

Chapter 17

Origin of the waters in the San Solomon Spring system, Trans-Pecos Texas

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Introduction

The San Solomon Spring System occurs between the Davis Mountains and the Toyah Basin. This spring system includes the Phantom Lake, San Solomon, Giffin, Saragosa, West Sandia, and East Sandia springs. These springs historically provided a considerable amount of water for this semi-arid part of Trans-Pecos Texas (Brune, 1981) and continue to provide water for irrigation and recreational purposes. The springs also support two federally endangered fish species: the Comanche Springs pupfish (*Cyprindodon elegans*) and the Pecos gambusia (*Gambusia nobilis*). Some of these springs (Phantom Lake, Saragosa, and West Sandia) have now dried-up or now flow at a reduced rate. Heavy pumping of the Toyah basin aquifer (LaFave and Sharp, 1987, 1990) led to drying up of the Irving, Buck, and Alamo springs near Pecos, Texas.

Most previous studies suggest that a large portion of the spring waters are derived primarily from the Davis Mountains (White and others, 1941; Couch, 1978); (Figure 17-1). Others indicate that the spring water could also be derived from the Capitan Reef rocks in the Apache Mountains and areas beyond (Couch, 1978; Harden, 1972). Later studies concluded that there are two components to the spring flow system: (1) a base-flow component that derives water from the bolson aquifer in Wild Horse Flat and (2) a storm-flow component that derives water from the Davis Mountains during intense rainfall events (Neilson and Sharp, 1985; LaFave and Sharp, 1987; Uliana, 2000). However, using computer simulation, Neilson and Sharp (1985) observed that only 2,850 acre-ft/yr of water could potentially flow from the Wild Horse Flat to the springs. This is much lower than the annual average spring flow of about 33,000 acre-ft. Understanding the source of the spring waters is important to understand what may have caused the cessation of flow in Phantom Lake Springs and may be causing declining spring flows.

We conducted a study to identify the source waters for the San Solomon Spring System. We did this by (1) expanding the area of investigation to include the Delaware Mountains; (2) analyzing groundwater compositions from wells completed in different

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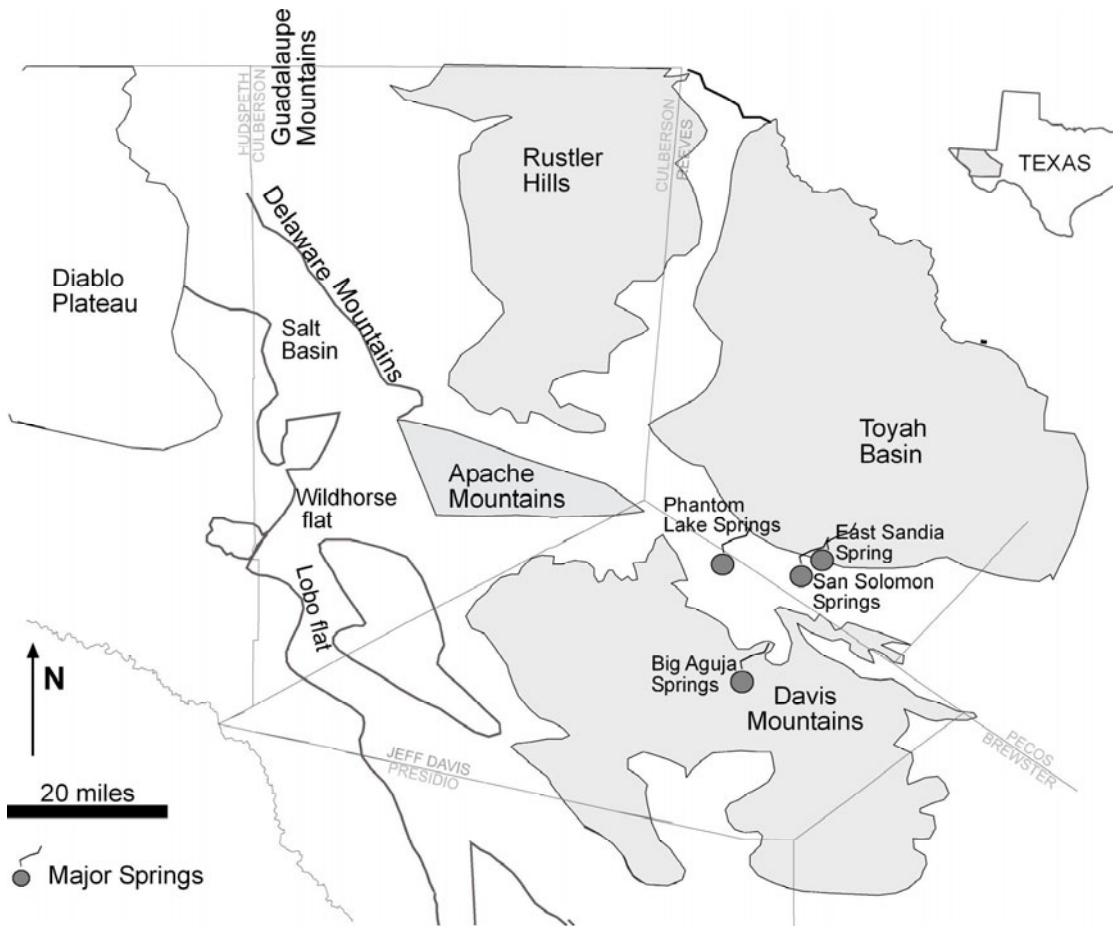


Figure 17-1: General geologic setting of the study area showing the topographic features and locations of the major springs (after Uliana, 2000).

geologic units to identify chemical processes and establish relationship between the different units; (3) using several additional isotopes of $\delta^3\text{H}$, $\delta^2\text{H}$, $\delta^{18}\text{O}$, $\delta^{13}\text{C}$, $\delta^{34}\text{S}$, and ^{14}C to identify the origin and the sources of the spring waters; and (4) simulating spring-water compositions using the NETPATH code. The purpose of this chapter is to discuss this work.

Previous work

Several researchers have studied the hydrogeology and geochemistry of groundwater in the Trans-Pecos region (White and others, 1941; Couch, 1978; Harden, 1972; Hiss, 1980; Neilson and Sharp, 1985; Sharp, 1989; LaFave and Sharp, 1987, 1990; Uliana, 1995; Sharp, 1998; Sharp and others, 1999). Most of the research was focused on identifying the sources of the water for these springs.

White and others (1941) believed that the spring waters were derived from an interconnected system of fissures and solution passages in the Lower Cretaceous limestone. They first suggested that the principal area of intake for the spring waters is the anticlinal valley that parallels the steep fronts of the Davis Mountains and the mountains west, northwest and southwest of the springs. They reported considerable increases in flow in the springs immediately after heavy rains.

Couch (1978) provided an extensive review of the regional groundwater flow system in relation to structure and lithologic characteristics of the various geological units. Couch (1978) postulated that water from the Capitan Reef aquifer west of the Pecos River could flow southeast through the faults into the down-faulted Lower Cretaceous aquifer. He observed that flow in Phantom Lake springs increases considerably after 24 hours of heavy rainfall, and flow in the San Solomon and Giffin springs increases another 24 hours later than the Phantom Lake springs. The changes that occur in all three springs during storm flow are increases in flow, decreases in water temperature, decreases in mineral content, and increases in turbidity. Couch (1978) thought that the springs hydrologic system is controlled by a constant-flow component that is fed by recharge from the volcanic terrain, alluvium and underflow from the stream gravels, and a stormflow component that consists of an extensive system of cavities and channels in superposition of the constant flow system.

Hiss (1980) reported on the groundwater movement in the Permian Guadalupian aquifer system in southeastern New Mexico and western Texas. He concluded that a combination of factors controlled groundwater flow distribution: (1) regional and local tectonics, (2) evolution of the landscape, (3) relative transmissivities of the aquifers, (4) the amount of recharge, and (5) exploitation of groundwater and petroleum over the last five decades. He indicated that groundwater moved east and southeastward through the shelf (Capitan Reef and associated limestone) and basin aquifers (Delaware Mountain Group).

Nielson and Sharp (1985) reported that the Capitan Reef aquifer complex is highly permeable and can provide a conduit for flow through the preferentially west–east aligned faults through the Apache Mountains. Using computer simulations, they reported that 2,850 acre-ft/yr of water could potentially flow from the southern portion of the Salt Basin. However, this volume is much less than the average flow of 33,000 acre-feet/yr observed in the springs.

LaFave and Sharp (1987) observed water quality from wells in the Davis Mountains that is markedly dissimilar from the springs. They reported that the groundwater from the Davis Mountains is fresh containing less than 500 mg/l total dissolved solids while the spring waters have total dissolved solids of 2,000 to 2,400 mg/l. Presence of sodium, chloride, and sulfate in the spring waters made them suggest that the waters must have interacted with evaporite sequence that is not found between the Davis Mountains and the springs. From limited isotope measurements, they observed that the spring has a $\delta^{18}\text{O}$ value of -8.52 ‰ SMOW compared to a $\delta^{18}\text{O}$ value of -5.71 ‰ SMOW from a spring on Limpia Creek in the Davis Mountains. A corrected C-14 age for one sample from the spring was found to be $8,954 \pm 235$ years before present. This information led them suggest that the spring water could not be of local origin but more likely from higher

elevations or cooler Pleistocene times. They also postulated that during a storm, spring flow could comprise as much as 73 percent from the Davis Mountains and 27 percent from a steady source, that is, the Capitan aquifer and associated limestones through a fault conduit through the Apache Mountains.

Uliana (2000) carried out a detailed investigation of the spring waters using $^{87}\text{Sr}/^{86}\text{Sr}$, $\delta^2\text{H}$, and $\delta^{18}\text{O}$ isotopes. He indicated that the spring waters were partially recharged from a regional system in the southern Salt Basin that flows through the Apache Mountains into the Toyah Basin.

Fracture trends in the bedrock largely control the regional flow system. Using the PHRREEQC geochemical model, he showed that 28 to 43 percent of the spring water could have been recharged from baseflow from the west and 57 to 72 percent from local meteoric recharge in the Davis Mountains.

Analytical Methods

We analyzed seventeen groundwater and spring water samples for chemical and isotopic compositions (Figure 17-2). Prior to selecting wells for groundwater sampling, we hypothesized potential groundwater flow paths from the inferred source areas from the Davis Mountains, the Apache Mountains, and northwest of the Delaware Mountains. We used potentiometric surfaces from the intervening aquifers and lineament distribution pattern to select wells that could potentially lie along the flowpath to the springs. We took groundwater samples from wells completed at shallow depths where the water is presumably fed from recent recharge event, wells completed at deeper depths where the water was likely to have flowed through the deeper stratigraphic units, and the spring waters. To get a better appreciation of the chemistry and isotopic compositions of the groundwater in the Permian limestones, we also sampled three wells along the western edges of the Delaware Mountains. In addition, we reviewed water compositions from wells completed in the Cretaceous and the Permian rocks in the adjacent four counties of our study area. We compiled ion ratios of the groundwater from each of the geologic units to observe whether any unique ratios emerge particular to any unit.

A NETPATH computer code (net geochemical reactions along a flow path) available through the public domain was used to determine geochemical evolution of the waters (Plummer and others, 1994). NETPATH uses equations for chemical mass balance, electron balance, and isotope mass balance to account for net geochemical reactions between the initial (recharge area) and the final water (discharge area) along a flow path. The geochemical reactions are constrained by using a number of appropriate products and reactant minerals characteristics of the geology of the study area. NETPATH can be used for determining mixing proportions, geochemical reactions, dilution, evaporation, and mass transfer in the chemical and isotopic evolution of the evolutionary waters. Even though waters may not be truly evolutionary, NETPATH will always report reactions that it can find. Therefore, caution must be exercised in selecting samples for NETPATH simulation. All groundwater and spring samples were analyzed by ion chromatography-

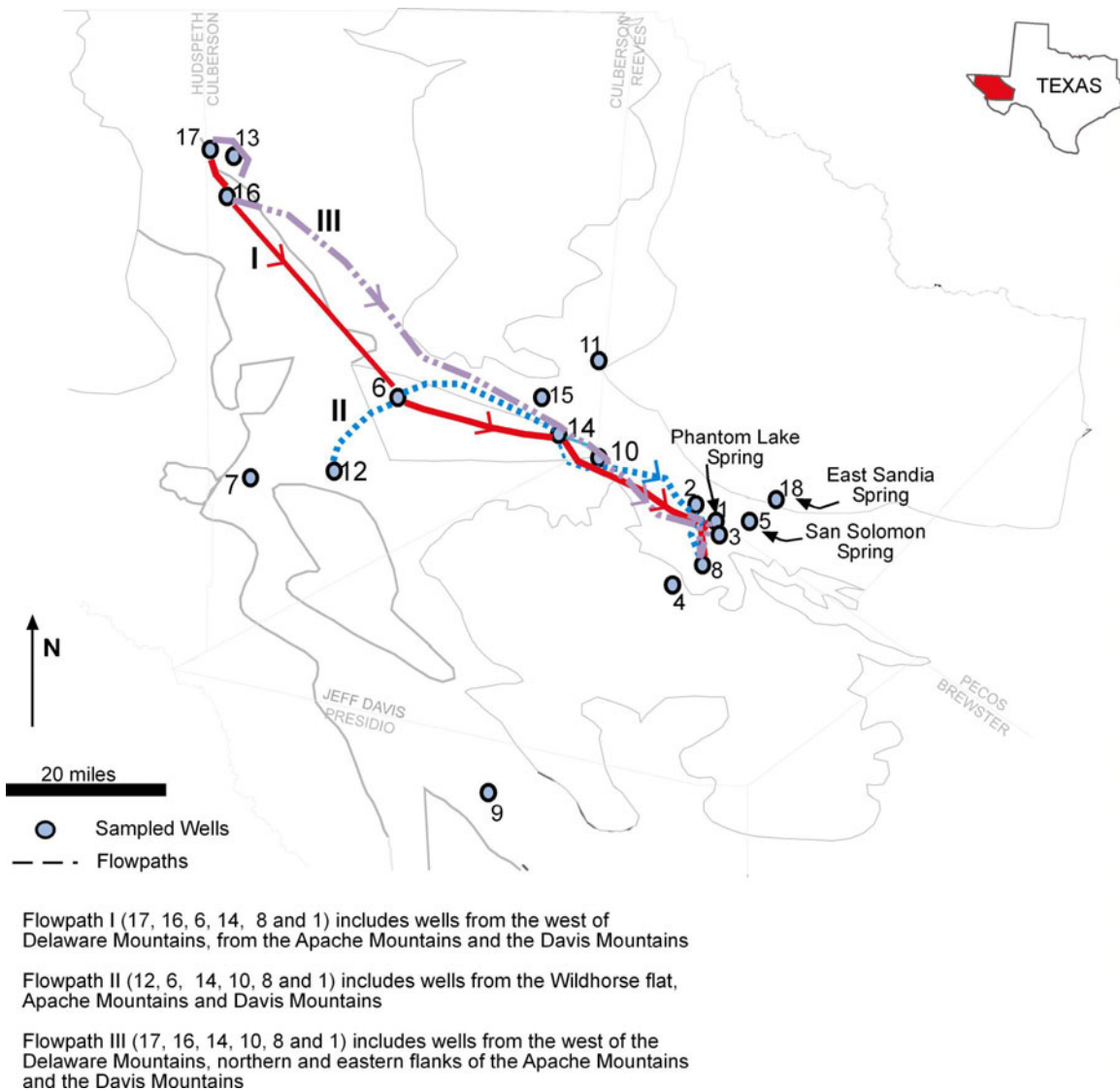


Figure 17-2: Map showing the locations of the sampled wells and the springs. For corresponding state well numbers and names, refer to Table 17-1.

mass spectrometry (ICP-MS) for chemical parameters at the Lower Colorado River Authority's (LCRA) Environmental Laboratory. $^{14}\text{C}_{\text{DIC}}$ isotope analyses were carried out at the Beta Analytic Inc. using an accelerator-mass-spectrometer (AMS), and the result was presented as apparent radiocarbon age before present (B.P. where present is 1950 A.D.) and percent of the modern standard (pmC). $\delta^{13}\text{C}/\delta^{12}\text{C}$ ratios were measured with reference to the PDB standard.

$\delta^3\text{H}$ analysis was done at the Tritium laboratory of the Rosenstiel School of Marine and Atmospheric Sciences, University of Miami. $\delta^3\text{H}$ was measured by chromium or zinc reduction to H_2 gas on a Micromas 602D mass spectrometer. $\delta^{18}\text{O}$ and $\delta^2\text{H}$ analyses were

carried out at the Coastal Sciences laboratory in Austin. $\delta^{18}\text{O}$ isotope was analyzed on a VG Micromass SIRA Series II mass spectrometer using the CO_2 equilibration method (Epstein and Mayeda, 1953). $\delta^{34}\text{S}$ was analyzed by extracting SO_2 from the settled BaSO_4 using a mass spectrometer VG Model 10, Series II.

Geologic Setting

Trans-Pecos Texas has been subjected to four major tectonic events: (1) formation of the Ouachita –Marathon fold and thrust belt in Early Pennsylvanian, (2) rifting of the Gulf of Mexico from the early Mesozoic through Cenozoic, (3) continued subduction that resulted in volcanism and lava flows and formation of the Davis and the Barilla mountains, and (4) basin and range faulting that formed the Salt Basin graben (Muehlberger and Dickerson, 1989). The Alpine earthquake of 1994 suggests that extensional to trans-tensional deformation may still be continuing (Uliana, 2000).

The Salt Basin graben is located between the Permian Delaware Basin and the Guadalupe Mountains and the Diablo Plateau to the west. The Delaware Basin contains more than 20,000 feet of Paleozoic sediments and is bounded by the Capitan Reef rocks exposed in the Guadalupe Mountains, Sierra Diablo, and the Apache mountains (Sharp, 1990). The reef trend continues into New Mexico and southeastward in the subsurface. Salt dissolution, extensional normal faulting, and Tertiary volcanism have been the three most important geological processes that led to the creation of the Toyah basin, flexure zones (Babb and Victorio), and the Rounsaville syncline trend/Stocks fault (Sharp, 1990).

The eastern margin of the Salt Basin is intensely faulted with faulting parallel the north trending basin boundaries. In the Rustler Hills, the fractures and fold axes have easterly trend (Sharp, 1990). Neilson and Sharp (1985) indicated that the Babb and the Victorio flexure zones created permeability barriers that shaped the surface drainage systems and controlled locations of the alluvial fans.

The Permian age strata in the northern Delaware Basin can be divided into three aquifers (Hiss, 1980):

- 1) low permeability Basinal aquifer containing sediments of the Delaware Mountain Group (Castile and the Rustler formations),
- 2) high permeability Shelf-margin facies with transmissivities exceeding $16,000 \text{ ft}^2/\text{day}$ consisting of the Capitan Reef and the underlying Goat Seep limestone, and
- 3) Shelf facies aquifer solely controlled by fracture porosity.

The rocks exposed in the vicinity of Balmorhea are comprised of the Lower and Upper Cretaceous marine sediments, Tertiary volcanic deposits and lava flows, and Quaternary alluvial deposits (White and others, 1941). The Lower Cretaceous sediments consist of massive thick-bedded limestone with some minor inter-bedded calcareous shale and sandstone at the base. The Lower Cretaceous section thins towards the northwest and has

a thickness of 500 feet near Balmorhea. The uppermost limestone exposed near the Phantom Lake springs contains several sinks or deep cavernous channels.

The Upper Cretaceous rocks are mainly composed of clay and are exposed beneath the lava on the steep front of the Davis Mountains and in the foothills. These rocks are 500 to 600 feet thick near Balmorhea.

The Tertiary aged volcanics cap the Davis Mountains and numerous hills and ridges in Balmorhea. These volcanics have a total thickness of 1,500 to 2,000 feet and the basal unit is marked by a white tuff. Much of these rhyolitic lava flow is densely fractured and jointed and is exceedingly porous. The volcanics dip below the base of the stream

gradient in structurally depressed areas where the lava may form a porous reservoir for the infiltrating rainfall as the base of the unit contains an impermeable tuff.

Alluvium and gravel of Tertiary, Pliocene, and Recent age overlie the bedrock of the lower mountain slopes and most of the lowlands and are generally 15 to 25 feet deep.

Water levels

Based on water-level measurements from the 1950s and 1960s, Neilson and Sharp (1985) indicated the presence of two groundwater divides in the Salt-Basin. The northern divide coincides with the Babb flexure zone and the central through the Victorio (Bitterwell Break) flexure zone (Goetz, 1980). They observed that the groundwater flow pattern is strongly influenced by the tectonics of the area that resulted in basin and range topography causing recharge from the alluvial fans on the mountain slopes flow towards the valley floor in the center of the closed basins. Thus, flow is preferentially towards the center in the north and the central areas of the salt flats, but, in the south near Wild Horse Flat, flow is from the alluvium towards the Apache Mountains in the east. Neilson and Sharp (1985) reported that groundwater flow was impeded east due to the presence of low permeability sediments of the Delaware Mountain Group and flow westward was prevented due to low fracture porosity of the Diablo Platform.

We reviewed water-level information from the Texas Water Development Board's (TWDB) groundwater database. We developed (1) a water-level map for the pre-development condition using water-level measurements from 1930 to 1960 (Figure 17-3) and (2) a water-level map using all water level measurements from 1930 through 2003 (Figure 17-4). The pre-development water level map constructed was based on limited water-level measurements but shows similar regional flow paths as seen from the water-level map constructed for 1930 to 2003. The groundwater divides reported to occur in the Salt Basin (Neilson and Sharp, 1985), although they appear to exist, may not be well developed as the gradient that defines the divides may be subtle and subject to change direction. While we support the contention expressed by earlier researchers (Neilson and Sharp, 1985) about the existence of groundwater divides in the Salt Basin, we believe that

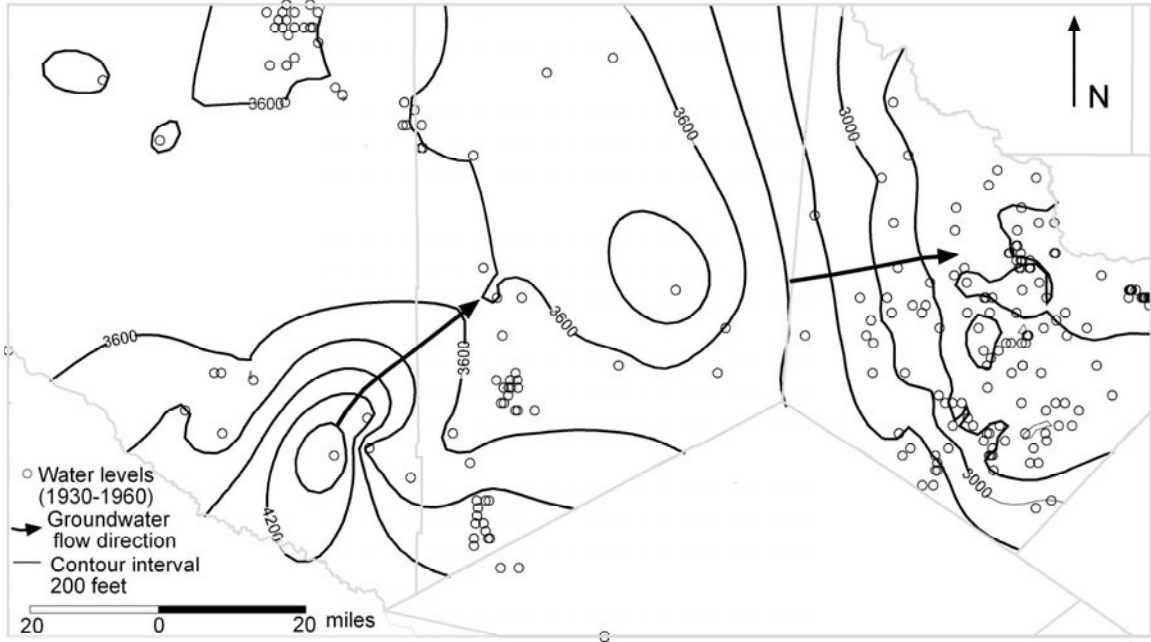


Figure 17-3: Water-level elevation maps of the study area for 1930-1960.

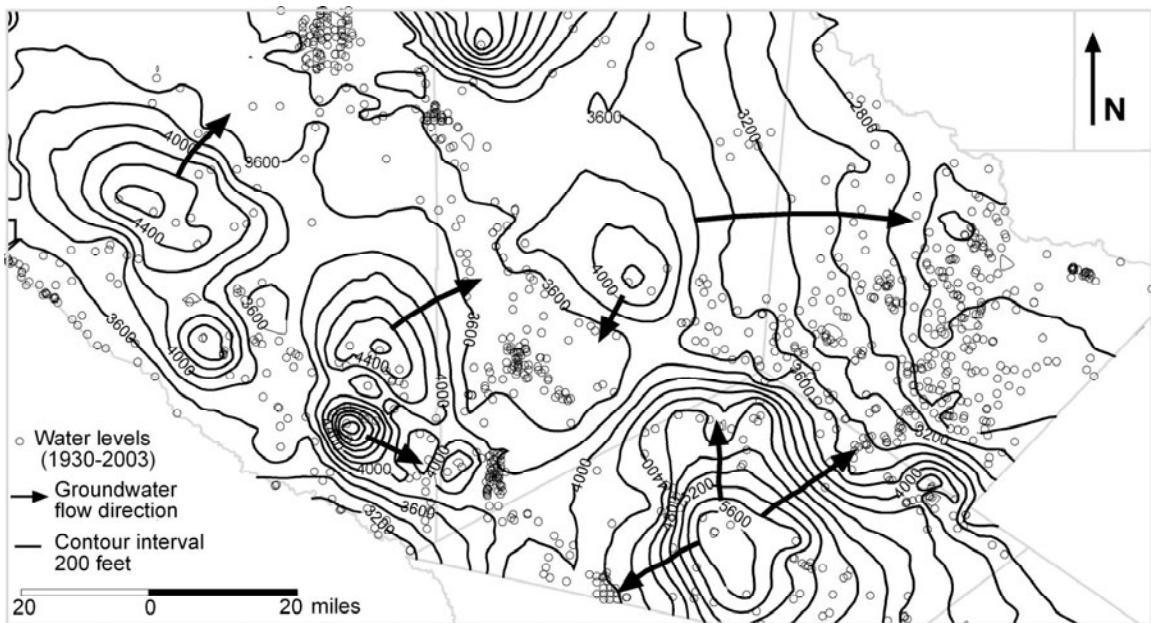


Figure 17-4: Water-level elevation maps of the study area for 1930 through 2003.

the divides may not be strongly developed and they may not readily apply to the deeper geological units below the Salt Bolsons. Numerous northwest-southeast and east-west trending fault zones occur between the Diablo Plateau and the Delaware Mountains across the salt flats. These fault zones can potentially act as flow conduits for the groundwater and could lend some support for groundwater flow to occur from areas along the western edges of the Delaware Mountains to the springs. In addition, if the groundwater that feeds the springs were recharged in a humid climate during the late Pleistocene as was supported by isotopic compositions (see later) then the water levels were likely to have existed at much higher elevations than that of today.

In a recent investigation, Lee and Williams (2000) reconstructed the paleohydrology of the Delaware Basin indicating that meteoric water that recharged from the uplifted western margin discharges basinward. Hydrocarbons migrated by pressure gradients and buoyancy, and discharged upwards along faults in the western basin. Thus, saline water from the deeper subsurface can move upwards into the overlying Delaware Mountain Group and the Capitan Reef aquifers.

Water Chemistry

Groundwater commonly evolves from an initial bicarbonate composition to waters dominated by sulfate and chloride. The initial calcium composition progressively changes to calcium-sodium then to mainly sodium composition through the processes of dissolution, precipitation, evapotranspiration, and cation exchange. These reactions can be evaluated by making cross-plots of the individual ions according to their stoichiometric compositions. When these ions plot on a straight line, then a specific reaction is implied and a deviation from it indicates changes to the chemistry due to other processes. A specific chemical type of a groundwater sample may roughly indicate its position in the geochemical evolution sequence, but the order can vary depending upon the sequencing of the processes and rock compositions through which the groundwater flowed.

We plotted the major cations and anions from the sampled wells on a piper diagram to observe similarities or differences in water composition between samples obtained from the different geologic units. We observed that the water composition plot into three areas of the Piper diagram (Figure 17-5; Piper, 1944). Water from the Davis Mountains is Ca-HCO₃ type with two water samples approaching Na-CO₃ composition. The remainder of the samples from the Cretaceous and the Permian rocks including the springs show a dominant Na-Cl-SO₄ composition. Waters from Phantom Lake, San Solomon, East Sandia, and Giffin springs have nearly identical compositions (Table 17-1).

Na/Cl ratios of the Phantom Lake, San Solomon, East Sandia, and Giffin springs are also nearly identical (0.63, 0.63, 0.70, and 0.74, respectively). SO₄/Cl ratios are also considerably lower in the Phantom Lake, San Solomon, East Sandia, and Giffin springs (0.69, 1.09, 1.08, and 1.08, respectively) than the rest of the samples. All of the wells sampled (3, 4, 9, and 10) downslope from the Davis Mountains across the springs have

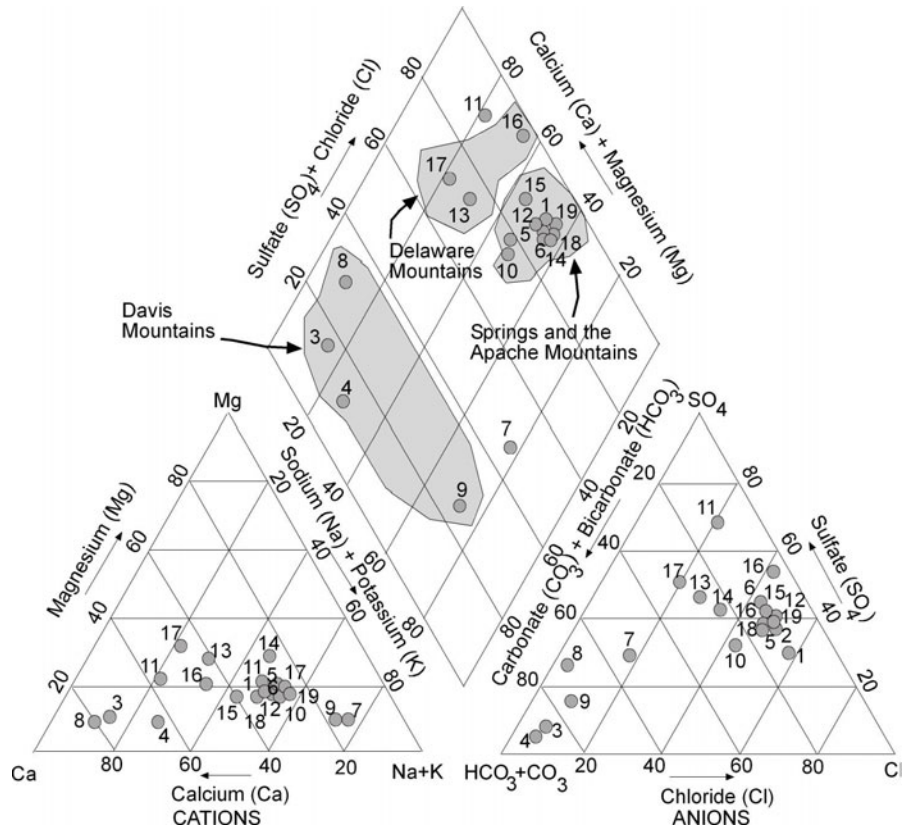


Figure 17-5: Piper diagram showing sampled groundwater and spring water compositions.

Table 17-1: Chemical composition of groundwater samples analyzed for this study. All values are in mg/l except for Sr that is in ug/l.

Sample Number	Sample Names	State	Chemical Composition (mg/l)												
			Na	K	Ca	Mg	Cl	HCO ₃	SO ₄	NO ₃	Sr (ug/l)	F	Na/Cl	SO ₄ /Cl	
1	Phantom Lake Springs	5202405	418	22	175	79.9	664	224	463	1.04	3430	2.24	0.63	0.70	
2	Madera-McIntyre, Reeves	5201302	181	8.56	112	34.5	276	190	303	0.4	1590	0.636	0.66	1.10	
3	Madera-Huelster	5202404	11.7	2.75	58.3	5.05	8.6	173	12.8	5.93	254	0.5	1.36	1.49	
4	Davis Boys Camp	5209501	14.3	2.18	31.9	3.02	4.54	114	4.97	2.33	99.6	1.4	3.15	1.09	
5	San Solomon Spring	5202611	392	20.2	182	77.2	620	223	678	1.4	3200	1.86	0.63	1.09	
6	Apache Ranch	4752602	411	21.4	166	88.7	646	211	666	0.31	3110	1.49	0.64	1.03	
7	City of Van Horn	4758505	116	6.86	18.9	8.08	38.5	200	86.7	9.83	342	2.22	3.01	2.25	
8	Timber Mountain	5209303	15	3.1	114	8.1	5.98	287	83	1.47	670	0.44	2.51	13.88	
9	Clay Evans	5138803	85	4.2	18	6.5	15.2	212.34	36	2.37	290	2.31	5.59	2.37	
10	Banky Stocks Ranch	4764401	239	12.6	128	48.4	356	256	412	1.34	2760	1.47	0.67	1.16	
11	T-diamond	4748701	173	9.48	422	96	217	213	1370	6.55	7350	1.69	0.80	6.31	
12	University Lands	4759603	375	18.4	124	76	541	263	557	0.51	2980	1.4	0.69	1.03	
13	Six Bar Cattle Co.	4718402	107	3.46	141	65	164	292	402	0.16	2460	0.82	0.65	2.45	
14	Yearwood Ranch	4755802	105	7.11	149	105	369	415	613	53.37	6090	1.18	0.28	1.66	
15	Yearwood Ranch	4755401	296		226	60	442	216	620	19		1.8	0.67	1.40	
16	Wilson (Wimberly well)	4726101	371	90.3	497	135	600	90.31	1032		1470	2.81	0.62	1.72	
17	Armstrong Farms	4717302	83		156	66	117	298	411	0.4		1.4	0.71	3.51	
18	East Sandia spring	5203115	444	23	202	88	630	281	680			2.1	0.70	1.08	
19	Giffin Spring	5202610	463	25	186	79	628	276	679	1	4000	2	0.74	1.08	

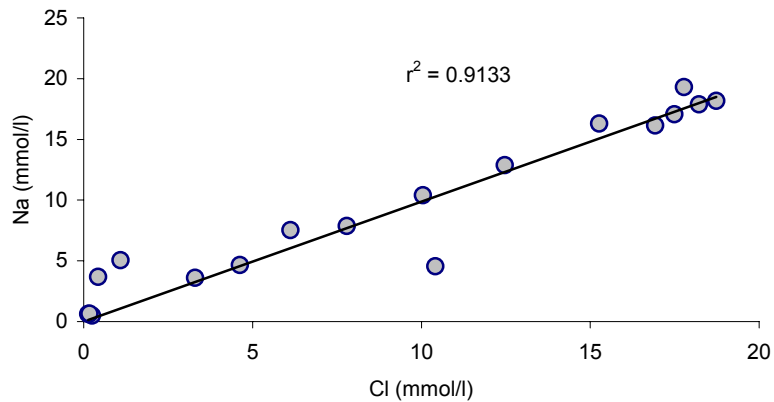


Figure 17-6: Na versus Cl plot of the groundwater from selected wells and the spring water.

the least salinity with considerably lower Na, Cl, SO₄, and Sr values indicative of their derivation from recent recharge events (Table 17-1).

When we plotted Na and Cl values of the waters, we observed that most of the samples fall on the 1:1 line (Figure 17-6). Samples 7 and 9 have slightly higher Na values compared to Cl, and sample 14 has a lower Na value compared to Cl. The close correlation for most of the samples indicates that most of the Na and Cl were derived from dissolution of halite minerals. The characteristic Na/Cl weight ratios (0.62 to 0.63) of the samples bear well with groundwater derived from halite dissolution. Also, Ca-Na exchanges appear insignificant except for samples 7, 9, and 14. The Na/Cl ratios we observed in the springs are close to what would be expected from dissolution of pure halite (0.65), which is maintained in solution unless significant cation exchange that reduces Na concentration occurs (Leonard and Ward, 1962; Hitchon and others, 1969; Richter and Kreitler, 1991). Similar Na/Cl ratios (0.63 to 0.65) in the salt springs of West Oklahoma were derived from halite solution (Leonard and Ward, 1962). Other researchers reported that high Na/Cl ratios could even be observed in shallow alluvium due to halite dissolution in the underlying aquifers (Gogel, 1981). A plot of Ca and SO₄ of the waters show a moderate correlation ($r^2 = 0.79$) perhaps indicating that gypsum must also have been a significant source for much of the calcium in the waters (Figure 17-7). Ca and HCO₃ of the waters indicate a poor correlation ($r^2 = 0.04$) indicating that most of the Ca in the studied waters was not derived from dissolution of carbonate sediments. A plot of Cl and NO₃ of the waters shows a wide scatter suggesting that they were not derived from the same irrigation source. When Cl and NO₃ are derived from the same irrigation source, Cl and NO₃ compositions often show uniform concentrations (Saffigna and Keeny, 1977).

A review of the fluctuations of the total dissolved solids (TDS) and Na/Cl ratios of the Phantom Lake and San Solomon spring waters over the historical record (1923-2003) of

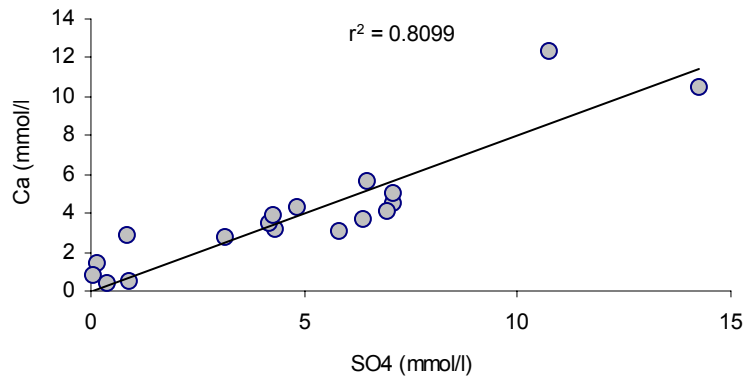


Figure 17-7: Ca versus SO₄ plot of the groundwater from selected wells and the spring water.

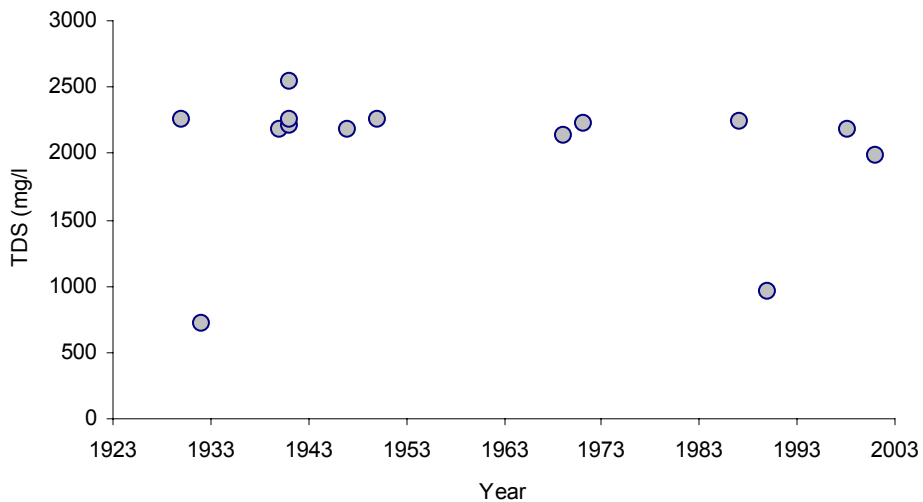


Figure 17-8: TDS concentrations from Phantom Lake Springs from 1923 through 2003. Note that freshening of the springs during intense rainfall (depleted TDS and Na/Cl values) is infrequent in the historical record (1932 and 1990).

measurement indicate that the spring water composition remains nearly uniform except during 1932 and 1990 when considerable freshening marked by increases in spring flow and rainfall occurred. This uniformity in spring-water composition, which largely was unperturbed over the last 80 years, may imply a sustained dominant flow from a regional source (Figure 17-8).

We also analyzed water chemistry information from wells completed in specific geologic units in adjacent four counties (Table 17-2). We observed that there is a high variability

Table 17-2: Groundwater compositions from wells completed in the Capitan Reef and associated limestone; Cretaceous System; and the Salt Bolson and the Delaware Mountain Group from Jeff Davis, Culberson, Reeves and Presidio counties. Mean and standard deviation (SD) values are shown in parenthesis. N represents number of total samples used in estimating the mean and SD.

Formation	Na/Cl	SO ₄ /Cl	Sr (mg/l)	F (mg/l)
Capitan Reef Complex and associated limestone	0.04 to 6.45 (1.28±1.38, n = 40)	0.37 to 368 (10.47 ± 40.30, n = 50)	0.34 to 5.52 (2.41± 1.60, n = 17)	0.55 to 3 (1.38± 0.71, n = 40)
Cretaceous System	0.6 to 1.64 (1.14±0.34, n = 9)	0.52 to 5.79 (3.24 ± 2.07, n = 10)	0.7 to 5.75 (4.06 ± 2.9, n = 3)	0.6 to 2.5 (1.38 ±0.78, n = 9)
Salt Bolson and Delaware Mountain Group	0.54 to 0.71 (0.63±0.07, n = 5)	1.67 to 4.51 (2.81± 1.09, n = 5)	6.7 to 14.4 (10.5 ± 5.42, n = 3).	1.5 to 1.89 (1.86 ± 0.35, n = 3)

in the water composition within each of the geologic units. A closer association appears to exist between water compositions (Na/Cl and SO₄/Cl ratios) from wells completed in the Salt Bolson and Delaware Mountain Group and those of the springs.

δ²H and δ¹⁸O isotopes

δ²H and δ¹⁸O isotopes behave predictably during their hydrologic evolution from evaporation, rainout, ice accumulation, melting, and runoff. Isotopic evolution of the waters through the various phases of the hydrologic cycle is reflected in the global meteoric water line (GMWL) (Craig, 1961a, b). Global meteoric water line is essentially an average of the numerous local and regional meteoric water line as defined by the following equation: δ²H = 8δ¹⁸O + 10 ‰ SMOW. Thus, how isotope values of groundwater are positioned with respect to the GMWL reflects the nature of the isotopic evolution.

Changes in precipitation and temperature control climate change. Temperate climates have undergone rapid changes in temperature since late Pleistocene times (Clark and Fritz, 1997). A good correlation between isotopes in the rainfall and isotopes in the groundwater exists that make it a useful tool to apply to paleogroundwaters for interpretation of climate change. A shift in the isotopic signatures at or below the GMWL may indicate the existence of a pluvial (humid) climate during recharge of the paleogroundwater. Isotopic partition that results in depleted isotopic waters in cold regions and enriched waters in warm regions lead to its use in recharge and groundwater source area studies (Craig, 1961; Clark and Fritz, 1997). Water also becomes progressively enriched with δ²H and δ¹⁸O during evaporation as occurs in a closed basin (Gonfiantini, 1986).

The analyzed groundwater and spring water samples have $\delta^{18}\text{O}$ values that range from -7.2 to -9.3 ‰ SMOW and $\delta^2\text{H}$ values that range from -52 to -72 ‰ SMOW. One rain sample analyzed is considerably enriched in both $\delta^2\text{H}$ and $\delta^{18}\text{O}$ isotopes (Figure 17-9, Table 17-3). We observed that most of the $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values plot parallel to but positioned lower than the GMWL. Plot of the isotope compositions parallel to but just below the GMWL line may suggest that much of the recharge may have occurred under a humid climate. When we use linear regression of the isotope values, we obtain an equation defined by $y = 6.22x - 7.45$ indicating a slight lowering of the slope compared to the GMWL reflecting evaporation effects due to infiltration.

Groundwater samples from wells 3, 4, 8, and 9 from the Davis Mountains have considerable similarities in both $\delta^{18}\text{O}$ (-7.4 ‰ to -7.6 ‰ SMOW) and $\delta^2\text{H}$ values (-52 ‰ to -57 ‰ SMOW) (Table 17-3). Similar $\delta^{18}\text{O}$ (-6.8 ‰ to -7.7 ‰ SMOW) and $\delta^2\text{H}$ (-52 ‰ to -54 ‰ SMOW) values are found in wells 11, 14, and 15 located along Jeff Davis, Culberson, and Reeves county lines. Wells from the Davis Mountains (3, 4, 8, and 9) occur at higher elevations than the wells located along the tri-county line (11, 14, and 15). There is nearly a thousand feet elevation difference between the two general locations. We observe that, overall, these waters are enriched in both $\delta^{18}\text{O}$ and $\delta^2\text{H}$ isotope values. The rest of the samples (1, 2, 5, 6, 7, 12, 13, 16, and 17) have considerably more depleted $\delta^{18}\text{O}$ (-8.5 to -9.3 ‰ SMOW) and $\delta^2\text{H}$ (-60 to -72 ‰) values (Table 17-3).

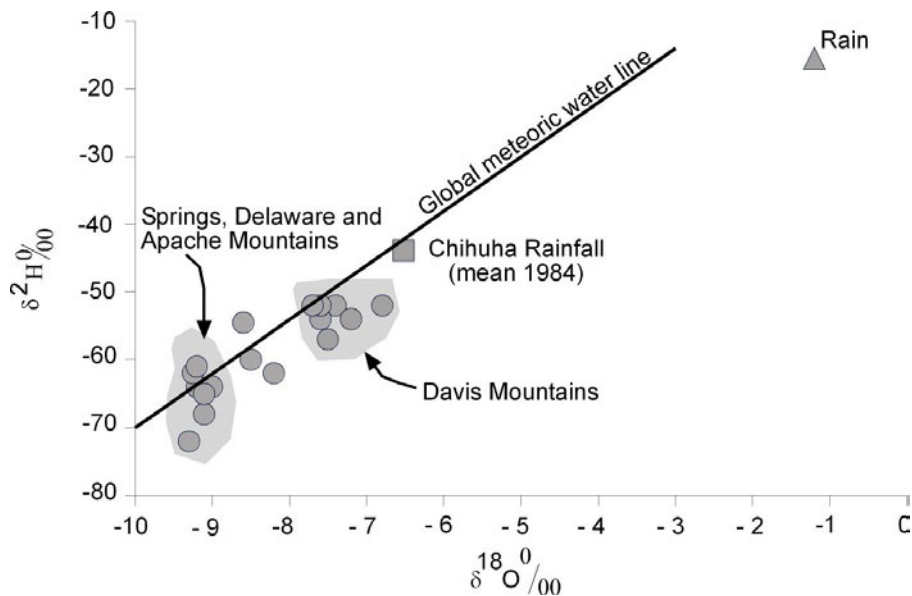


Figure 17-9: $\delta^{18}\text{O}$ versus $\delta^2\text{H}$ isotope compositions of groundwater and spring water from selected wells. The square represents the mean value of the rainfall for 1984 from the Chihuahuan desert. Triangle represents the only rain sample available from the study area.

Table 17-3: Isotope values of the analyzed water samples from the study area. SMOW refers to standard mean ocean water, TU to tritium unit, BP to before present, fmdn to fraction modern, and PDB to Pee Dee Belemnite standard.

Sample Number	State Well Number	$^{18}\text{O}/\text{‰}$ (SMOW)	$\delta^2\text{H}/\text{‰}$ (SMOW)	Tritium (TU)	Apparent ages (BP)	^{14}C fmdn	$^{14}\text{CpmC}$	$\delta^{13}\text{C}/\delta^{12}\text{C}/\text{‰}$ PDB	$\delta^{34}\text{S}/\text{‰}$
1	5202405	-9.2	-64	0.06	17,580	0.112	11.2	-7.4	10.6
2	5201302	-8.5	-60	0.12	11,290	0.245	24.5	-7.3	
3	5202404	-7.4	-52	1.87	2,670	0.717	71.7	-11.8	
4	5209501	-7.5	-57	0.24	8,830	0.333	33.3	-12.7	
5	5202611	-9.1	-68	0.17	15,360	0.148	14.8	-7.3	10.3
6	4752602	-9.3	-72	-0.06	19,200	0.092	9.2	-6.8	11.3
7	4758505	-8.2	-62	0.01	17,950	0.107	10.7	-6.6	8.2
8	5209303	-7.6	-54	1.36	11,410	0.242	24.2	-8.7	
9	5138803	-7.6	-52	0	14,630	0.162	16.2	-8.2	
10	4764401	-8.6	-54.5	2.12	10,220	0.2801	28.01	-7.4	
11	4748701	-7.7	-52	0.61	4,250	0.5889	58.89	-7.8	
12	4759603	-9.25	-62	0.12	17,140	0.1183	11.83	-6.2	
13	4718402	-9.2	-61	0.02	16,970	0.1209	12.09	-8.7	
14	4755802	-7.2	-54		17,690	0.1105	11.05	-9	3.2
15	4755401	-6.8	-52	4.26					10
16	4726101	-9.0	-64	0.08					11.1
17	4717302	-9.1	-65		16,090	0.1349	13.49	-8.6	11
	Rain water	-1.2	-15.5	2.92					

Rainfall occurs as an air mass rises over a landscape and cools by expansion. The cooler temperatures at higher altitudes cause depletion in both the $\delta^{18}\text{O}$ and $\delta^2\text{H}$ isotope values. For every 300 feet rise in altitude, $\delta^2\text{H}$ isotopes decrease from -1 to -4 ‰ and $\delta^{18}\text{O}$ isotopes decrease from -0.15 to -0.5 ‰ (Clark and Fritz, 1987). Thus, recharge from direct rainfall in the Davis Mountain wells (at $\sim 4,400$ feet) would likely be more depleted than wells located in the areas along the tri-county line (at $\sim 3,400$ feet). However, we observed only slight differences in $\delta^{18}\text{O}$ and $\delta^2\text{H}$ isotope values from these two areas, perhaps due to mixing from a second source.

$\delta^{18}\text{O}$ and $\delta^2\text{H}$ isotope values (-1.4 ‰ and -15.5 ‰ SMOW, respectively) of the only rain sample are much heavier than the groundwater. This rain sample was collected in August

at the start of the rainy season in West Texas when most of the heavy isotopes could potentially be trapped in the initial vapor mass. Thus, this isotope value perhaps represents one of the heavier end-members that could be encountered in a wider spread of isotopic compositions in any rainfall. For example, $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values of rainfall (1962-1988) from the closest GNIP stations in Chihuahuan desert located in northwestern Mexico indicate that the isotope values in the rainfall can vary widely. In the Chihuahuan desert, $\delta^{18}\text{O}$ values of the rainfall range from 0 to -14.3 ‰ (-6.52 ± 3.40 ‰ SMOW) and $\delta^2\text{H}$ values range from -9.9 to -96.9 ‰ (-43.9 ± 25.25 ‰ SMOW).

Several researchers have suggested that the ground temperatures may have fluctuated from 5 to 8 °C between the last glacial maximum and the present (Dutton, 1995; Stute and others, 1995). Dansgaard (1964) reported a relationship between surface air temperature and $\delta^{18}\text{O}$ values with a slope of 0.695 ‰ / °C. Uliana (2000) reported that

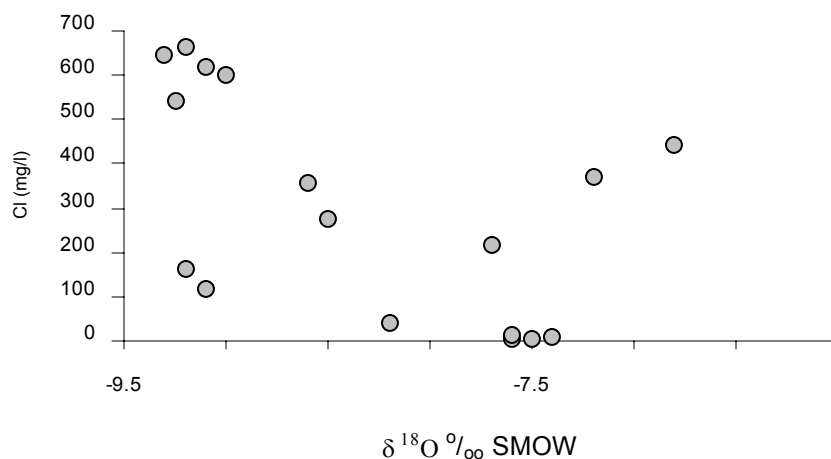


Figure 17-10: Cl versus $\delta^{18}\text{O}$ plot of the groundwater from selected wells and the spring water.

this temperature reduction might cause a reduction in $\delta^{18}\text{O}$ isotope values of the rainfall during the last glacial maximum by about 3 to 5 ‰ SMOW for our study area. If we add this conversion to our lone rainfall value, the $\delta^{18}\text{O}$ value of the rainfall in the last glacial maximum could have been about -6.2 ‰ SMOW. If we apply this conversion to the Chihuahuan samples, we observe that $\delta^{18}\text{O}$ isotope values in the rainfall during the last glacial maximum could well range from about -6 to -20 ‰. These values are within the range of values observed in the groundwater and spring water samples from our study area. A plot of Cl versus $\delta^{18}\text{O}$ values indicates that the waters with higher Cl concentrations, an indicator of increased water-rock interaction and therefore increased residence time, show lighter $\delta^{18}\text{O}$ values (Figure 17-10). Cl versus $\delta^{18}\text{O}$ composition of the groundwater from wells west and northwest of the springs (6, 12, and 16), as well as the springs (1 and 5), clusters together in the plot indicating a common source. Although wells 13, 16, and 17 are located in close proximity, they show considerable differences in Cl but not in $\delta^{18}\text{O}$ values (Figure 17-10). Samples 13 and 17 have higher Na/Cl values than sample 16 indicating addition of Na through cation exchange. Most of the samples from the Davis Mountains have low Cl salinity and plot along the x-axis.

Tritium Isotopes

The bulk of the tritium ($\delta^3\text{H}$) isotopes was produced from atmospheric testing of nuclear bombs between 1951 and 1980. Most of the “bomb” tritium has been washed away leaving tritium levels in global precipitation closer to natural levels (Clark and Fritz, 1997). Only qualitative interpretations can be made from tritium isotopes due to mixing

with pre-bomb groundwater and the evolution of tritium due to its natural decay (Clark and Fritz, 1997).

Tritium isotope values of the samples range from 0 to 4.6 TU. The higher values occur in the Davis Mountains and in areas where the Jeff Davis, Culberson, and Reeves county lines meet. $\delta^3\text{H}$ concentrations in the groundwater from wells (3, 4, 8, and 9) in the Davies Mountains are 0, 0.24, 1.36, and 1.87 (respectively) indicating that the waters represent contributions from pre-1952 to a mixture of sub-modern and recent recharge. Further west, samples 10 and 15 contain much higher values (2.12 and 4.26 TU, respectively).

The spring waters (Phantom Lake and the San Solomon) and the rest of the groundwater samples west of the Delaware Mountains and the Apache Mountains have lower $\delta^3\text{H}$ values (~ 0) (Table 17-3) indicating that they are produced from pre-1952 recharge events. Thus, the considerable differences in the $\delta^3\text{H}$ values similarly identify two sources of water: one in the south from the Davis Mountains and the other from the Apache and the Delaware mountains.

The tritium isotope value of the lone rain sample collected from the rain gage at the rest stop on IH-10 in Pecos County is 2.92 TU. This value is somewhat lower than what could potentially be present in a modern rainfall, particularly when one groundwater sample has considerably more tritium than the rain sample. This depletion may indicate that much of the bomb tritium is slowly being washed away from the atmosphere. $\delta^3\text{H}$ values in the rainfall from the Chihuahuan desert GNIP station ranged from 7 to 17.5 TU in 1984.

Carbon isotopes

$^{13}\text{C}/^{12}\text{C}$ is a good tracer for determining open versus closed system evolution of the carbonate in the groundwater. This is because there are large differences between $^{13}\text{C}/^{12}\text{C}$ values in the soils and the carbonate matrix of the aquifer. Under an open system condition of an unconfined aquifer, $^{13}\text{C}/^{12}\text{C}$ in the groundwater approach the soil values (-15‰ PDB). However, under a closed system condition of a confined aquifer,

$^{13}\text{C}/^{12}\text{C}$ values commonly become heavier reflecting reactions with the aquifer matrix ($>-15\text{‰}$ PDB). Samples 3 and 4 have the most depleted $^{13}\text{C}/^{12}\text{C}$ values (Table 17-3). A cross-plot of the $^{13}\text{C}/^{12}\text{C}$ and the ^{14}C values indicates that $^{13}\text{C}/^{12}\text{C}$ progressively decreases with an increase in the ^{14}C pmC values (Figure 17-11). Therefore, we suggest that the depleted values (samples 3 and 4) reflect groundwater derived under shallow, unconfined conditions that retained the $^{13}\text{C}/^{12}\text{C}$ signatures of the soils. The heavier isotopes probably indicate increased carbonate reactions within the aquifer matrix due to their longer residence time.

^{14}C activity for the groundwater and the spring water samples range from 9.2 to 71.7 pmC (Table 17-3). Samples in the Davis Mountains (3, 4, and 8) have the maximum ^{14}C pmC values (71.7, 33.33, and 24.2, respectively). Samples 10 and 11, located along the Culberson/Reeves county line, also have higher ^{14}C pmC values (28 and 58.89,

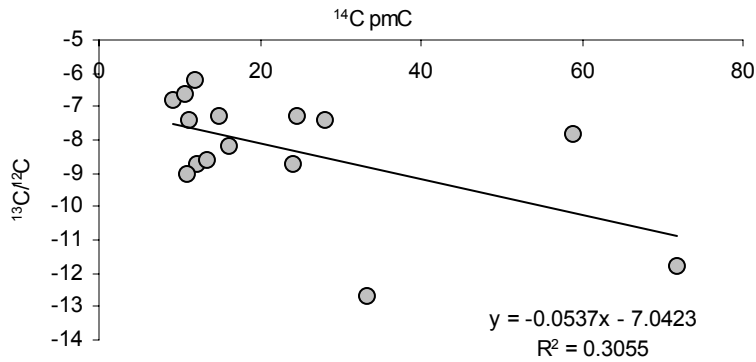


Figure 17-11: ^{14}C versus $^{13}\text{C}/^{12}\text{C}$ values of the groundwater from selected wells and the spring water.

respectively). The rest of the samples to the west and the northwest of the springs have lower ^{14}C pmC values (9.2 to 24.5).

The higher ^{14}C pmC and tritium values in the groundwater from the Davis Mountains confirm contribution of modern to sub-modern water. Groundwater samples from the west and the northwest and the spring water samples have lower ^{14}C pmC values, indicating their derivation from older paleogroundwater.

^{34}S isotopes

Sulfur compounds in the subsurface can occur in the form of sulfate and sulfide minerals, dissolved sulfate, dissolved sulfide, and hydrogen sulfide gas. Sulfur compound from these sources participate in the geochemical evolution of groundwater and contributes to groundwater salinization. Sulfur-34 is generally fractionated between sulfur compounds due to biological cycling. Values exceeding +20 ‰ CDT are found in association with evaporites and limestones. Permian CaSO_4 can have $\delta^{34}\text{S}$ values in the range of 11 to 23 ‰ CDT (Krouse, 1980). Negative $\delta^{34}\text{S}$ values are formed under diagenetic conditions where reduced sulfur compounds are formed (Krouse, 1980). The dissolution of gypsum or anhydrite occurs without measurable isotopic fractionation; therefore, isotopic compositions of SO_4 can be used as a tracer of the sulfate origin (Clark and Fritz, 1997). The $\delta^{34}\text{S}_{\text{SO}_4}$ values of the modern seawater have a composition of 21 ‰ CDT.

We analyzed for $\delta^{34}\text{S}_{\text{SO}_4}$ of the Phantom Lake and San Solomon spring waters and the groundwater from wells west and northwest of the springs. We observed that the $\delta^{34}\text{S}_{\text{SO}_4}$ values of the Phantom Lake springs, San Solomon spring, and sample 15 have identical values (+10 to +10.6 ‰ CDT). Samples 6, 16, and 17 have nearly identical values (~11 ‰ CDT). Sample 14 has a $\delta^{34}\text{S}_{\text{SO}_4}$ value of +3.2 ‰ CDT, and sample 7 has a value of +8.2 ‰ CDT. Most of the $\delta^{34}\text{S}_{\text{SO}_4}$ values indicate that they are derived from dissolution

of Permian evaporites. Samples 7 and 14 show slight depletion due to biogenic sulfate reduction.

Age dating

Tritium-free paleogroundwater (recharged at >50 years) can be dated for its age by ^{14}C isotopes. ^{14}C is derived from the decay of photo-synthetically fixed-carbon in the soil that reaches the groundwater either in the form of dissolved inorganic carbon (DIC) or dissolved organic carbon (DOC). The age dating method involves determination of the loss of radionuclide (^{14}C) in the sample assuming that the initial concentration of the parent is known and that no gains or loss occurred except through decay. The half-life of ^{14}C is about 5,730 years, and the effective dating range for groundwater is about 30,000 years (Clark and Fritz, 1997).

To determine the correct ^{14}C ages, we considered different age correction models to revise the apparent radiocarbon ages. Apparent radiocarbon ages do not account for the chemical reactions that may alter ^{14}C values: they only consider natural decay. The correction method incorporates various models used to resolve carbonate reactions effect on ^{14}C values (for example, alkalinity, statistical, ^{13}C -mixing, and matrix-exchange).

The alkalinity model uses a correction that incorporates the initial and the final dissolved inorganic carbon (DIC) concentration, which normally amounts to about 50 percent in the vast majority of the samples for closed system dissolution of calcite (Tamer, 1975). This is because most of the H_2CO_2 is consumed by limestone dissolution, and the original ^{14}C activity of the soil CO_2 gas is diluted by about 50 percent. We used this value for estimating alkalinity correction.

The statistical correction model assumes that, during infiltration of the water, some the ^{14}C -free carbon may dilute the ^{14}C activity. This value can be estimated statistically over the recharge area, which could act as the ^{14}C activity of the aqueous carbonate. Vogel (1970) presents the dilution values for different geologic systems (karst = 0.65-0.75, fine-grained carbonates = 0.75-0.90, and crystalline rocks = 0.90-1.00). We used the median value (0.7) for karst system as this may better represent the carbonate terrain of the study area.

The $\delta^{13}\text{C}$ -mixing model incorporates the ^{14}C -active DIC during open-system dissolution and its dilution under closed-system conditions, as is common in nature (Pearson and Hanshaw, 1970). However, the dilution factor is heavily weighted on pH-dependent enrichment between soil CO_2 and aqueous carbon in the recharge areas. We used a pH of 7 for calculating the dilution.

The matrix exchange model considers ^{14}C -enrichment between carbonate minerals of the aquifer matrix and the DIC (Fontes and Garnier, 1979). In this method, ^{14}C activity is apportioned between contributions from ^{14}C -free matrix and $^{14}\text{C}_{\text{DIC}}$ that exchanged with CO_2 in the soil and the carbonate matrix. The $\delta^{13}\text{C}$ isotope model and the matrix

exchange model consider open and closed system carbonate reaction that is more realistic to carbonate systems.

The corrected ages of the waters from the sampled wells and the springs are presented in Table 17-4 and Figure 17-12. The statistical and the alkalinity models assume simplified carbonate evolution with little carbonate reactions resulting in a lower dilution of ^{14}C . This results in ages that are closer to uncorrected ages. $\delta^{13}\text{C}$ -mixing model is highly dependent on the pH of the recharge water. Clark and Fritz (1997) show that when pH is varied from 6 to 7, it can result in differences in ages by about 50 percent. Estimating pH is complicated for paleowaters such as these. The matrix exchange model includes both carbonate dissolution and exchange and does not require specified input parameters. Thus, the corrected ages from the matrix-exchange model may prove to be better estimates for the actual ages of the waters.

Nearly all of the models considered show negative ages for well samples 3 and 11, indicating that the ages for these waters were overcorrected to the future (Table 17-4). These samples have high tritium and ^{14}C pmC values indicating contribution from modern to sub-modern waters.

Geochemical Modeling

Model runs involved speciation of the different elements, determining their saturation states, and exploring various mixing and dissolution/precipitation reactions. Saturation indices (SI) refer to the saturation states of the water with respect to a given mineral phase (Table 17-5; Plummer and others, 1996).

A mineral precipitates from the water if it is saturated ($\text{SI} > 0$) and dissolves when under-saturated ($\text{SI} < 0$). Saturation states of the waters with respect to the different mineral phases are presented in Table 17-5. Only four samples are saturated with respect to calcite, but the remainder of the samples are under near-saturation (< -0.3) except for samples 3, 4, 8, and 10. Samples 3, 4, 8, and 10 are also considerably under-saturated with respect to the rest of the minerals reported in Table 17-4. This level of under-saturation with respect to all mineral phases perhaps indicates that these waters were derived from recent recharge events.

Most of the samples are also under near-saturation conditions with respect to aragonite and dolomite, and only two samples (12 and 17) show near-saturation with respect to gypsum. Although one sample (16) is over-saturated with respect to fluorite, several samples (1, 5, 7, 9, 12, and 17) show near-saturation.

Table 17-4: Corrected ages of the sampled waters using various 14-C dilution models.

Sample Well ID	State Well Number	Measured ¹⁴ C DIC (pmc)	Unadjusted age* (¹⁴ C years)	Selected adjustment models			
				Statistical ¹ (Vogel, 1970)	Alkalinity ² (Tamers, 1975)	¹³ C Mixing model ³ (Pearson and Hanshaw, 1970)	Matrix-exchange ⁴ (Fontes and Garnier, 1981)
1	5202405	11.2	17,580	15,150	12,368	13,117	9,766
2	5201302	24.5	11,290	8,679	5,897	6,566	5,713
3	5202404	71.7	2,670	-198	-2,980	685	-2,256
4	5209501	33.3	8,830	6,142	3,360	7,513	4,392
5	5202611	14.8	15,360	12,846	10,064	10,733	10,918
6	4752602	9.2	19,200	16,776	13,995	14,252	14,190
7	4758505	10.7	17,950	15,528	12,746	12,832	10,896
8	5209303	24.2	11,410	8,781	5,999	7,721	5,569
9	5138803	16.2	14,630	12,099	9,317	10,678	8,450
10	4764401	28.01	10,220	7,572	4,790	5,539	5,165
11	4748701	58.89	4,250	1,429	-1,353	-293	-813
12	4759603	11.83	17,140	14,698	11,916	11,651	11,851
13	4718402	12.09	16,970	14,518	11,736	13,458	11,969
14	4755802	11.05	17,690	15,261	12,480	14,411	15,515
17	4717302	13.49	16,090	13,612	10,830	12,481	10,597

*Unadjusted age calculated using A₀ of 100 pmc and ¹⁴C half life of 5,730 years

¹¹⁴C remaining after dilution 0.7, median value for karst systems

²¹⁴C remaining is 0.5 percent as per carbonic acid dissolution of limestone

³pH = 7, enrichment for ¹³C_{DIC-CO2 (soil)} = 6

⁴¹³C of matrix carbonates = 3, ¹³C_{soil-CO2} = 21, and enrichment ¹³C_{CO2-CACO3} = -11.8

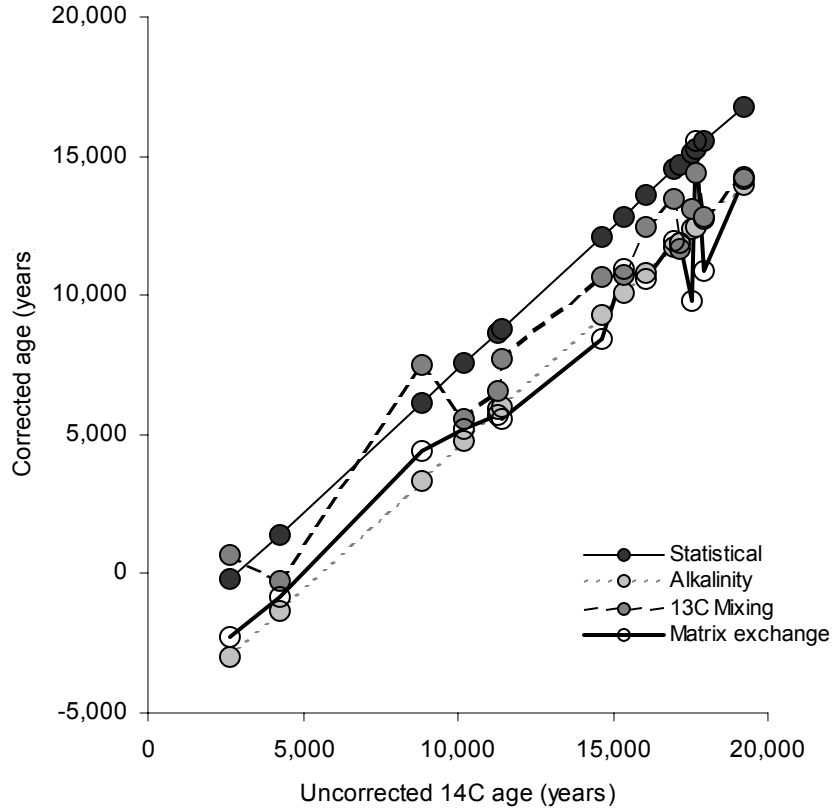


Figure 17-12 Plot showing uncorrected vs. corrected ages of the spring waters and the groundwater using different C-14 dilution models

We made several scenario runs to identify the best match between suspected source area groundwater composition and the spring-water composition using NETPATH (Table 17-6):

- 1) Flowpath I: Simulation includes groundwater samples from wells west of the Delaware, Apache, and Davis mountains (following solutions through well locations 17, 16, 6, 14, and 8);
- 2) Flowpath II: Simulation includes groundwater samples from wells in Wild Horse Flat and the Apache and Davis mountains with no contributions from the Delaware Mountains (following solutions through well locations 12, 6, 14, 10, and 8); and
- 3) Flowpath III: Simulation includes groundwater samples from wells west of the Delaware and from the Davis mountains with no contributions from the Apache Mountains (following solutions through well locations 17, 16, 14, 10, and 8).

Table 17-5: Saturation states of the waters with respect to different mineral phases. Subscript SI refers to the saturation states of each mineral phase where SI = IAP/KT, IAP = ion activity product, and KT = equilibrium constant.

Sample Number	Well Number	Calcite _{SI}	Aragonite _{SI}	Dolomite _{SI}	Gypsum _{SI}	Anhydrite _{SI}	Celestite _{SI}	Fluorite _{SI}
1	5202405	-0.12	-0.26	-0.24	-0.92	-1.14	-0.91	-0.24
2	5201302	-0.29	-0.44	-0.75	-1.13	-1.35		-1.4
3	5202404	-0.42	-0.56	-1.56	-2.48	-2.7	-3.13	-1.6
4	5209501	-0.82	-0.97	-2.32	-3.07	-3.29		-0.92
5	5202611	-0.13	-0.27	-0.29	-0.76	-0.98	-0.81	-0.44
6	4752602	-0.19	-0.34	-0.32	-0.82	-1.04	-0.83	-0.67
7	4758505	0.016	-0.13	-0.001	-0.91	-1.14	-1.86	-0.22
8	5209303	-0.91	-1.05	-1.84	-2.19	-2.41	-1.93	-2.27
9	5138803	0.005	-0.14	-0.79	-1.52	-1.74	-2.45	-0.1
10	4764401	-0.86	-1	-1.82	-2.54	-2.75	-1.64	-1.2
11	4748701	-0.15	-0.29	-0.38	-1.01	-1.234	-0.54	-0.56
12	4759603	0.13	-0.014	-0.05	-0.22	-0.44	-0.66	-0.4
13	4718402	-0.2	-0.34	-0.27	-0.97	-1.19	-0.96	-1.28
14	4755802	-0.04	-0.18	-0.07	-0.97	-1.19	-0.63	-0.83
15	4755401	0.09	-0.05	0.37	-0.86	-1.08		-0.61
16	4726101	-0.035	-0.179	-0.31	-0.68	-0.91	-1.15	0.06
17	4717302	-0.17	-0.31	-0.57	-0.29	-0.51		-0.27

We used the same ion, isotopic, and phase constraints in all the above simulations. We used Ca, ¹³C, ¹⁴C and ³⁴S, calcite, and gypsum as constraints unless otherwise stated. We allowed dissolution and precipitation of both calcite and gypsum to occur.

Results of the above simulations along flowpaths I, II, and III are presented in Table 17-6. Flowpath I includes groundwater from west of the Delaware Mountains (17 and 16), the Apache Mountains (6), and the Davis Mountains (8). Simulation results for Flowpath I indicate that about 14 percent of the spring water could probably be derived from the Delaware Mountains, 73 percent from the Apache Mountains, and 13 percent from the Davis Mountains. This simulation closely reproduces measured $\delta^{13}\text{C}$, ^{14}C , and $\delta^{34}\text{S}$ values of the Phantom Lake spring water.

Flowpath II includes groundwater from Wild Horse Flat (12), the Apache Mountains (6), and the Davis Mountains (8). Simulation results for Flowpath II suggest that about 5 percent of the spring water could probably be derived from Wild Horse Flat and the remainder from the Apache Mountains with no contribution from the Davis Mountains. This simulation produces $\delta^{13}\text{C}$, ^{14}C , and $\delta^{34}\text{S}$ values that do not closely match to the measured values of these isotopes from the Phantom Lake spring water.

Table 17-6: NETPATH geochemical modeling results showing mixing proportions of well waters necessary to match the Phantom Lake spring water composition.

Model	Groundwater Mixing to Yield Phantom Lake Spring Water Composition ¹									¹³ C ‰ PDB		C-14 (percent modern carbon)		³⁴ S ‰ CDT	
	Well 17	Well 16	Well 14	Well 12	Well 10	Well 8	Well 6	computed	measured	computed	measured	computed	measured	computed	measured
Flowpath I	0.1	0.04	0.31			0.13	0.42	-7.71	-7.4	11.67	11.2	9.25	10.6		
Flowpath II			0.25	0.05	0.08	0	0.62	-7.51	-7.4	16.24	11.2	5.69	10.6		
Flowpath III	0.27	0.12	0.52		0.1	0		-7.61	-7.4	12.76	11.2	8.43	10.6		

¹fields left blank indicate that these wells were not included in that specific simulation

Flowpath III includes water from west of the Delaware Mountains (17 and 16), northern and eastern flanks of the Apache Mountains (14 and 10), and the Davis Mountains (8). Simulation results for Flowpath III suggest that about 39 percent of the spring water could probably be derived from the Delaware Mountains and 61 percent from the Apache Mountains with no contribution from the Davis Mountains. This simulation produces $\delta^{13}\text{C}$, ^{14}C , and $\delta^{34}\text{S}$ values that do not agree with measured values from the Phantom Lake spring water.

The simulation for Flowpath I includes all components of groundwater from the Delaware, Apache and the Davis Mountains; and the computed values closely match the measured $\delta^{13}\text{C}$, ^{14}C , and $\delta^{34}\text{S}$ values of the Phantom Lake spring water. Given our conceptualization of the flow system, where water could potentially flow from these three areas to the springs, we suggest that the spring waters were probably derived along Flowpath I.

Discussion

Based on the water-quality information alone, two different source areas of the spring waters (Phantom Lake, San Solomon, and East Sandia springs) can be identified. We observed that the Na/Cl ratios of the Phantom Lake, San Solomon, and East Sandia springs are nearly identical (0.63, 0.63, and 0.70, respectively). SO_4/Cl ratios are also considerably lower in the Phantom Lake, San Solomon and East Sandia springs (0.69, 1.09, and 1.08, respectively) than the rest of the samples. This compositional trend is in sharp contrast to the fresh waters derived from wells sampled (3, 4, 9, and 10) down-dip from the Davis Mountains. The Na/Cl and SO_4/Cl ratios clearly indicate that the spring waters derived most of the minerals from dissolution of halite and gypsum. In the shallow subsurface between the springs and the Davis Mountains, no gypsum or halite deposits occur (White and others, 1941), which precludes the Davis Mountains to be a dominant source area for the spring waters under any regular steady-state conditions.

Isotopic information from the springs and the groundwater wells from the Apache Mountains and west of the Delaware Mountains indicate these areas to be part of the provenance of the springs. $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values of the groundwater samples from the Davis Mountains wells are more enriched, indicative of modern to sub-modern groundwater. $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values of the rest of the samples west of the Delaware Mountains and in the Apache Mountains indicate that recharge occurred under a humid climate during the late Pleistocene period. Tritium and C-14 values also support a similar conclusion, consistent with our water chemistry interpretation. Isotopic data suggest that the waters from the Davis Mountains are much younger, but the rest of the samples to the west and northwest of the springs are about 10,000 to 16,000 years old. S-34 data suggest that the spring waters were derived from dissolution of gypsum, as much of the sulfate bore characteristic isotopic signatures of Permian evaporites that occur in the Apache Mountains and west of the Delaware Mountains.

From our detailed investigation, we can conclude that the elemental and isotopic compositions between the springs and wells from areas in the Apache Mountains and west of the Delaware Mountains are similar. However, is this sufficient to suggest that these waters could find a fault zone conductive enough to bring them to the spring? We observe that several northwest-southeast trending faults occur in this area that could potentially act as pathways. These waters also lie at an elevation higher than the elevation at the springs. Water-level data also indicate that the area is only weakly disconnected hydraulically from areas further south in the Salt Basin and that the groundwater divides may not exist in the deeper units below the Salt Bolson. Also, if these waters were recharged under a humid climate as evidenced from isotope data, a higher rate of infiltration may have more favorably altered the current potentiometric surface to allow groundwater flow through the fault conduits to the springs. Geochemical modeling supports that the final water composition in the springs can be achieved if groundwater from the western edges of the Delaware Mountains and the Apache Mountains flowed southeast towards the springs.

Based on the above lines of evidence, we suggest that groundwater from west of the Delaware Mountains follows the fault zones and mixes with the waters from the Apache Mountains to reach the springs under a baseline condition when no flash flood events occur. During intense rainfall events, which are rather rare on a historic scale, changes occur to the traditional supply source when the spring waters may temporarily receive much of their flow from the Davis Mountains.

Conclusions

Based on our hydrochemical analyses, we conclude that:

- 1) Two sources of water were identified in the study area—one derived from the south in the Davis Mountains and the other from the Apache Mountains and west of the Delaware Mountains. A significant component of discharge from the Davis Mountains probably fails to reach as far down as Phantom Lake or San Solomon springs unless excess local recharge occurs during intense rainfall events.
- 2) Groundwater from wells in the Davis Mountains is mainly composed of Ca, Na-HCO₃ types, and the groundwater from the wells in the Apache Mountains and west of the Delaware Mountains is mainly Na-Cl-SO₄ types. Na/Cl, SO₄/Cl, Ca, and SO₄ concentrations support that groundwater from the west and northwest was derived from dissolution of halite and gypsum (Permian evaporites and limestone) while the groundwater from the south in the Davis Mountains is fresh with little salinity.
- 3) $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values indicate that groundwater from the west and northwest were recharged under a humid climate, possibly during late Pleistocene times.
- 4) Groundwater from the Davis Mountains has higher concentrations of tritium, ¹⁴C pmC, and ¹³C/¹²C, suggesting contribution from modern to sub-modern waters probably derived at shallow depth. Most of the waters from the west and northwest of

the Apache Mountains and the spring waters have depleted tritium, low ^{14}C pmC, and heavier $^{13}\text{C}/^{12}\text{C}$ values, suggesting that they were derived from a deeper, older paleogroundwater system. $\delta^{34}\text{S}$ of the gypsum indicates that groundwater from the west and the northwest was derived from Permian evaporites.

- 5) NETPATH geochemical modeling indicates that a substantial portion (~80 percent) of the spring water could probably be derived from as far as the Apache Mountains and west of the Delaware Mountains with only minor contributions from the Davis Mountains.

Acknowledgments

We would like to thank Doug Coker for groundwater sampling, Ian Jones for review and comments, and the U.S. Fish and Wildlife Service and Texas Parks and Wildlife Department for partial funding of this project.

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