is greater than expected for meteoric water—there is an overlap between the shallow water and deep water. The deviation of deep water from the modern meteoric water line may indicate a small amount of evaporation of deep water prior to transfer to deeper parts of the aquifer. Alternatively, this overlap may imply that the shallow water recharges the deep water (vertical recharge).

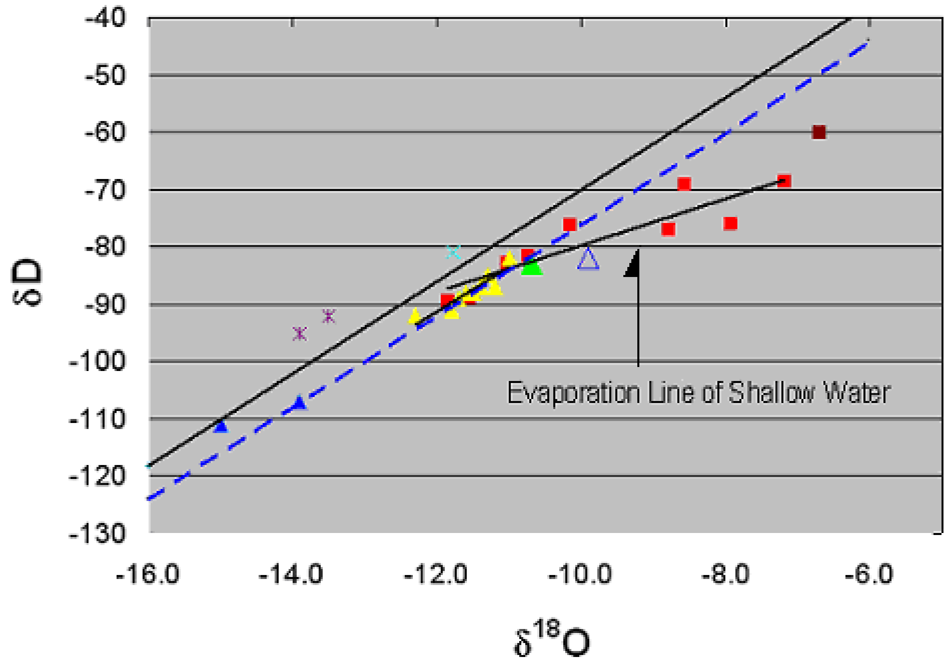


Figure 3-15: The isotopic composition of water samples from the study area. The filled green triangle is sample TSN03 and the empty blue triangle is sample 04PWW2. The isotopic composition of snow are shown in pink asterisks, summer run off in blue asterisk, and summer rain in brown square. The blue-dashed line is the Pleistocene Local Meteoric Water Line (Lopes Hoffman 1997). The other symbols and assigned numbers are from table 3-1.

Since the deep water is lighter than the shallow water there should be a lighter water source which has been mixed with the shallow water and shifted the deep water isotopic composition to the right. The overlap between the alluvium deep water of PCW (yellow triangles in fig. 3-16) and some samples of bedrock deep water from Black Mesa suggests that the deep water may recharge by old bedrock water from the surrounding bedrocks. Figure 3-15 also shows good consistency between the isotopic compositions of deep water samples with the Pleistocene Local Meteoric Water Line, indicating that the deep water is old and might reflect recharge of bedrock water from surrounding formations.

One possible light end-member for the deep water samples are the very light samples from bedrock wells; samples 04PWW19 and TSN037 (filled blue triangles) on the δD-$\delta^{18}O$ diagram (fig. 3-15). Water samples with very light oxygen and hydrogen isotopic compositions are seen in Black Mesa Aquifers as well (Lopes and Huffman 1997) (fig. 3-16). These samples have the lowest D and^{18}O values but they are unlikely to be the light end member that mixed with evaporated shallow water and generated the deep water because no water samples plot between this possible end member and the mixed ground water (fig. 3-15). If light deep water and heavy shallow water generated the deep mixed water, a continuous range of isotopic compositions is expected to range from the light end member and ending at the heavy shallow water is expected.

Water from atmospheric precipitation is another possible light end member for the mixed deep water. The intercept of the evaporative line for the shallow water and the modern global meteoric line has a light isotopic composition. The intercept can be the light end member for the deep water (fig. 3-15) since most deep water samples are heavier than this water, it is possible to make a mixture of this water with heavy water to generate the isotopically intermediate deep waters. However, most of the deep water samples are not on the evaporative line of shallow water and are consistent with the equation determined by regression:

$$H = 7.8O + 2.8$$

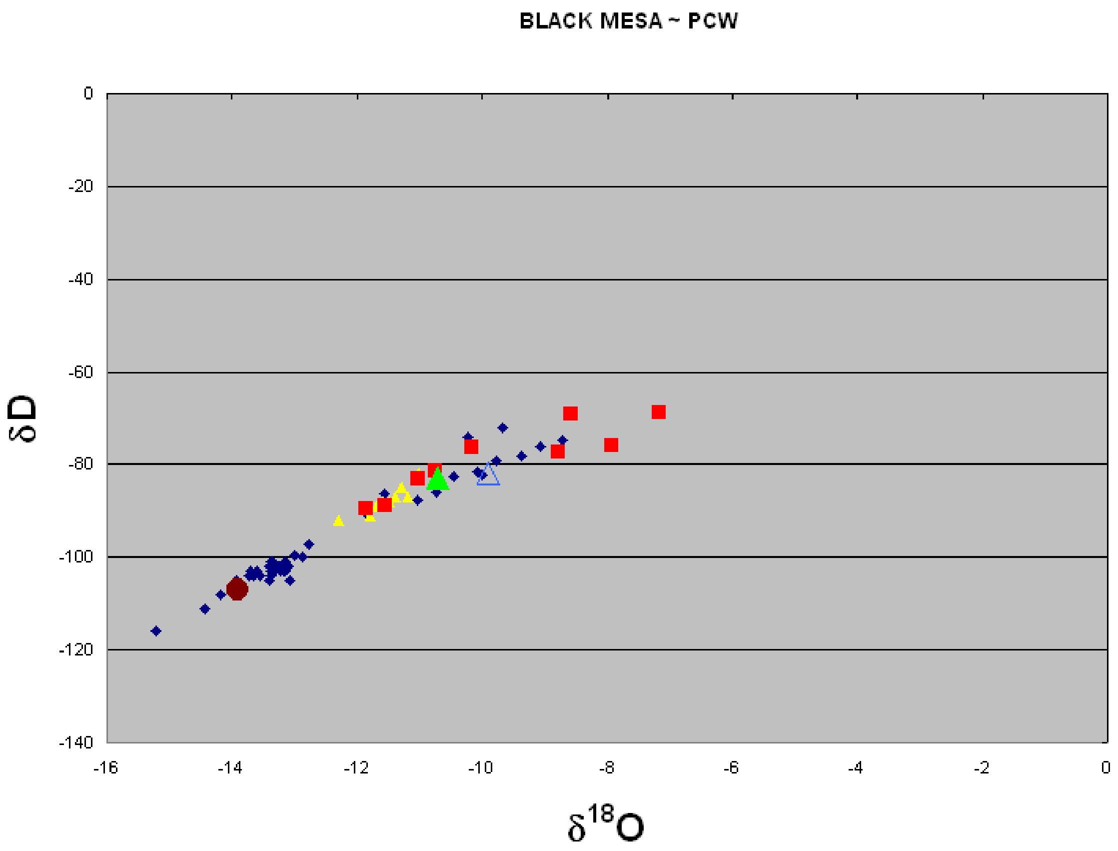


Figure 3-16: The isotopic composition of water samples from Pueblo Colorado Wash and water samples from Black Mesa. The water samples from Black Mesa are shown in filled blue diamonds. TSN03 is shown as filled green triangle and 04PWW2 is shown as empty blue triangle. The other symbols are from table 3-12.

This line is the general trend of the deep water in the Pueblo Colorado Wash. The lightest water on this line is sample 04PWW3 in Cornfield and the heaviest are 04PWW7 and 04PWW6. The shift toward heavier values from a simple mixing line of precipitation and heavy shallow water indicates that mixing of atmospheric water and isotopically evolved shallow water does not define a simple linear pattern. Another point that has to be considered is that evaporation is not a uniform process and can take place to varying degrees from water with varying initial compositions. As will be mentioned later in this section, the atmospheric water in the study area has a broad range of isotopic composition and the contribution of winter and summer precipitations are not similar in recharging the ground water in Pueblo Colorado Wash. Therefore, the shallow water has different sources with different initial isotopic compositions. Moreover, shallow water might have experienced different extent of evaporation in different seasons and even in different years. In other words, at each sample site, the isotopic composition of the shallow water will likely vary in response to seasonal and yearly changes in weather to produce what is shown on figure 3-15.

In addition to the graphical support for the complex mixing hypothesis, other evidence suggests that the measured isotopic composition is not fully explained by simple mixing. First, several shallow water samples are located on the deep water line. As the temperature and pressure are roughly constant all over the wash, having a broad range of stable composition in shallow water can not be explained by uniform evaporation. The isotopic composition of shallow water that falls on the deep water line are very similar to the deep water samples from the same area. This shows that the deep water is being recharged by modified shallow water that has an atmospheric source or the shallow water is being recharged by deep water. The intercept of the shallow water line and the deep water has the following isotopic composition:

$$\delta^{18}O = -11 \quad \delta D = -83$$

Samples 04PWW6 and 04PS26 have the same isotopic compositions as the intercept values and both samples are within 3000 meters of each other near Greasewood.

The other evidence for a complex mixture is that water from the atmospheric precipitation that might recharge the aquifer has a broad range of possible isotopic ratios. This range starts with very light snow, goes through intermediate summer runoff water, and ends at a very heavy summer rain. Since all deep water samples are isotopically lighter than the summer runoff and the summer rain, the direct contribution of these two types of atmospheric water in the deep water recharge is unlikely. On the other hand, the composition range of the shallow water samples that are not located on the deep water line falls in the range between the summer runoff and the summer rain. This indicates that contributions of summer rain and the summer runoff can account for the shallow water in alluvium. The other result from figure 3-15 is that snow and winter precipitation contribute more to the deep water than the summer runoff and summer rain.

Therefore, summer precipitation is likely to be the main source of recharge for the shallow water and winter precipitation should be the main source of recharge for the deep water. These results are supported by the general weather patterns of precipitation in northern Arizona. The are two main sources of moisture for northern Arizona are summer rain or monsoon, which originated mostly from the tropical Pacific Gulf of California (Douglas et al. 1993, Adams and Comrie 1997) and Gulf of Mexico (Schimtz and Mullen 1996), and winter precipitation, which mostly originates from the northern and western parts of Pacific (Woodhouse 1997). Since summer storms originate from lower latitudes, they are rich in ^{18}O compared with the winter precipitation. Williams et al. (2005) mentioned that the δ^{18}O value for the summer precipitation is about -6‰ and that of winter is about -16‰. The comparison of shallow water and deep water with the δ^{18}O values of the summer precipitation and winter precipitation reveals that, while the shallow water samples are scattered roughly near the -6‰ of summer precipitation, deep water samples—excluding the confined water—are between -11 to -13‰, similar to, but heavier than, the expected winter precipitation values. The small difference (about -3‰ to -5‰) between the average winter value and the isotopic range of deep water values is probably due to the mixture of deep water with some shallow water and/or evaporation/sublimation of snow and snowmelt. Additionally, the lower elevation of PCW than the elevation of sampled sites of the Williams' study area may be another factor for this difference.

3-13 Comparison of Ground Water in Pueblo Colorado Wash with Black Mesa

Lopes and Huffman (1997) comprehensively studied the ground water of Black Mesa. The chemical facies identified in aquifers beneath Black Mesa are generally similar to those in the Pueblo Colorado Wash. The dominant anion facies in both areas is bicarbonate. There is a compositional change from calcium facies to sodium facies down hydrologic gradient in the Black Mesa aquifer (Lopes and Hoffman 1997) a similar change apparent in ground water from Pueblo Colorado Wash. Lopes and Hoffman (1997) proposed that these water compositions can be explained by dissolution of carbonate minerals, breakdown of silicate minerals, and cation exchange. Other factors, such as water mixing and similar sources of recharge, might contribute to similar trends of in both aquifers.

Some waters from Black Mesa and Pueblo Colorado Wash have similar isotopic compositions (figure 3-16). Lopes and Hoffman (1997) divided the Black Mesa waters into two classes, confined water and unconfined water. The isotopic composition of unconfined water from Black Mesa is very similar to the unconfined water in Pueblo Colorado and the isotopic composition of confined water from Black Mesa is similar to sample 04PWW19, a confined bedrock water in the PCW study area. These similarities allow that the age and the origin of water in Pueblo Colorado Wash and Black Mesa might be the same.

Black Mesa confined water is older than 10,000 years and was recharged during the glacial periods (Lopes and Hoffman 1997). Based upon comparison between these two areas, it is likely that bedrock well sampled near Greasewood and several USGS wells in adjacent aquifers might have a similar recharge history and based on the δD and $\delta^{18}O$ they might be as old as confined water in Black Mesa and possibly recharged during the glacial periods. On the other hand, the confined water makes just a small portion of the ground water in the study area. Since most of the ground water in Pueblo Colorado Wash is in the alluvium, it is expected to be from post glacial recharge. This hypothesis is supported by the higher permeability of alluvium in Pueblo Colorado Wash than the Black Mesa. On the other hand, the recharge of deep water of PCW by bedrock aquifers should be considered as discussed in section 3-16.The δD and $\delta^{18}O$ data therefore support the recharge of deep water in the PCW alluvium by both young shallow water and old bedrock water.

3-14 $\delta\ ^{13}C_{DIC}$ Composition of Ground Water

The effects of vegetation, bacterial activities, water-sediment interactions and dissolution of carbonates can be evaluated by using $\delta^{13}C$ values (Clark and Fritz 1997). The atmospheric CO_2 has a $\delta^{13}C$ value of -7‰. This value changes during the photosynthetic uptake of CO_2 which fractionates and depletes ^{13}C. The amount of fractionation depends on the pathways that plants follow for photosynthesis (O'Leary 1988). There are three principle photosynthesis pathways: C_3, C_4 and CAM. The C_3 pathway operates in about 85% of plant species and dominates in most terrestrial ecosystems (Ehleringer et al. 1991). Most C_3 plants have $\delta^{13}C$ values between -24 to -30‰ with an average value of about -27‰ (Vogel 1993). The C_4 plants have $\delta^{13}C$ values from -10 to -16‰ with a mean value of about -12.5‰ (Vogel 1993). Most agricultural plants such as sugar cane, corn and sorghum are C_4 plants. The CAM plants mostly dominate in the desert areas and the $\delta^{13}C$ values of these plants are between the C_3 and C_4 plants since the photosynthesis pathway they use is a combination of C_3 and C_4 pathways (Clark and Fritz 1997). As vegetation dies and accumulates in the soil aerobic bacteria and fungi break down most of its organic matter into CO_2. Soils have CO_2 concentrations 10 to 100 times higher than atmosphere. The microbially-respired CO_2 has the same $\delta^{13}C$ values as the vegetation, but, outgassing and diffusion of CO_2 imparts a diffusive fractionation on the soil CO_2. Therefore, the $\delta^{13}C$ values of soil CO_2 is about -23‰ in most C_3 landscapes (Aravena et al. 1992).

The other modifying factor of $\delta^{13}C$ is the dissolution of carbonate minerals. The $\delta^{13}C$ values from carbonate minerals vary from 20 to -40‰ (Hudson 1977), depending on the source of carbon. While $\delta^{13}C$ values in marine carbonates are close to zero, in freshwater limestones these values are negative. Therefore, the $\delta^{13}C$ value in groundwater is the sum of these modifying factors. The carbonate minerals of the alluvium in Pueblo Colorado Wash originated from surrounding formations, which comprise marine clastic units(Turini et al (2003) reported $\delta^{13}C$ for several units in the Black Mesa area and most are consistent with a marine origin with $\delta^{13}C$ values near 0 per mil) and lacustrine limestones. The detrital carbonate contribution to the PCW alluvium is expected to have a relatively uniform isotopic composition therefore variations from a constant value may indicate processes other than mineral dissolution.

In Pueblo Colorado Wash both shallow water and deep water have wide ranges of $\delta\,^{13}C_{DIC}$ values. The range for the shallow water is from -3.2 to -9.1 per mil (table 2-10) and for the deep water is from -4.1 to –11.7 per mil (table 2-9). Generally, the $\delta^{13}C_{DIC}$ values in Pueblo Colorado Wash are much higher than values resulting from oxidation of plant matter. C3 and C4 plant activities bring the $\delta\,^{13}C$ value to -20‰. The difference between the ^{13}C values from plant activities and the $\delta\,^{13}C$ in the ground water from Pueblo Colorado Wash is consistent with the sparse vegetation in the area and contributions from carbonate mineral dissolution. Additionally, the values higher than -6‰ are best explained by the dissolution of marine carbonate minerals, which in the study area are present as cements in clastic units. Three samples have the highest values: 04PSD1, 04PS18 and 04PWW19. The first two samples are shallow water from the dug wells located close to sand dunes. The higher permeability in the sand dunes results in more effective water-sediment interactions. These interactions result in the dissolution of marine carbonates and drive the $\delta\,^{13}C$ values toward zero.

A similar explanation for high $\delta\,^{13}C$ values is seen in sample 04WW19, which is confined water with high pH. Based on its D and ^{18}O isotopic composition this water is old and has had time for dissolution of carbonate cements. Therefore, the δ ^{13}C value has been modified toward higher values.

As a result, the δ ^{13}C values greater than -7‰ are considered to result by dissolution of marine carbonate cements with infiltrated water, while values lower than -7‰ are the result of the interaction of bacterial activity in the ground water (section 3-16) that release isotopically light CO_2 from the breakdown of plant accumulations or animal and human wastes. Values near -7‰ are consistent with atmospheric CO_2 that is partitioned into the water. It should also be considered that there is a fractionation between gaseous CO_2 and the CO_2 dissolved in water which is about 0.7‰. This implies that the range of $CaCO_3$ precipitated by surface water, which is also organic carbon poor, is likely to be closer to -5‰ to -6‰.

3-15 Trace Element Composition of Pueblo Colorado Wash Sections

In the Pueblo Colorado Wash aquifer, some trace elements, including uranium, arsenic, iron, selenium, manganese, and barium, have high concentrations in some wells. The concentrations of trace elements in Section 1, in which all water samples belong to bicarbonate facies and calcium is the dominant major cation, are not high. In section 2, the concentration of Ba is high in samples 04PWW3 and 04PWW5. Selenium has low concentrations in all wells except sample 04PWW2 (table 2-7). Sample 04PWW2 has high a concentration of sulfate (table 2-5). Since selenate anion has chemical properties similar to sulfate there might be a correlation between the high concentrations of selenate and sulfate in this well, although wells in other sections, TSN03 and TSN04, have high concentrations of sulfate without elevated selenium concentrations (tables 2-5 and 2-7). In section 3, all wells have higher Ba concentrations than the samples from other sections. Additionally, the concentrations of Fe and Mn are high in most wells in section 3 (table 2-7). The reasons for higher concentrations of these cations are discussed in section 3-16. In section 4, sample 04PWW17 has high concentrations of arsenic and uranium. Sample 04PWW2 has high concentration of barium and sample TSN03 has high concentrations of iron and manganese (tables 2-5 and 2-7). No correlations were found between the hydrofacies and the elevated concentrations of the above-mentioned elements in the section 4. Table 3-8 presents the medians and ranges of selective trace elements, major cations, and major anions of the water samples from different sections of Pueblo Colorado Wash Aquifer.

3-16 Evidence of Chemical Reduction in Pueblo Colorado Wash

The direct study of bacterial activities and the identification of bacteria living in the Pueblo Colorado Wash Aquifer are beyond the scope of this project, but an attempt was made to assess the importance of bacteria activity in ground water. To do this, dissolved species sensitive to the presence or absence of bacterial activity and the reduction-oxidation condition in the ground water were evaluated.

Microbial activities affect the chemical composition of groundwater. This activity is a function of availability and abundance of nutrients in the groundwater and electron acceptors and electron donors from which the organisms derive energy by electron transfer. The availability of electron acceptors and electron donors limit the activity of specific organisms. Organic materials, as the sources of energy for bacteria, are broken down during metabolism of bacteria. The breakdown of organic materials takes place in several steps and is associated with release of electrons. The released electrons are transferred to electron acceptors which, as the last step of respiration, absorb the electrons released by the organic matters (Pratt and Cornely 2004). There are several common electron acceptors and different bacteria use different electron acceptors. The aerobic and facultative bacteria use oxygen as the electron acceptor, whereas anaerobic bacteria use elements that can be chemically reduced under natural conditions such as ferric oxides (Fe III), Mn (IV), nitrate (N(V)) and nitrite (N(III)) and sulfate (Chapelle 2000; Cowan and Talaro 2006).

Some water samples from Pueblo Colorado Wash alluvium contain ammonia and nitrate (tables 2-3, 3-1, and 3-2). The presence of ammonia and nitrate are consistent with bacterial degradation of organic materials and release of nitrogen compounds. Ammonia and nitrate are components of fertilizers but the lack of cultivation along the wash suggests the most likely source of these two compounds is organic wastes. The sources of organic wastes might be either agricultural or residential. There are typically several houses and livestock shelters near wells and springs that produce water with high concentrations of nitrate and detectable ammonia. Thus ammonia and nitrate may identify water sources exposed to organic matter contamination.

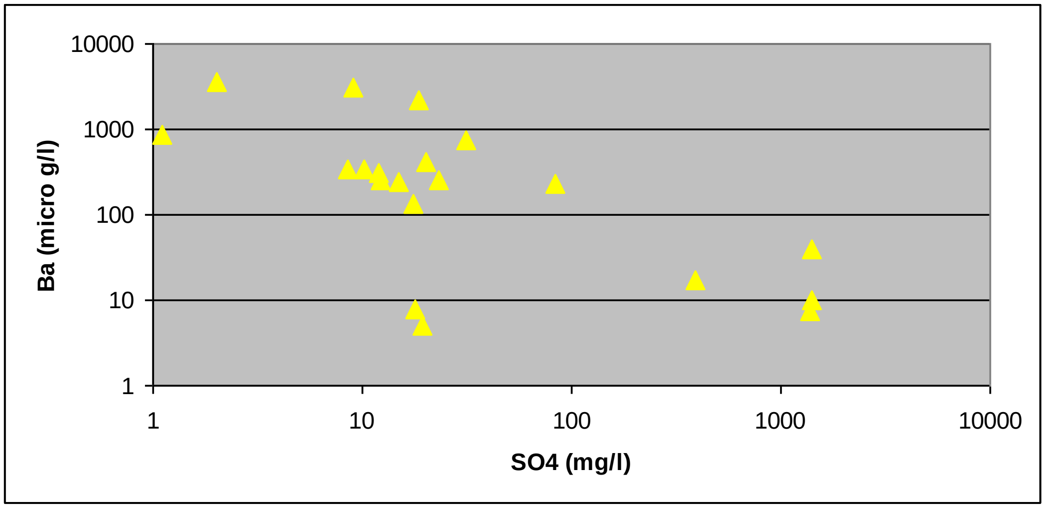
Chemically reducing conditions within the alluvium are proposed to account for the high contents of dissolved Ba, Mn, and Fe in some water samples. Since barite has very low solubility detectable sulfate generally limits the barium concentration to low values ($Ksp_{Barite} = 1.1 \times 10^{-10}$). Lowering of dissolved sulfate by bacterial sulfate reduction will therefore cause an increase in the Ba concentration in ground water if barite is present in the sediment (fig 3-17). Therefore the higher concentrations of Ba in some wells are probably the result of sulfate reduction. The presence of reducing conditions in the alluvium is also consistent with high concentrations of Mn and Fe ions in samples that have high concentrations of Ba (table 3-9).

The concentrations of Fe and Mn in these wells are between 5 to 200 times more than the wells where concentration of sulfate is high. Therefore, the pE range of ground water in wells with high concentrations of Ba, Mn, and Fe should be between +5 and -6 (Drever 2002). In the other wells and springs, the pE values should be greater than +11 and -2 depending on pH (considering the pH range of waters in the PCW consider limiting the pE range to conditions in the ground water pH= 7 to 10), if the concentrations of Mn are limited by the stability of manganese oxides (Drever 2002). A comparison between the Ba and sulfate concentrations and $\delta^{13}C_{DIC}$ values show the wells with high Ba concentration and low sulfate concentration have $\delta^{13}C$ values less than -7‰ which supports the importance of bacteria respiration in portions of the aquifer producing water with high contents of Ba, Fe and Mn.

Three samples, 04PF15, 04PF and 04PF13, are close to a former/active sewage impoundment near the town of Greasewood. Sample 04PWN22 is surrounded by shrubs and sample 04PWW5 is from a major place for livestock watering and the top soil and sediments are mixed with animal waste. Therefore, the sources of organic materials might be from the leakage of the sewage impoundment, animal waste and decomposing organic materials.

	Na^+	**Ca^{++}**	**Mg^{++}**	**K^+**	**SO_4^{--}**	**Cl^-**	**HCO_3^-**	**U**	**As**	**Se**	**Mn**	**Ba**	**Fe**	**pH**	**Specific Conductance**
Section 1 Median	10.35	62.5	7.31	1.76	11	15	219.1	1.69	1	2.4	4	338	50	7.62	394
Section 1 Range	8.3	30.9	4.8	1.58	3.5	14.1	50.2	0.88	2	1.5	10.6	157	0	0.15	66
Section 2 Median	197.6	57.3	22.7	2.7	15.3	230.3	363.7	28.48	6	12	142	373.5	50	7.44	1141
Section 2 Range	874.3	59.3	16.5	3.25	1381	440.5	275.6	6.24	6.2	91.2	205.4	3032.4	3050	0.85	1725
Section 3 Median	84.3	43.2	26.9	4.53	13.4	91.1	371.5	0.98	4	3.6	211.5	1084.5	446	7.82	829.5
Section 3 Range	127.2	34.42	17.9	6.1	31.3	149	88.3	30.4	19.8	5.6	304.7	3368	980	0.25	436
Section 4 Median	200.9	47.6	30.7	6.82	83	215	330.8	42.5	9.4	8.8	82.2	227	50	7.94	1391
Section 4 Range	6874.6	982	840	27.2	1377	14937	226.8	24.6	16.7	7.8	450	210	1150	048	25861

Table 3-9: The medians and ranges of cations, and selective anions and trace elements of different sections of Pueblo Colorado Wash Aquifer.



3-17: The concentration of Ba is inversely proportional to the concentration of sulfate in deep water of PCW.

Sample	Ba (µmol/l)	Mn (µmol/l)	Fe (µmol/l)	SO_4 (mol/l)
04PF15	25.93	4.2	18.39	0.02
04PWW5	22.52	5.29	55.36	0.09
04PF16	16.44	4.56	4.07	0.19
04PN21	9.63	5.71	11.8	0
04PN22	6.44	3.49	11.96	0.01
04PN20	5.52	4.8	18.39	0.33
04PF13	1.79	1.79	2.11	0.15

Table 3-4: the concentrations of Ba, Mn, Fe and sulfate in the deep water samples in which the concentrations of Ba, Mn, Fe are higher and the concentrations of sulfate is lower than the other deep water samples from PCW.

3-17 Possible Sources of Recharged Water in Pueblo Colorado Wash Aquifer

The ground water in the Pueblo Colorado Wash Aquifer can be recharged by several sources, including rain water, snow melt, and base flow from surrounding aquifers. To assess the possibility of these sources, the isotopic composition and the major ion concentrations will be considered.

-Rain and Snow Melt: There is no data on the concentrations of major ions from snow melt and rain of the study area. However, the data from the two rain composition monitoring sites, AZ03 at Grand Canyon and AZ97 at Petrified Forest National Park-Rainbow Forest were chosen as representative (data from National Atmospheric Deposition Program 2004). It was assumed that the chemical composition of precipitation in the study area should be close to these two data sets (table 3-5). The concentrations of HCO_3 were calculated by using charge balance and measured cations.

Site	**Ca**	**Mg**	**K**	**Na**	**NH_4**	**NO_3**	**Cl**	**SO_4**	**HCO_3**
AZ03	0.31	0.044	0.022	0.089	0.29	1.12	0.15	0.67	0.21
AZ97	0.72	0.045	0.032	0.061	0.39	1.48	0.09	1.13	0.91

Table 3-5: The chemical composition of rain in two monitoring sites in northern Arizona for 2004 (all units are in mg/l). AZ03 at Grand Canyon National Park and AZ97 at Petrified Forest National Park-Rainbow Forest

The datasets show high concentrations of nitrate and ammonia in the precipitation of the two monitoring sites. In the study area, ammonia and nitrate were detected in some wells. Since these two species can have other sources, such as animal waste, it is difficult to attribute the presence of these two species to only rain water. In addition, if precipitation was the principal source, then all ground water would be expected to show similarly high values. The absence of these two species may indicate that the precipitation may not be the main recharge source for that specific well or these two species have been removed from the water by either bacterial activity and/or cation exchange (NH_4^+ has high affinity to be adsorbed by clay minerals Drever (2002)). Therefore, to evaluate the contribution of rain and snow melt, this study relies on the isotopic composition of the precipitation and the water samples

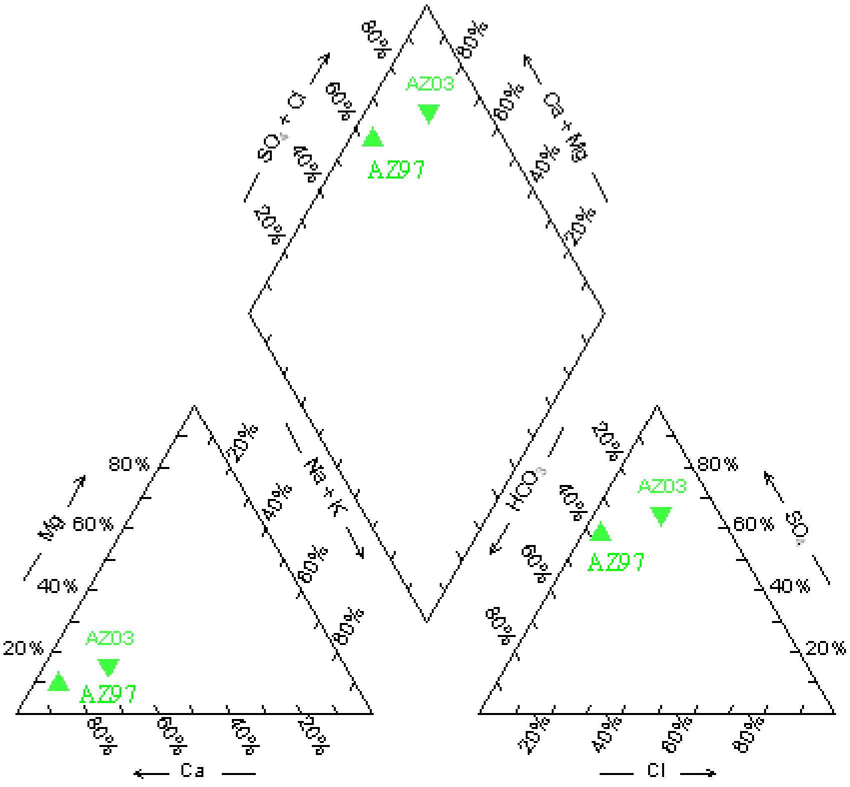


Figure 3-18: The hydrofacies of precipitation in northern Arizona.

Field observations indicate that, although the alluvium is generally fine-grained (silt and sand), in some places, such as in the section 3 and along the Pueblo Colorado Wash channel, the sediments are coarser and, therefore, rain and snow melt might contribute more readily to ground water recharge. The surficial heterogeneity of alluvium likely continues into the subsurface based on sediment descriptions in drillers logs. Intervals of coarser particles would have increased permeability that would enhance recharge particularly during intense summer storms.

There are few data on the isotopic composition of snow, summer rain, and summer run-off in the study area (fig. 3-15). The isotopic composition of these samples is distinct from the isotopic composition of the deep water and shallow water samples. This dissimilarity is likely the result of inadequate data collection in areas of recharge. Therefore, to evaluate the contribution of snow melt and summer rain the datasets of Grand Canyon were used. Monroe et al. (2004) reported that the isotopic composition range of precipitation in Grand Canyon area for summer is from $\delta^{18}O$ = -12.5 ‰, δD = -80 ‰ to $\delta^{18}O$ = 0 ‰, δD = -10 ‰ with most samples have values between $\delta^{18}O$ = -10 ‰, δD= -80 ‰ and $\delta^{18}O$ = -5 ‰, δD = -40 ‰, and that of winter is from $\delta^{18}O$ = -22.5 ‰, δD = -180 ‰ to $\delta^{18}O$ = -5 ‰, δD = -40 ‰ most samples are located between $\delta^{18}O$ = -20 ‰, δD = -140 ‰ and $\delta^{18}O$ = -10 ‰, δD = -60 ‰. The shallow water and deep water from Pueblo Colorado Wash Aquifer have isotopic values close to the range of winter precipitation (tables 2-9 and 2-10). This is consistent with winter precipitation contributing more recharge than summer precipitation, although both summer and winter precipitation experience some evaporation before recharging the ground water.

-Basal Flow: There are three likely areas that may contribute base flow into Pueblo Colorado Wash alluvium through bedrock and alluvial aquifers; Ganado Lake in the north, Defiance Plateau on the east side, and Steamboat- Joseph Spring Wash on the west side.

a) Ganado Lake is located near the Kinlichee spring and well 04PWW2. Table 2-8 presents the isotopic composition, and the concentrations of the major cations and anions of Ganado Lake. The isotopic composition of water from the lake reveals that the water has experienced evaporation and is distinct from the Kinlichee spring and deep water of well 04PWW2 (table 2-9 and 2-10). Additionally, the anion facies of water from the lake belongs to the bicarbonate facies and the cation facies is mixed facies (fig. 3-19). Therefore, the isotopic composition and the concentrations of major cation and anion composition do not show that the lake is a major source of basal recharge for section 2. The heavier isotopic composition of water in sample 04PWW2, compared with other deep water samples in the section 2, may be either the result of mixture of heavy water from the lake—probably through structural fractures since the lake is underlain by the clay rich Petrified Forest member of Chinle Formation, and leakage through that unit is not likely without structural fracturing—and the deep water at the location of 04PWW2. Alternatively, surface water that provides recharge to the aquifer in the area of well 04PWW2 may have evaporated.

b) The basal flow from the Defiance Plateau located on the east side of the Wash is the other possible source of recharge for sections 2, 3 and 4 (Appendix 1). The Plateau forms the south and east rim of the Wash, from section 2, all along the east side of the PCW along sections 3 and 4. Figure 3-20 shows the location of water samples from the Defiance

Plateau and section 2 on the Piper diagrams. No significant similarities between the section 2 water samples and Defiance water samples are apparent. The isotopic compositions of the water in these two sets of samples are different as well (tables 2-9 and 2-10).

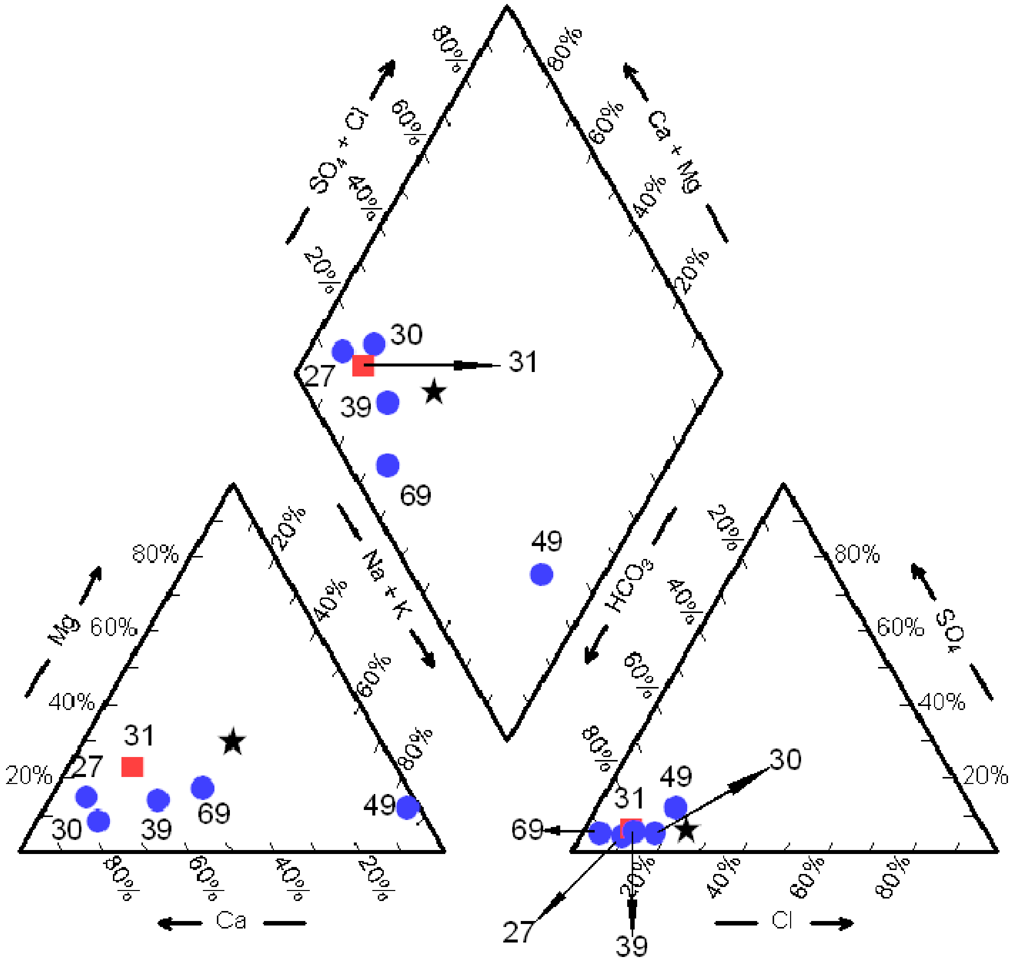


Figure 3-19: The major ions of water samples from Ganado Lake and Defiance Plateau. The symbols and assigned numbers are from table 3-1. The water sample from Ganado Lake is shown as a black star.

In contrast, there are significant similarities between the hydrofacies of water samples from section 3 and water samples form Defiance Plateau. Samples 04PGW27, 04PPGW30, TSN39CS are from Defiance Plateau. Figure 3-21 shows the composition of these samples compared with samples from section 3. The anion facies of all samples belong to bicarbonate facies. The cation facies vary from calcium dominant for the Defiance Plateau samples to no-dominant-type and eventually sodium dominant type for samples from the section 3. The change in relative abundance of the cations is attributed to cation exchange between water and sediments. The isotopic composition of samples in both populations are very similar (tables 2-9 and 2-10). As a result, Defiance Plateau is proposed as a significant source of recharge water in section 3. Section 4 does not show any similarities in isotopic composition or the concentrations of major cations and anions with any samples from Defiance Plateau (fig. 3-22 and tables 2-9 and 2-10). Therefore, the contribution of Defiance Plateau water into this section is unlikely.

c) The basal flow from Steamboat Wash and Joseph Spring Wash on the west side of the aquifer is the other possible source for recharge for section 2, 3 and 4. The deep water samples from the Steamboat area were drawn from bedrock. Isotopic data and major cations and anions do not show any similarities between the deep water of Pueblo Colorado Wash Aquifer and Steamboat-Joseph Spring Wash Aquifers for sections 2 and 3 (figs. 3-23 and 3-24, and tables 2-9 and 2-10). However, samples from section 4—04PWW7, 04WW17, and TSN03—have similar isotopic composition to samples TSN11CD and TSN04, which may indicate a contribution of basal flow from Steamboat-Joseph Spring Wash alluvium into the deep water of section 4 (tables 2-9 and 2-10).

In summary, summer rain, snow melt and basal flow all contribute recharge to the Pueblo Colorado Wash Aquifer, and different sections of Aquifer are recharged by different sources. While snow melt and summer rain are probably the most important sources of recharge for section 2, the high dissolved solids of some samples in this interval require contact to reactive salts in the subsurface. Section 3 is largely recharged by basal flow from Defiance Plateau. Basal flow is the most important contributor in section 4, to account for the rapid salinity increases from north to south. However, the composition and isotopic composition of water from the southern parts of Steamboat-Joseph Spring Wash Aquifer are not completely consistent with the water composition measured in section 4. This might be due to contribution of saline water from diatremes to the south and west of the Wash.

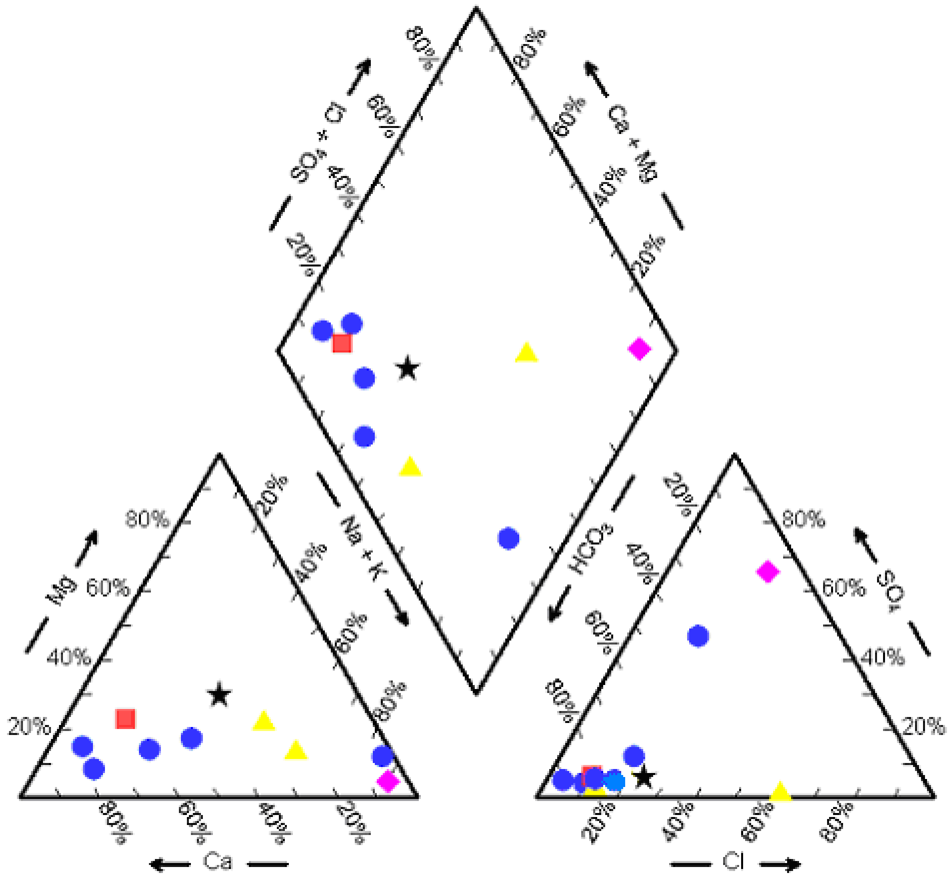


Figure 3-20: The major cation and anion composition of water samples from section 2 and Defiance Plateau. Symbols are from table 3-1. The black star is water sample from Ganado Lake and the pink diamond is sample 04PWW2.

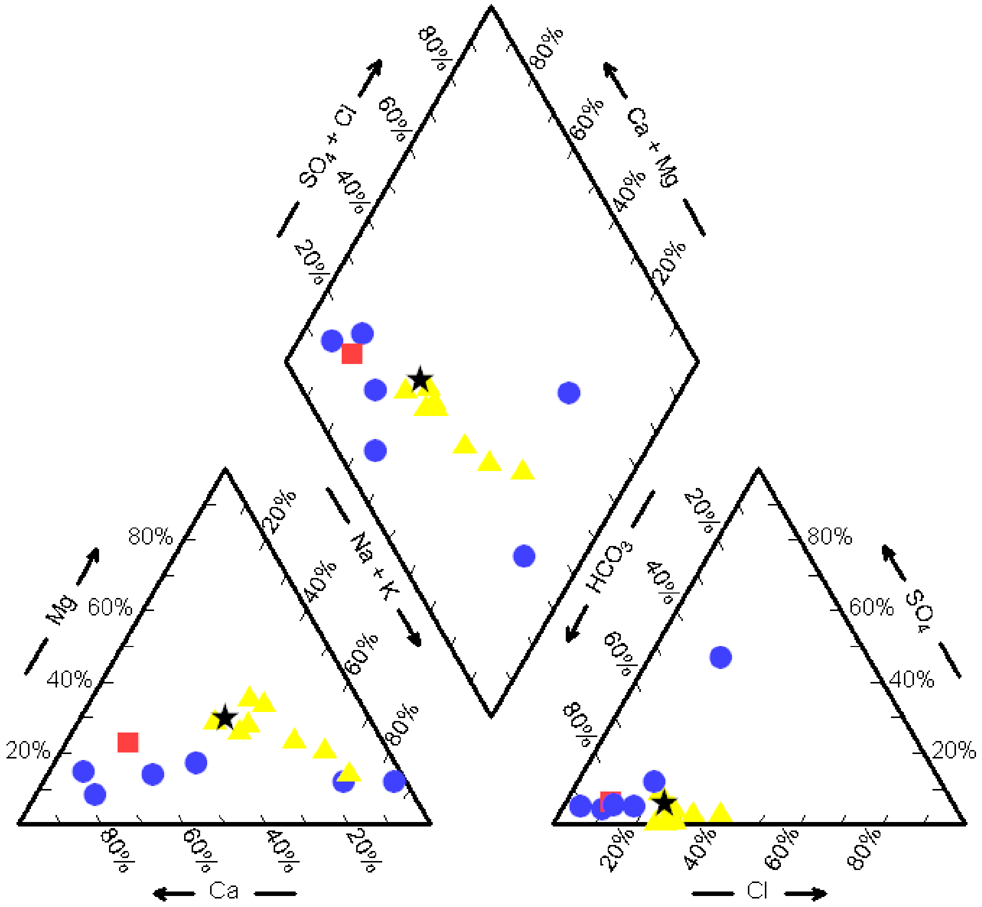


Figure 3-21: The major cation and anion composition of water samples from section 3 and Defiance Plateau. The black star represents Ganado Lake. Other symbols are from table 3-1.

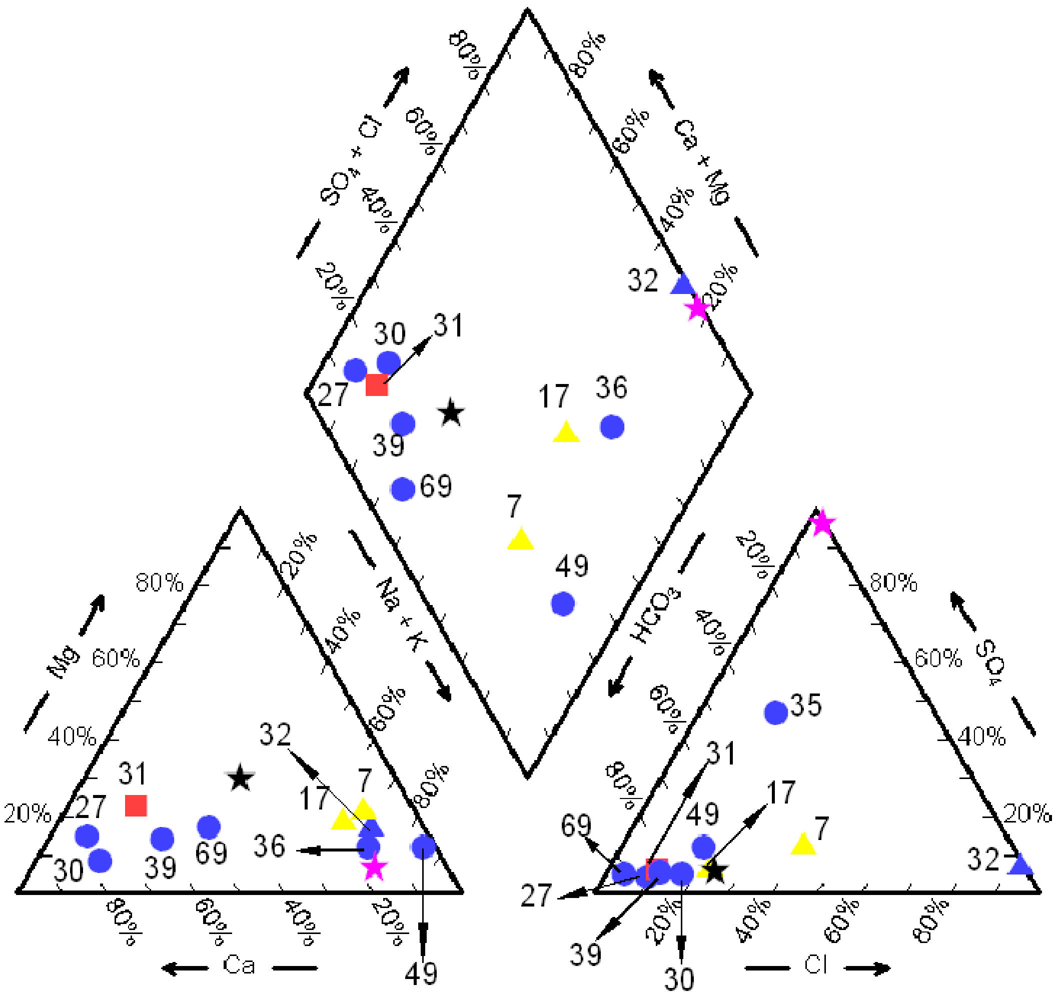


Figure 3-22: The major cation and anion composition of water samples from section 4 and Defiance Plateau. The pink star represents the water composition from a diatreme (from Akers et al. 1971) and the blue triangle is sample TSN03. Other symbols and assigned numbers are from table 3-1.

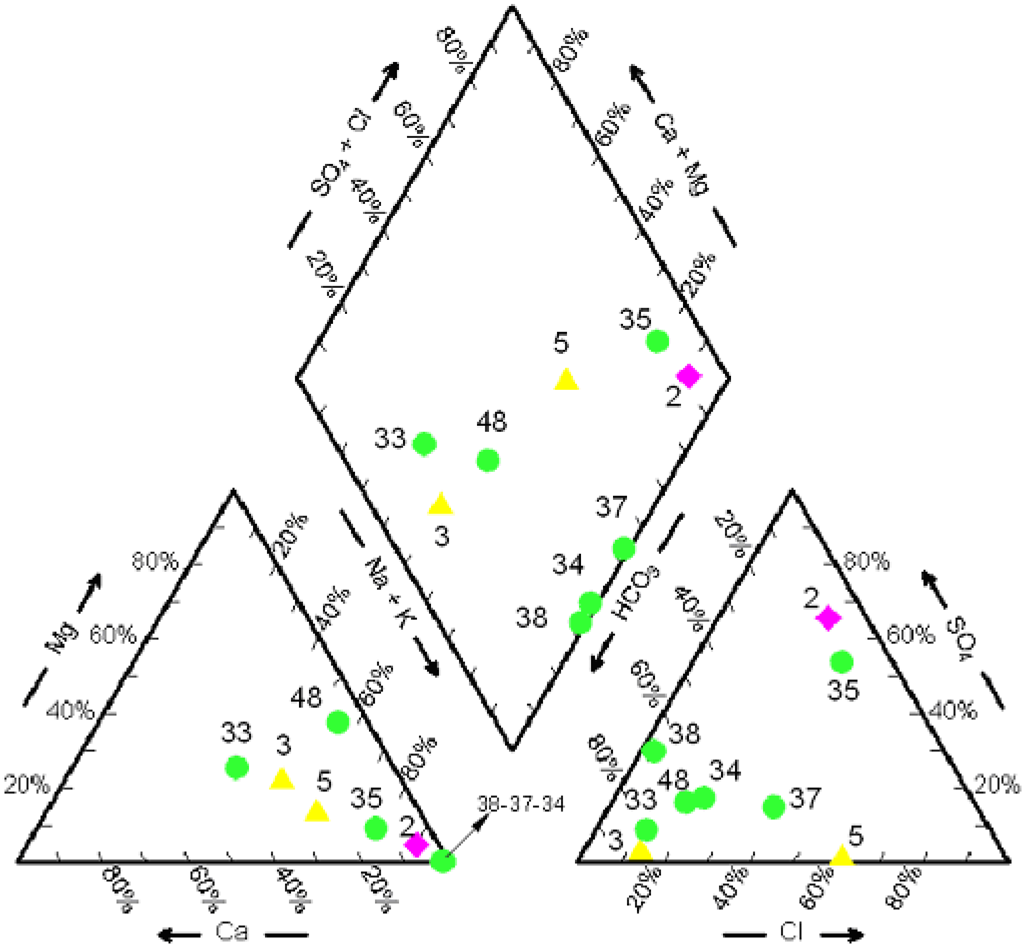


Figure 3-23: The major cation and anion composition of water samples from section 2 and the Steamboat-Joseph Spring Washes samples. Sample 04PWW2 is shown as a pink diamond. Other symbols and assigned numbers are from table 3-1.

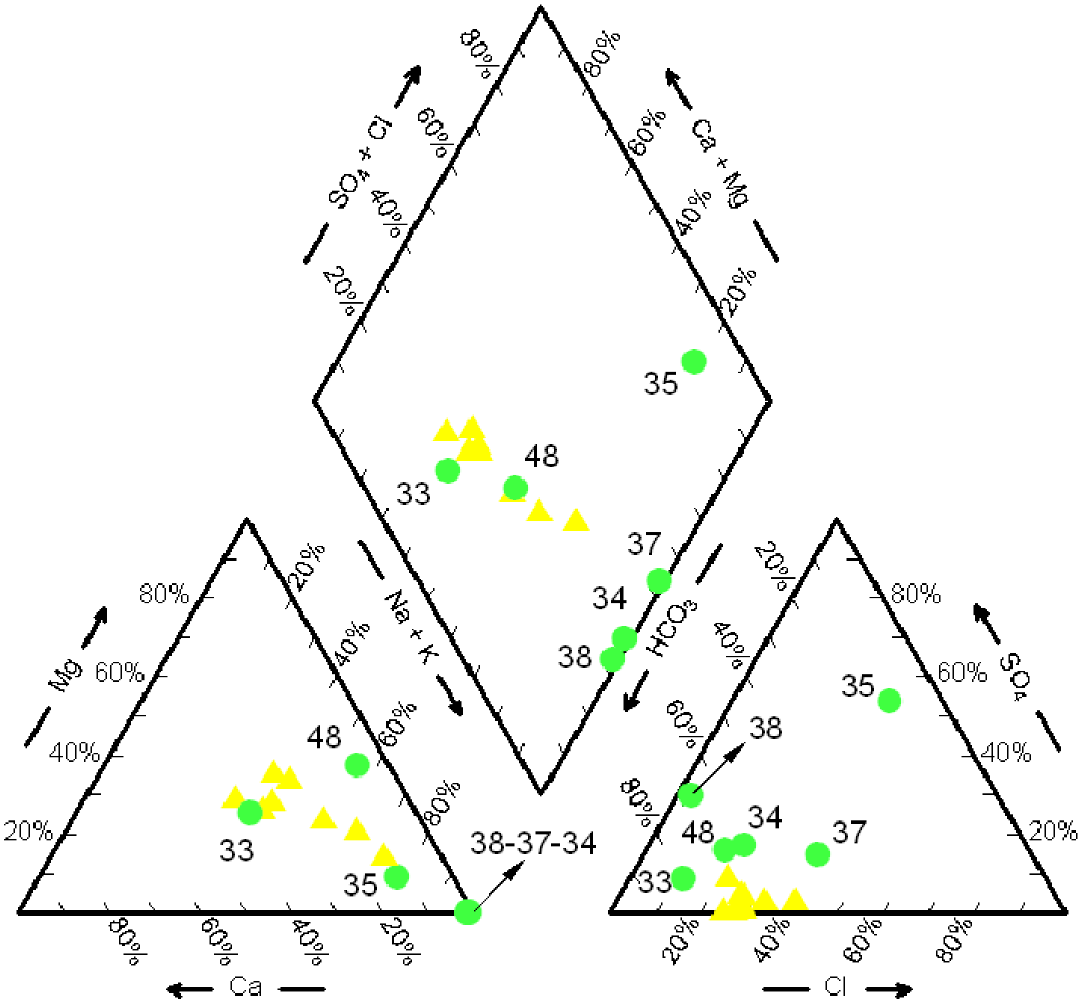


Figure 3-24: The major cation and anion composition of water samples from section 3 and the Steamboat-Joseph Spring Washes. Symbols and assigned numbers are from table 3-1.

3-18 Bedrock Aquifers in the Study Area

As mentioned earlier Pueblo Colorado Wash Aquifer is defined as an alluvial aquifer. The alluvium overlies bedrock, which also contains water (sample 04PWW19). Additionally, PCW is flanked by bedrock. On the east side, the Defiance Plateau, and on the west side, the Steamboat-Joseph Spring Wash host several wells.

The bedrock water is subdivided into two classes; unconfined water and confined water.

The unconfined waters have higher Ca contents, lower pHs and heavier deuterium and oxygen compositions than the confined water. The unconfined water from Defiance Plateau is a source of recharge for the deep water of PCW (see section 3-12). Samples 04PGW27 and 04PGW30 from Defiance Plateau and TSN33SWE from Steamboat-Joseph Spring wash are examples of unconfined bedrock water.

The confined water in the study area is similar to that described by Lopes and Hoffman for Black Mesa area. Sample 04PWW19 of Pueblo Colorado Wash (a bedrock sample) and samples TSN37, TSN11 and TSN34 from Steamboat-Joseph Spring Wash area, and sample TSN49TC from Defiance Plateau are interpreted to be confined water. Piper diagram (fig. 3-25) shows (sample TSN49TC is shown on fig. 3-22) that all samples belong to bicarbonate facies, and sodium-dominant facies. These samples are spread over the study area indicating that some bedrock aquifers beneath most of the drainage basin of the PCW are isolated from the alluvium.

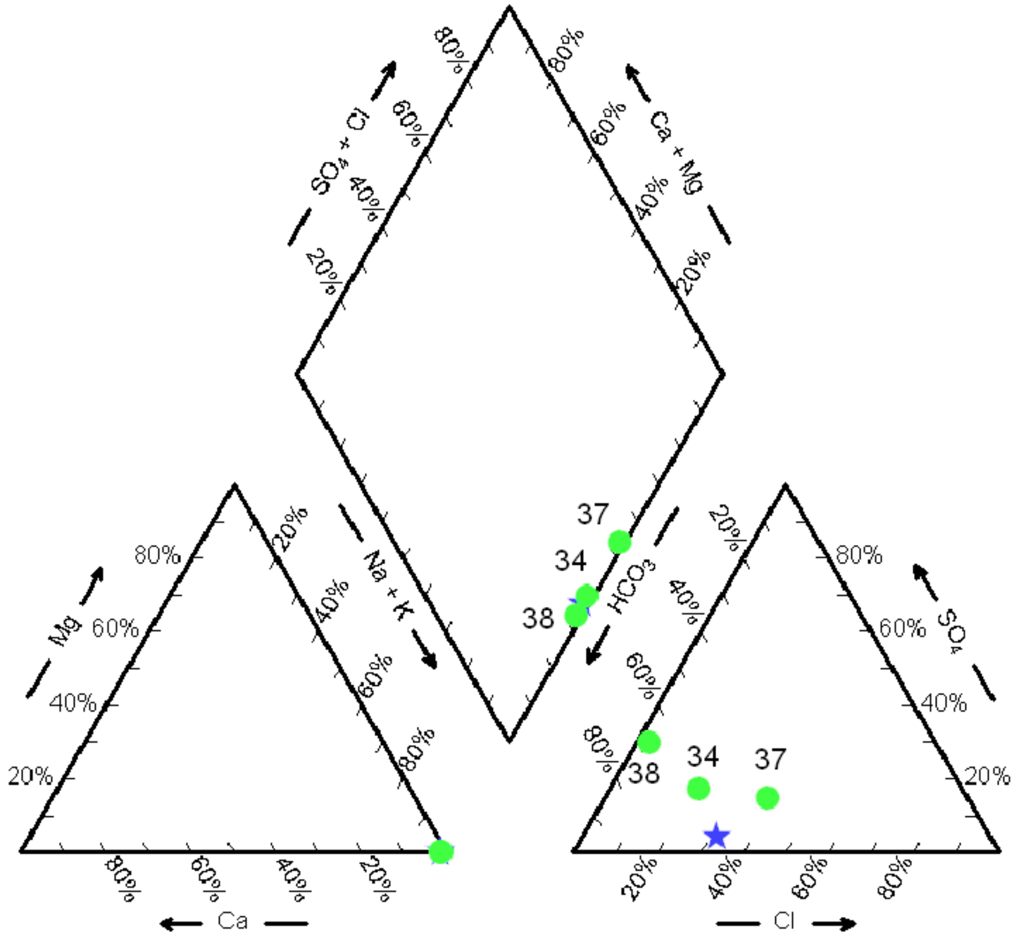


Figure 3-25: The major cation and anion composition of confined water samples on the Piper diagram. Sample 04PWW19 is shown as a blue star. Other symbols and assigned numbers are from table 3-1.

3-19 Saline Intrusion and Increased Salinity

The salinity of water in the southern part of PCW, section 4, increases rapidly from north to south. At Twin Buttes, well TSN03 (17K-306), water is saline and has the highest salinity in the study area. A comparison between the water composition from 1950's and 2001 of this well reveals that the specific conductance has increased about 500% (table 3-6).

	1950's (mg/l)	**2001 (mg/l)**
Na^+	1060	7000
Cl^-	565	15000
Mg^{2+}	69	860
SO_4^{--}	1240	1400
Specific Conductivity	5.5 ms/l	26.6 ms/l

Table-3-6: The composition comparison of well 17K-306, located at Twin Butte Pueblo Colorado Wash, in 1950's (from Kister and Hatchett1963) and 2000.

In layered aquifers, where both fresh water and saline water exist, the saline water typically underlies the fresh water through a transitional interface zone, since saline water is denser than fresh water (Schwartz and Zhang 2002). Overexploitation of fresh ground water may lead to two phenomena; salinization-upconing and saline water intrusion. In the salinization-upconing phenomenon the deep saline water locally moves upward and replaced the removed the freshwater. Saline water can also move laterally as the fresh water layer is depleted.

In section 4 of PCW, the composition of water in the aquifer may be starified. The saline water probably originates from the diatremes, located in the south and south west of Twin Buttes, and underlies the fresh water. The removal of the fresh water by pumping from numerous wells upgradient in the PCW might have depleted the supply of fresh water. Therefore, increased salinity of the deep water at Twin Buttes well might have been due to the advancement of saline water. The remarkable increase of chloride in well TSN03 supports this hypothesis. The specific conductivity of wells 04PWW17 is significantly less than well TSN03 and slightly higher than well 04PWW7. Additionally, well 04PWW17 belongs to bicarbonate facies while well TSN03 belongs to chloride facies. Therefore, the well 04PWW17 might indicate the northern boundary of the saline underlying water at the time of sampling. If the section 4 of Pueblo Colorado Wash Aquifer is a fresh/saline water system, it may limit the amount of water pumping out of section 3 since the ground water probably flows along the topographic slope from north to south. The removal or thinning of freshwater in section 3 may cause the advancement of saline water toward north, provided enough permeability and hydrologic pressure.

Chapter 4

4-1 Summary

Major cations and anions, isotopic composition of water samples, and trace elements were used to provide and identify the major controls on the inorganic chemical composition of ground water occurring within the Pueblo Colorado Wash Aquifer.

The three main objectives of this study have been fulfilled. The first objective was to identify and sample the current wells and springs being used by local residents in the study area. During this study thirteen sites were sampled, from which no data had been available before this study. Thirteen additional sites were sampled, for which the USGS had records of the chemical compositions, and this study provided additional records for the USGS database.

The second objective was to evaluate the geochemistry of the water to construct a conceptual model that accounts for the spatial variations in dissolved concentrations, identify probable reactions within the alluvium, and identify areas of contamination among the sample sites. This objective was addressed by analyzing the water samples for major cations, major anions, trace elements, and ^{18}O, D and ^{13}C isotopes. The WATEQ4F program version 2.63 was used to evaluate accuracy of the compositional data and develop a geochemical model.

The third objective was to investigate the possible roles of the clay minerals of the alluvium and the water-sediment interactions on the water chemistry.

4-2 Conclusions

Pueblo Colorado Wash Aquifer is an alluvial aquifer, in which the chemistry of water is determined by simple dissolution and breakdown of minerals, water mixing, cation exchange, evaporation, bacteria activity, and recharge from different sources.

The alluvium is a heterogeneous mixture of silt and fine sand, with intercalated lenses of gravel and coarse sand. These lenses, which are located at different depths, host the ground water. The thickness of alluvium is not uniform along the wash, and it varies from about 20 to 70 meters. The alluvium thickness pinches out in the south of Twin Buttes and disappears. The width of the Wash along its main course varies from about 1 to 5 km. The silt and fine sand partially isolate the lenses from each other. This heterogeneity is evident in parts of Wash, such as section 3, where wells are very close to each other, the chemistry of the water in adjacent wells are different, especially for concentrations of some trace elements.

The water samples from the Pueblo Colorado Wash aquifer is divided into two groups: shallow water and deep water. Each group has different chemical compositions. Most samples of shallow water belong to the bicarbonate facies. Some shallow wells, located near sand dunes, show high concentrations of arsenic, high Na/Ca ratios, and high concentrations of sulfate, which is probably from dissolution of windblown minerals such as sodium sulfate. Shallow water has also experienced evaporation and cation exchange, which caused the depletion of Mg and Ca. The composition of other shallow water samples can be largely explained by the simple dissolution of carbonate minerals.

The chemistry of deep water is very different in the different parts of the Wash; hence, the Wash is subdivided into four geochemical sections:

Section 1: This section is located in the northern and northeastern parts of the Pueblo Colorado Wash and reflects the composition of shallow bedrock on the Defiance uplift. The water samples in this section have low specific conductance values and belong to the calcium and bicarbonate facies.

Section 2: This section is located between the Sunrise Spring and Road 261 in the northern parts of the wash. In this section, the specific conductance values increase very rapidly from north to south. The dominant cation in most samples of this section is sodium, and one sample has calcium as the dominant cation. One sample in this section belongs to the sulfate facies, and the other samples belong to bicarbonate facies. The sample that belongs to the sulfate facies has high concentrations of selenium. The high concentration of selenium might be attributed to the same source as the dissolved sulfate. Bacterial activity causes high concentrations of barium, magnesium, and iron in some of the samples of this section.

Section 3: This section has chemical characteristics very similar to water samples from section 1. The isotopic compositions of samples from this section are very close to the samples from section 1. There are also significant similarities between the chemical composition of water samples from section 3 and water samples from Defiance Plateau. The specific conductance value drops significantly at the boundary of this section with section 2 and increases very slightly compared with the rate of increase of sections 2 and 4. This drop is attributed to the significant recharge of water from section 1 into section 3. Some wells in this section have high concentrations of barium, iron, and manganese and low values of $\delta^{13}C$, which is attributed to bacterial activity.

Section 4: This section starts south of Greasewood and ends at Twin Buttes. The major cation in the water samples of this section is sodium and the dominant anion is chloride for the most southern sample, and bicarbonate for the other two samples. The specific conductance values increase from north to south very rapidly so that the water sample from Twin Buttes has the highest specific conductance value among the water samples of the study area. Since this section is close to the volcanic diatremes, it is likely recharged by saline water from diatremes, and therefore water mixing is an important factor in the water chemistry of this section. The over pumping of fresh water has caused the saline intrusion in Twin Buttes well.

Isotopic compositions of water samples indicate that winter precipitation is the important source of recharge. The plotting of deuterium and oxygen composition of deep water shows an excellent match with the Pleistocene Local Meteoric Water Line. This suggests that the deep water is recharged by old bedrock water.

The bedrock flanking and underlying the PCW alluvium contain water. The bedrock water is subdivided into two classes; unconfined water and confined water. The unconfined water has higher Ca and Mg concentrations than the confined water. In confined water the Ca and Mg were removed by cation exchange. Comparison between the confined bedrock water of Pueblo Colorado Wash with the confined water samples from Black Mesa also shows the similarity in chemistry and isotopic composition. Therefore the confined water of PCW might be as old as 10,000 years.

4-3 Recommendations and Suggestions

This study focused on the chemical composition of Pueblo Colorado Wash Aquifer. The age of water samples was suggested by comparison with the Black Mesa data. To have precise results age determination of the water by dating methods is required. The results from dating the water would help to examine whether the deep water is recharged by Pleistocene water, and also help to determine the ratio of recharging young shallow/old deep water.

Section 3 is the most productive section of PCW and has good water quality in the study area. This section is recharged by section 1, Defiance Plateau. To avoid contamination and pollution of water in section 3, it is necessary to manage any agricultural, industrial, and housing development in the Defiance Plateau. Because deep water in section 3 is recharged by section 1, Defiance Plateau, it is also necessary and important to limit the amount of water pumping out from Defiance Plateau.

Saline intrusion is seen in the southern part of PCW, section 4. To avoid the advancement of saline water from section 4 to section 3, the pumping of water in section 3 must be managed properly. A comprehensive study on the possible presence of saline water in the deeper parts of Pueblo Colorado Wash Aquifer is recommended to determine the wells with higher risk of saline intrusion.

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