

Tracing regional flow paths to major springs in Trans-Pecos Texas using geochemical data and geochemical models

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Abstract

San Solomon, Giffin, and Phantom Lake Springs, located in Trans-Pecos Texas, have a high TDS, Na–Cl–SO₄ baseflow component derived from a regional flow system and a low TDS, mixed cation–mixed anion stormflow component derived from local precipitation events. The hypothesis that the regional flow system maintaining baseflow spring discharge originates in the Salt Basin and flows through the Apache Mountains towards the springs is tested with historical geochemical data from wells and springs. Data from over 1400 wells in the study area over a 50-year period were analyzed and used to delineate 11 hydrochemical facies based on the predominant ions.

Geochemical data from samples along the hypothesized regional flow path indicate a trend of increasing dissolved solids and Cl–HCO₃ ratios and decreasing Na–Cl ratios. These are consistent with evolution of groundwater in an unconfined regional system dominated by carbonates and evaporites. In the bicarbonate facies, the waters represent recent recharge modified by mineral dissolution and cation exchange. In the sulfate zones, the hydrochemical facies are controlled by gypsum, anhydrite, and halite dissolution, cation exchange, and mixing with Na–Cl waters. In the chloride zones, the hydrochemical facies are controlled by halite dissolution and irrigation return flow. Spring discharge chemistry is most similar to chloride zone waters; Na–Cl and Ca–SO₄ ratios suggest that baseflow is derived from the chloride zone waters upgradient along the hypothesized flow path.

PHREEQC modeled groundwater evolution along the hypothesized flow path and spring discharge under stormflow and baseflow conditions. Results indicate that: (1) hydrochemistry along the regional flow path is controlled by dissolution of halite, gypsum, dolomite, and CO₂ and by precipitation of calcite; (2) baseflow spring discharge is derived primarily from this regional flow system; and (3) spring discharge after major storm events can constitute as much as 72% local recharge that is further modified by dissolution of calcite, gypsum, and CO₂. Data analysis and model results suggest that cave formation in this system is occurs during major storm events. © 2001 Published by Elsevier Science B.V.

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1. Introduction

Trans-Pecos Texas is the area of Texas west of the Pecos River (Fig. 1). This is a subtropical arid climate region (Larkin and Bomar, 1983) with an average annual rainfall of 30 cm (Schuster, 1996). Surface water resources are rare, so the region is

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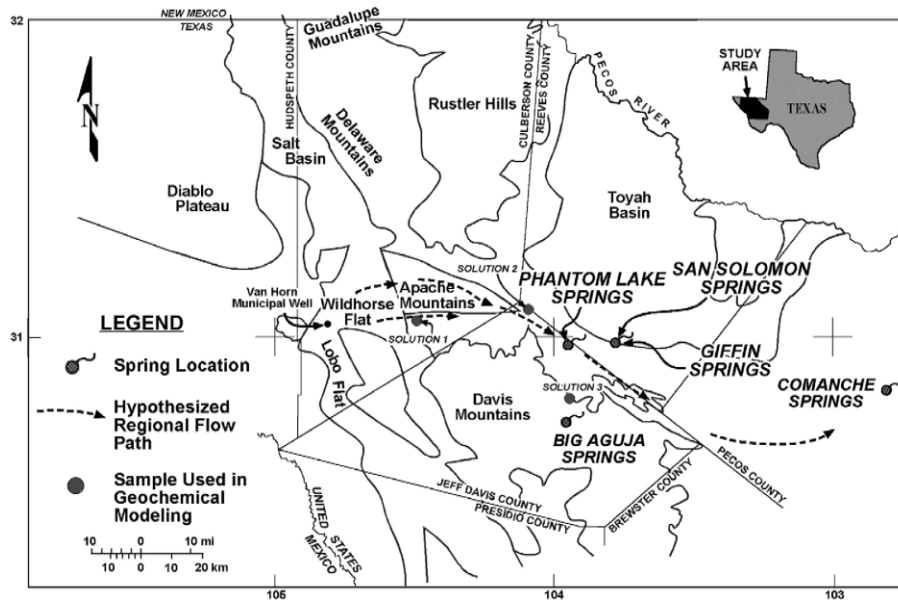


Fig. 1. Map of Trans-Pecos Texas showing the major physiographic features and locations of major springs. The dashed arrows indicate the hypothesized regional flow path. Solutions 1, 2, and 3 are locations of samples used for geochemical modeling (simplified from Barnes, 1976, 1979, 1995a,b).

almost exclusively dependent on groundwater to meet municipal and agricultural needs.

Usable surface water discharges from several springs located in Reeves, Pecos, and Jeff Davis Counties (Fig. 1). The springs include San Solomon and Giffin Springs, located in the village of Toyahvale, and Phantom Lake Springs, located at the Kingston Ranch in Jeff Davis County. Comanche Springs, located in the city of Fort Stockton, TX, ceased to flow in the 1960s and now only discharge irregularly and at very low rates. Numerous minor springs, such as Big Aguja Springs, occur in the Davis Mountains to the south.

Flow and geochemical data provide evidence for a mixed source at the springs. San Solomon, Giffin, and Phantom Lake Springs respond to local precipitation events with increases in discharge and turbidity, indicating that they are fed by a local flow system (Brune, 1981). Under baseflow conditions spring flow maintains consistent temperatures (25–26°C) and high total dissolved solids concentrations (TDS) (~2000 mg/l) suggesting a regional flow component. Groundwater heads (Fig. 2) suggest that groundwater in the Wildhorse Flat section of the Salt

Basin is flowing out of the basin through the permeable reef facies limestones of the Apache Mountains towards the springs and into the Toyah Basin. Neilson and Sharp (1985) used water balance calculations and modeling results to show that water discharges from Wildhorse Flat into the Apache Mountains. Discharge from San Solomon and Giffin Springs has remained relatively constant over the period of record. In contrast, Phantom Lake Springs have exhibited a decline in discharge and, for the first documented time, ceased to flow in February of 1998 (Sharp et al., 1999). There was not, however, a corresponding decline in local precipitation and recharge.

Groundwater chemistry data, collected and archived by the Texas Water Development Board (TWDB) over the last 50 years, test the hypothesis that discharge from San Solomon, Giffin, and Phantom Lake springs is partially sourced from a regional flow system (Fig. 1). Over 2800 sampling records were reduced to a set of composite records that characterize the distribution of hydrochemical facies based on the predominant ions. These data also trace chemical changes along the hypothesized flow path.

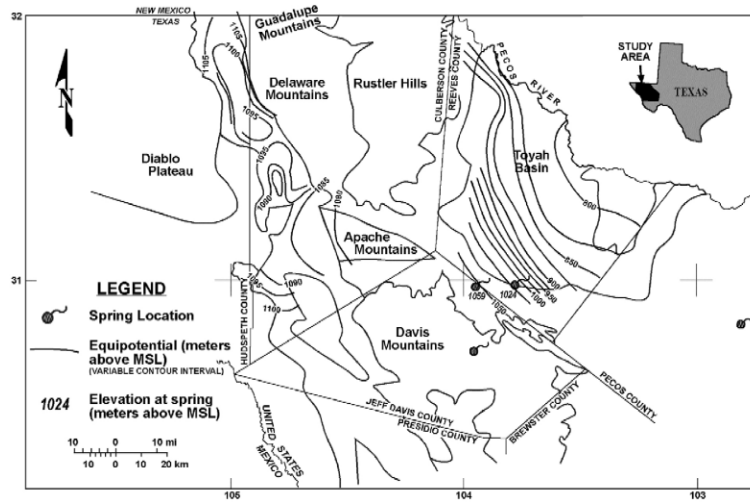


Fig. 2. Pre-development groundwater heads in Trans-Pecos Texas (modified from Sharp, 1989).

Geochemical models developed with the program PHREEQC (Parkhurst et al., 1980; Parkhurst, 1995) identify reactions that may explain the observed

groundwater chemistry and estimate percentages of spring discharge derived from regional flow system and local recharge.

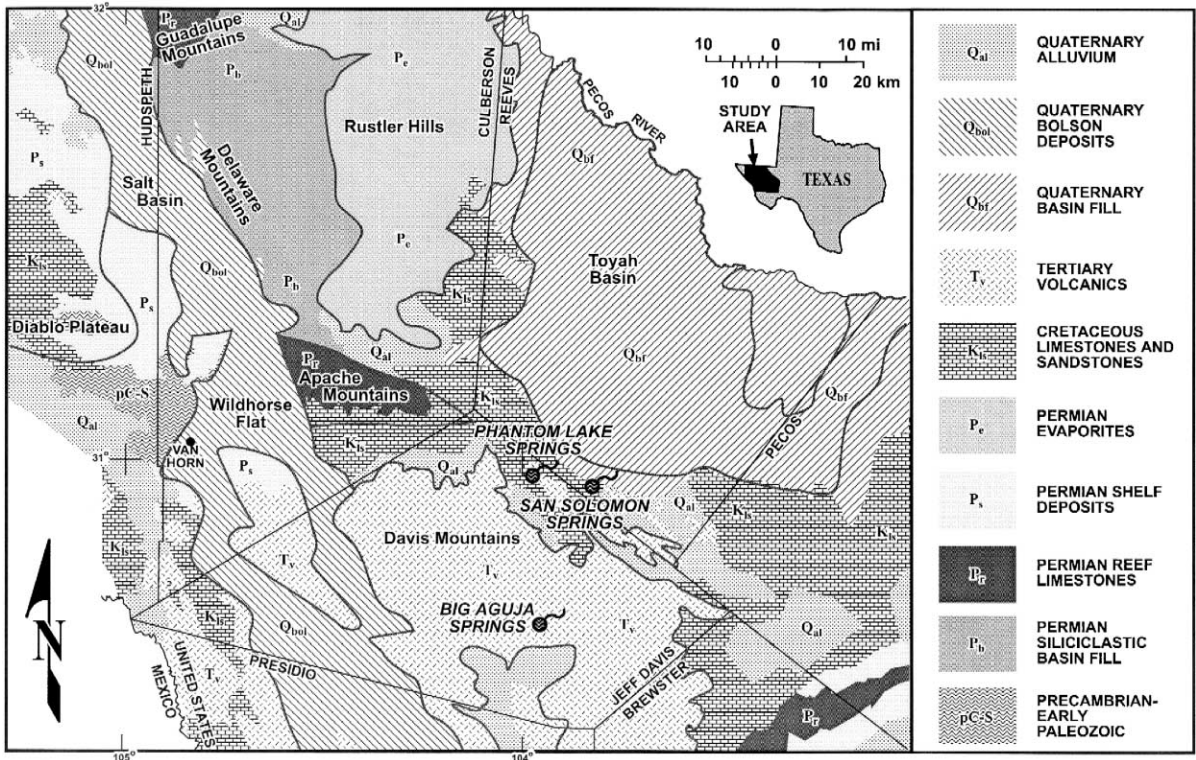


Fig. 3. General regional geology of the study area (simplified from Barnes, 1976, 1979, 1995a,b).

2. Physiography and geology

Trans-Pecos Texas lies within the Basin and Range physiographic province. Ground elevation ranges

from about 700 m (2300 ft) above sea level (ASL) along the Pecos River to 2667 m (8751 ft) ASL at Guadalupe Peak in the Guadalupe Mountains. The Apache and Guadalupe Mountains are portions of

Table 1

Chemistry data from spring samples and the Van Horn Municipal Well

The Van Horn Municipal Well is located in Wildhorse Flat and represents the upgradient end of the hypothesized flow system.

All units are in mg/l unless otherwise noted.

Date	Ca	Mg	Na	K	Sr	HCO ₃	SO ₄	Cl	F	NO ₃	Temperature (°C)	pH	Specific conductance (µmho/cm)	TDS	Calcite SI
<i>Phantom Lake Springs (State Well # 52-02-405)</i>															
10/28/30	191	86	453	20.0		285	691	655		0.6	26.0			2255	0.00
9/12/32 ^a	81	27	139			170	205	186		1.4	22.0			722	-0.47
10/27/40	182	87	468			253	672	636		1.0			3410	2185	-0.08
1/14/41	193	86	470			282	687	646		0.8			3510	2221	-0.02
1/30/41	193	87	458	30.0		282	689	646	0.8	0.5	25.0		3500	2260	-0.02
5/14/41	190	83	614			269	633	900		0.8			3220	2553	-0.05
10/15/47	191	90	451			230	692	650		1.0			3560	2188	-0.11
1/28/50	187	95	473			282	695	660		0.2		7.40	3410	2264	0.36
6/6/69	182	72	456			207	670	640	2.1	0.4	26.0	7.70	4320	2143	0.54
4/28/71	192	91	467	1.9		278	680	650	2.2	0.4	26.0	7.40	4400	2237	0.38
3/27/87	205	70	467	20.0		277	674	647	1.7	1.0		7.90	4316	2239	0.89
10/31/90 ^a	105	30	163	13.0	1.7	209	267	247	0.9	6.1	23.0	7.26	1530	966	-0.04
3/28/98 ^b	183	83	453	22	3.6	321	650	619			25.4	7.18	3600	2287	0.21
<i>San Solomon Springs (State Well # 52-02-611)</i>															
10/28/30	190	80	432	16.0		286	651	610		0.1				2138	-0.01
9/13/32 ^a	102	35	200			264	270	238						974	-0.19
1/30/41	184	78	405	18.0		284	612	570	0.5	1.0			3120	2031	-0.02
10/15/47	168	81	402			156	638	590		2.1			3290	1957	-0.31
1/28/50	179	90	421			273	635	600		1.1		8.10	3180	2079	1.02
7/10/69	192	87	429			282	650	600	2.0	0.4		7.80	4185	2119	0.78
7/15/70	197	87	434			279	680	640	2.2	0.4		7.40	4309	2198	0.39
4/14/90	185	75	440	24.0	4.3	284	650	628	1.7	1.2	26.0	7.29		2169	0.28
11/1/90 ^a	99	23	133	12.0	1.4	247	213	178	1.1	7.3	21.0	7.20	1298	827	-0.05
3/27/98 ^b	177	78	420	20	3.3	275	621	587			24.7	7.2	3520	2015	0.15
<i>Giffin Springs (State Well # 52-02-610)</i>															
12/6/30	189	80	437			284	635	608						2088	-0.01
7/10/69	186	86	433			277	660	600	2.1	0.4		7.90	4185	2121	0.85
5/29/90	186	79	463	25.0	3.8	275	679	628	1.7	0.9				2221	-0.04
11/1/90 ^a	114	30	166	13.0	1.7	233	269	245	0.9	7.2	23.0	6.90	1550	990	-0.31
<i>Big Aguja Springs (no state well #)</i>															
3/27/98 ^b	42	5	22	3.7	0.2	197	7	7		1.2				285	-0.50
<i>Comanche Springs (no state well #)</i>															
3/27/98 ^b	256	113	358	14.9	5.8	322	881	512		23.2				2495	0.14
<i>Van Horn Municipal Well (State Well # 47-58-505)</i>															
1/11/65	19	7	122			255	81	21	3.10	8.0		8.00	681	386	0.19
3/27/98 ^b	20	9	121	7.3	0.4	261	77	46		9.9				554	-0.77

^aData in italics represents samples influenced by recent storm events.

^b1998 samples analyzed at the University of Texas (all other samples are from Texas Water Development Board).

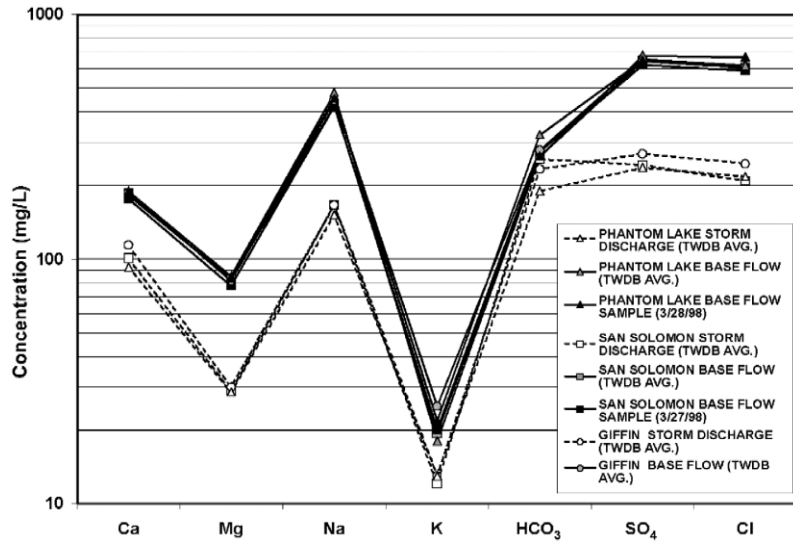


Fig. 4. Schoeller diagram of samples from San Solomon, Giffin, and Phantom Lake springs. Dashed lines and open symbols represent samples influenced by recent local precipitation.

the reef that circled the Late Permian Delaware Basin (Fig. 3). The Delaware Mountains consist of Mid- to Upper Permian (Leonardian–Guadalupian) limestones and sandstones deposited in the Delaware Basin. The Rustler Hills are primarily evaporites (gypsum and anhydrite) that were deposited after the Delaware Basin was cut off from the ocean in the Late Permian. The evaporites dip to the east and are

present at depth in Reeves and Pecos counties. Lower Cretaceous limestones overlie the Permian rocks south and east of the Apache Mountains. Cretaceous rocks crop out to the south and east of the Apache Mountains along the Reeves–Jeff Davis county line and in Pecos County. The Davis Mountains consist of Eocene to Oligocene lava flows and ash-flow tuff deposits that overlie Cretaceous rocks in Jeff Davis

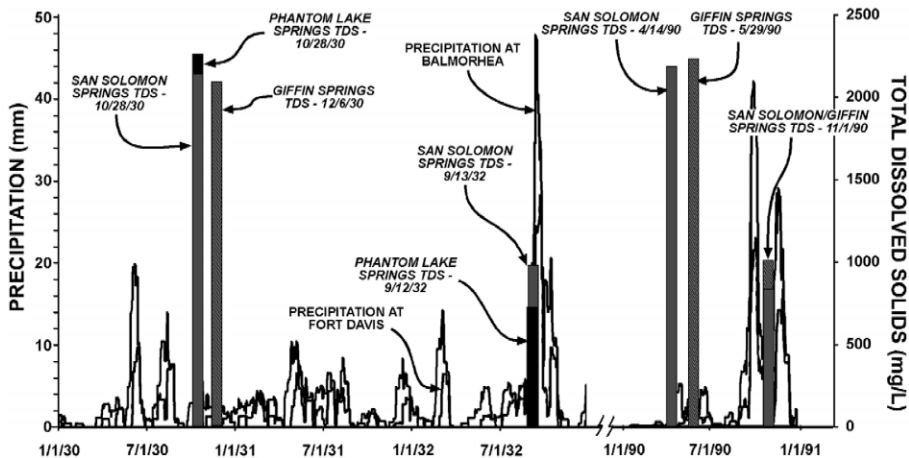


Fig. 5. Graphs of local precipitation (solid lines) and spring discharge TDS (columns). Low TDS values in spring discharge are associated with major precipitation events.

County. Cretaceous limestones in the Toyah Basin are overlain by a thick sequence of Cenozoic alluvium that is up to 470 meters (1500 ft) thick in the center of the basin (Ashworth, 1990). The alluvial sediments filling in the Salt Basin graben reach a thickness of over 750 m (2400 ft) (Gates et al., 1980).

3. Geochemical data

Two sets of water chemistry data were analyzed: a set of historical data obtained from the TWDB and a set of samples collected by the authors in 1998. Both data sets are described below.

3.1. Historical data

Water chemistry data from over 2800 records from wells and springs in the study area were obtained from the TWDB. A record refers to all the data from a single sampling event; a field refers to a specific type of data (e.g., Ca^{2+} concentration, pH, temperature, etc.) within a record. The data fields in each record include state well number (a unique well ID), TDS, pH, water temperature, specific conductance, cation (Ca^{2+} , Mg^{2+} , Na^+ , K^+ , Sr^{2+}) concentrations, and anion (HCO_3^- , SO_4^{2-} , Cl^- , F^- , NO_3^-) concentrations. Each record also includes well location coordinates (in latitude and longitude) and an aquifer code that identifies the hydrostratigraphic unit in which the well is completed. From 1402 wells, 1621 of these records have balanced analyses (charge balance < 5%) and complete values for the primary cations (Ca^{2+} , Mg^{2+} , and Na^+) and anions (HCO_3^- , SO_4^{2-} , and Cl^-). Only these records were used in the following analyses.

3.2. Spring water quality

Samples taken in March of 1998 from San Solomon Springs, Phantom Lake Springs, Big Aguja Springs, Comanche Springs, and a municipal supply well in the town of Van Horn were analyzed for major cations and anions. Cation analyses were performed at the University of Minnesota, Department of Geology and Geophysics by ICP-MS. Anion analyses were performed at The University of Texas at Austin using Ion Chromatography. These results are

presented in Table 1 with comparable analytical results from the TWDB database.

These data show that San Solomon, Giffin, and Phantom Lake Springs have similar major ion compositions (Fig. 4). Most of the samples have TDS values that range from 2000 to 2300 mg/l; however, samples taken on September 12, 1932 and November 1, 1990 have TDS values of 800–1000 mg/l. The 1932 and 1990 samples were associated with large precipitation events and may represent stormflow conditions influenced by local recharge to the system

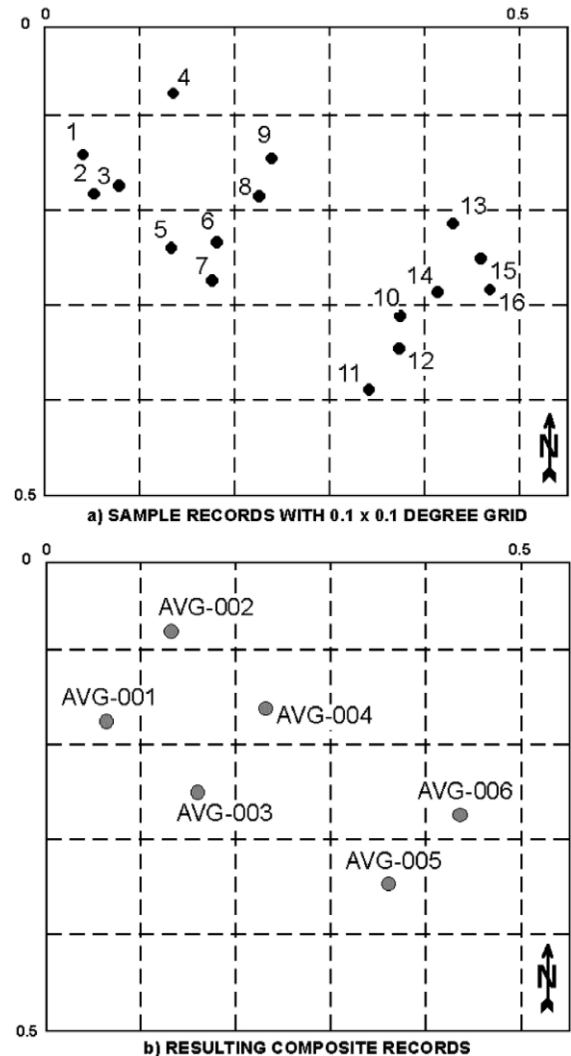


Fig. 6. Schematic diagram illustrating the reduction of the sampling data to a set of composite records.

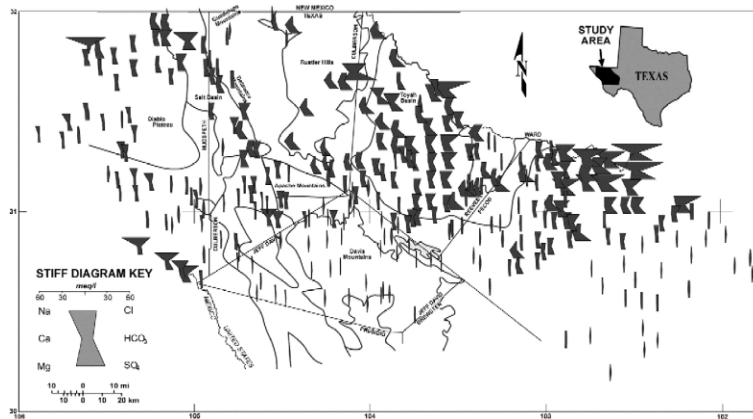


Fig. 7. Map of composite record stiff diagrams illustrating regional variations in groundwater chemistry (base map from Barnes, 1976, 1979, 1995a,b).

(Fig. 5). Higher TDS samples are correlated with baseflow conditions and may represent discharge from the hypothesized regional system (Fig. 5). LaFave (1987) examined the 1932 spring discharge rate and chemistry data and calculated that 73% of spring discharge during the storm was related to local storm recharge.

4. Data reduction methods

The methods of data reduction, area distributions and averaging of the data, predominant ion classifications, and delineation of the predominant anion zones are discussed below. The 1621 balanced records were reduced to a set of 295 composite

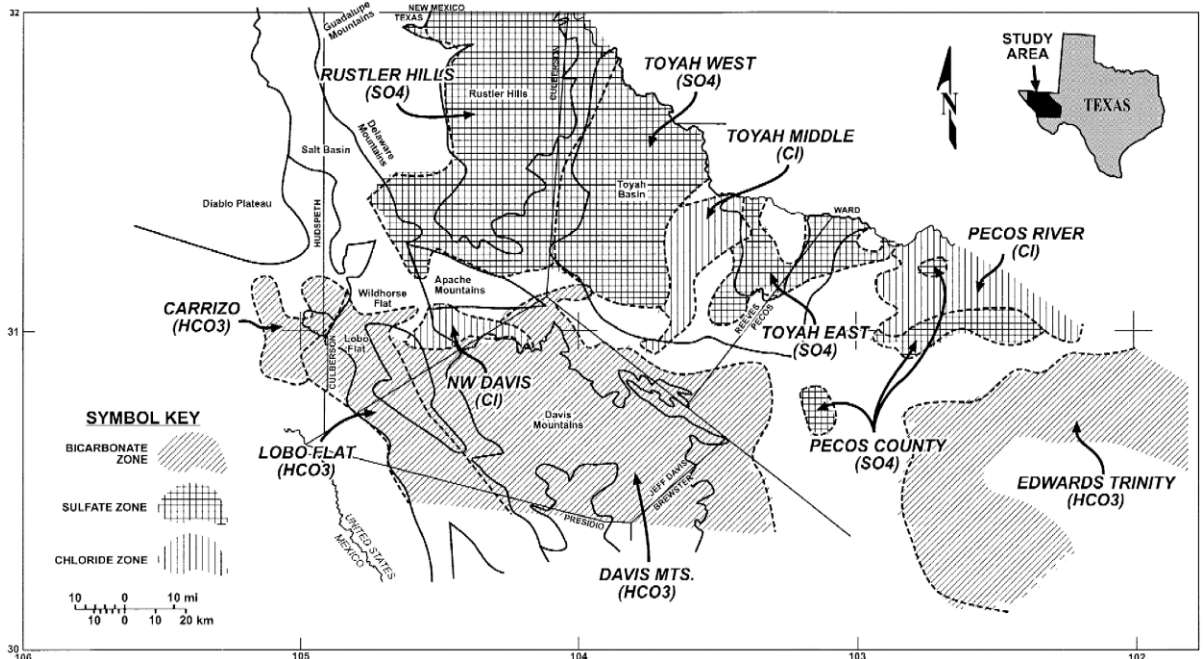


Fig. 8. Map of predominant anion zones and hydrochemical facies (base map from Barnes, 1976, 1979, 1995a,b).

Table 2
Hydrochemical facies shown on Fig. 8

Hydrochemical facies name	Predominant cation–anion
Lobo Flat	Na–HCO ₃
Carrizo	mixed-HCO ₃
Davis MTS	Ca–HCO ₃
Edwards Trinity	Ca–HCO ₃
Rustler Hills	Ca–SO ₄
Toyah West	Na–SO ₄ and mixed-SO ₄
Toyah East	Ca–SO ₄
Pecos County	Ca–SO ₄ and mixed-SO ₄
NW Davis	Na–Cl
Toyah Middle	mixed-Cl
Pecos River	Na–Cl

records by grouping and averaging sets of records within 0.1° longitude by 0.1° latitude grid cells (Fig. 6). A Stiff diagram was plotted for each composite record on Fig. 7 to display the regional variations in groundwater chemistry.

Composite records were classified based on the predominant ions of the three major cations (Ca²⁺, Mg²⁺, and Na⁺) and three major anions (HCO₃⁻, SO₄²⁻, and Cl⁻). The predominant ion is the ion with the greatest concentration (in meq/l), providing that the concentration is greater than 50% of the sum of the major ions. Records were classified as ‘mixed’ if the ion with the greatest concentration was less than 50% of the sum of the concentrations of the major ions. These classification numbers were plotted at the composite records locations. Zones containing samples with similar predominant anions were delineated on the map with hatch patterns. From these predominant anion zones, 11 specific hydrochemical facies (Back, 1961) were defined (Fig. 8, Table 2).

5. Data analysis

Below we discuss the analyses of geochemical trends along the hypothesized flow path and the areal distribution of geochemical data using Stiff diagrams, anion zones, and spring discharge chemistry.

5.1. Geochemical trends along the hypothesized regional flow path

A set of 251 sample records along the hypothesized regional flow path (Fig. 1) was selected. Con-

centrations of total dissolved solids, Ca²⁺, Mg²⁺, and SO₄²⁻ were plotted versus their position along the flow path (Fig. 9A,B,C and D). Fourth-order polynomial regression lines fit to the data on each plot indicate that these parameters follow a general trend that suggests that TDS and specific ion concentrations increase along the flow path from Van Horn to San Solomon and Phantom Lake Springs. Beyond these springs along the flow path, concentrations decrease to reach a local minimum at the Reeves–Pecos County line and then increase towards Comanche Springs to reach concentrations similar to those at San Solomon and Phantom Lake Springs.

Increasing dissolved constituents along the hypothesized flow path from Van Horn to San Solomon and Phantom Lake Springs is consistent with the trend expected from water evolving along a flow path (Chebotarev, 1955; Mifflin, 1968). The variability in the data (i.e., deviations from the trendlines) represents local recharge at various points along the flow path. Down gradient from the springs, lower TDS water indicates an area receiving a significant amount of local recharge, most likely originating in the Davis Mountains. This may represent a local flow system from the Davis Mountains mixing with water in the regional flow systems as it flows towards Comanche Springs. An alternate explanation is that the overall trend represents two separate flow systems—one originating in the Salt Basin and flowing to San Solomon and Phantom Lake Springs and eventually to the irrigation wells in the Toyah Basin, and a second originating in the Davis Mountains and flowing towards Comanche Springs.

Ratios of Cl–HCO₃ and Na–Cl concentrations were calculated for each sample and plotted versus location on the hypothesized flow path (Fig. 9E and F). The samples near the Van Horn Municipal Well have low Cl–HCO₃ values. This ratio increases along the flow path towards San Solomon and Phantom Lake Springs, follows a decreasing trend beyond San Solomon and Phantom Lake Springs, and then increases along the flow path towards Comanche Springs. The Cl–HCO₃ trend is similar to the trends on graphs 9A, 9B, 9C and 9D; with increasing ratios between Wildhorse Flat and San Solomon and Phantom Lake Springs suggesting the evolution of groundwater. The lower ratios along the flow path beyond San Solomon and Phantom Lake Springs

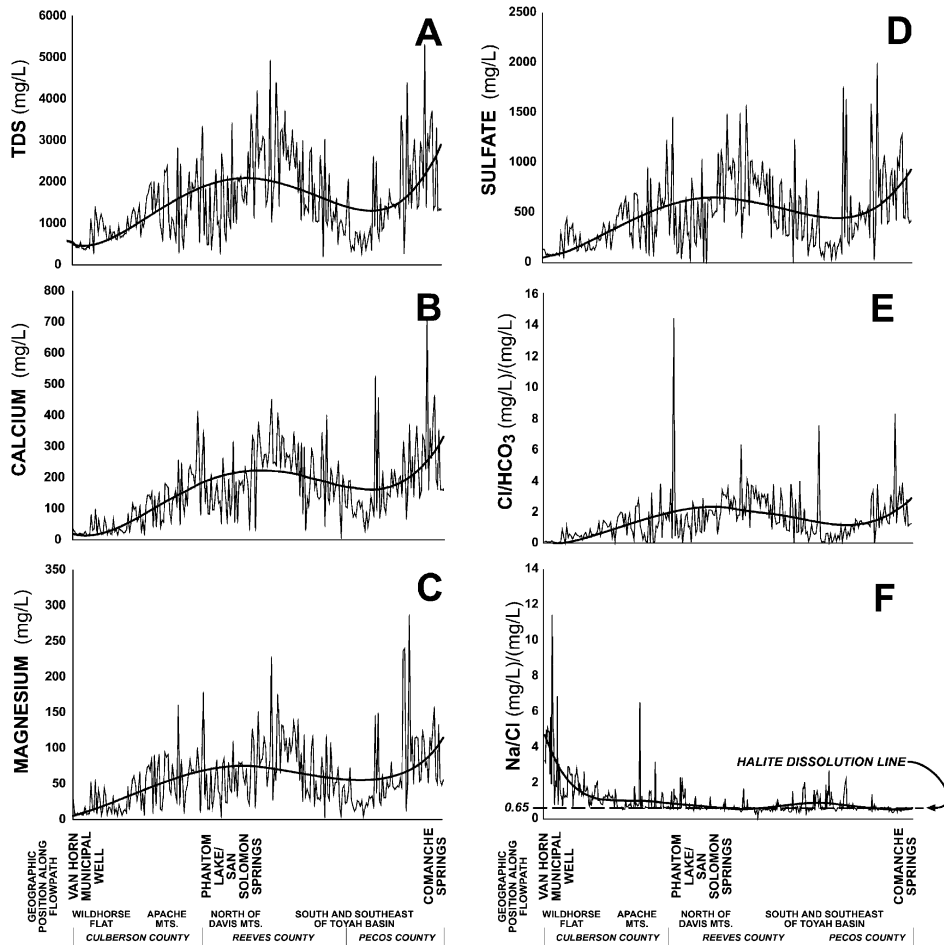


Fig. 9. Graphs of geochemical parameters and ion ratios plotted against position along the hypothesized regional flow path. Curves fit to the data are polynomial trendlines; these lines illustrate the overall trends within the variability of the data.

probably represent an influx of recharge originating in the Davis Mountains.

Samples near the Van Horn Municipal Well have high Na–Cl values (up to 11.5) that decrease along the flow path (Fig. 9F). A polynomial regression line fit to these data indicates a general trend of Na–Cl values approaching the halite dissolution line (0.65 by weight) near the springs. This trend represents modification of the Na–HCO₃ waters near Van Horn by either dissolution of halite or mixing with Na–Cl waters. Ratios become slightly elevated along the flow path past the springs then approach the halite dissolution line again near Comanche Springs. This slight elevation in Na–Cl values is consistent with

recharge of low chloride waters from the Davis Mountains.

5.2. Stiff diagram map

Groundwater from the Rustler Hills has a Ca–SO₄ signature that reflects the extensive evaporite deposits in that area. The low TDS Ca–HCO₃ signature that predominates in the Davis Mountains reflects the low solubility of the rhyolitic lava flows and tuffs. Lobo Flat and Wildhorse Flat data are low TDS Na–HCO₃ waters, suggesting that the water is primarily recent recharge in the alluvial fill. Na⁺, Cl⁻, SO₄²⁻, and TDS values increase along the hy-

pothesized flow path towards and into the Apache Mountains. Groundwater from the vicinity of the southwest corner of the Apache Mountains has high sodium and chloride concentrations, and high sulfate levels appear to be associated with Ca–SO₄ waters flowing east from the Rustler Hills.

Samples from the area near San Solomon and Phantom Lake Springs reflect mixing of local, low TDS water from the Davis Mountains with Na–Cl–SO₄ water moving from the west out of the Apache Mountains and Rustler Hills. Samples along the western edge of the Toyah Basin have Ca–SO₄ signatures similar to the samples from the upgradient Rustler Hills. Waters become progressively higher in sodium and chloride down gradient and towards the center of the Toyah Basin. This enrichment of groundwater in Na⁺ and Cl⁻ is caused by either: (1) concentration of dissolved salts from evaporation of water applied for irrigation, (2) dissolution of halite evaporites in the subsurface, or (3) movement of brines from depth up into the shallow groundwater

system. High concentrations of sodium, chloride, and sulfate in samples taken from near the Pecos River in Pecos County are from a combination of irrigation return flow and influx of saline water from the Pecos River.

5.3. Hydrochemical facies

Eleven hydrochemical facies were delineated (Table 2). The chemistry of each is discussed below.

5.3.1. Predominantly bicarbonate facies

Bicarbonate facies occur in Lobo Flat, the Carrizo Mountains, the Davis Mountains, and in eastern Pecos County where Cretaceous carbonates crop out on the Edwards Plateau. Bicarbonate waters are low in TDS (< 700 mg/l). The Lobo Flat waters tend to a Na–HCO₃ facies and have higher Na–Cl ratios. The Carrizo Mountains waters are mixed cation–HCO₃ and tend to have higher SO₄²⁻ concentrations, higher TDS, and more variability than the other

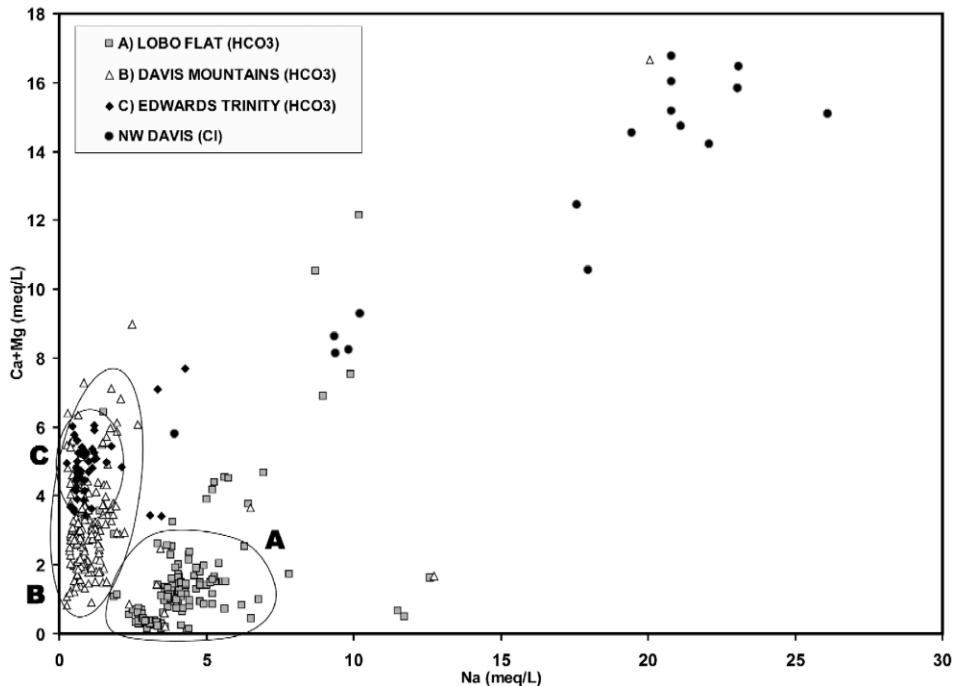


Fig. 10. Plot of Na versus Ca + Mg for all the Bicarbonate zones and for the NW Davis chloride zone. The Lobo Flat samples (A) tend to cluster in a group shifted in the direction of increasing Na and decreasing (Ca + Mg) from the other Bicarbonate zones (B and C), suggesting that a process like cation exchange may be removing Ca and Mg from solution and adding Na to solution. In the NW Davis chloride zone, both Na and Ca + Mg increase linearly, suggesting that the NW Davis samples are not modified by cation exchange.

bicarbonate facies. The Davis Mountains and Edwards Trinity facies contain Ca–HCO₃ waters.

Low TDS and high bicarbonate concentrations suggest that these waters represent recent recharge (Chebotarev, 1955; Back, 1961; Mifflin, 1968). Whole rock analyses of the flood rhyolites and trachybasalts in the Davis Mountains associated with the Paradise Mountain Caldera (Cameron et al., 1996) suggest that these rocks are the source of calcium and sodium in waters from the Davis Mountains zone. Mole ratios of Ca–SO₄ in the Davis Mountains average 8.3. Waters dominated by gypsum and anhydrite dissolution should have Ca–SO₄ mole ratios close to 1. Thus, the Ca–SO₄ mole ratios suggest that gypsum and anhydrite dissolution are not significant factors contributing to the Davis Mountains zone chemistry. Ca–SO₄ mole ratios in Lobo Flat average 0.88 and indicate that dissolution of gypsum and/or anhydrite in the alluvial fill is occurring. The plot of Na⁺ versus Ca²⁺ Mg²⁺ (Fig. 10) shows that the Lobo Flat waters are shifted towards higher sodium concentrations and lower calcium and magnesium concentrations than the other bicarbonate zone waters. The relatively high sodium concentrations and low TDS are inferred to be the result of either dissolution of volcanic and metasedimentary siliciclastic minerals, or by cation exchange with clays in the alluvial fill. Loss of Ca²⁺ from solution by cation exchange would account for Ca–SO₄ mole ratios lower than 1.

5.3.2. *Predominantly sulfate facies*

Sulfate facies occur in the Rustler Hills, in the western half of the Toyah Basin, and along the eastern edge of the Toyah Basin. In addition, several small noncontiguous zones in Pecos County were identified and grouped as one facies. Water samples from the sulfate facies are brackish. Most TDS values range between 1000 and 6000 mg/l; some have values as high as 8800 mg/l. The Rustler Hills facies contains primarily Ca–SO₄ waters; the adjacent Toyah West facies has mixed cation–SO₄ and Na–SO₄ waters with generally higher TDS values than the Rustler Hills facies. Samples from the Toyah East facies are more variable than the other zones and show a wide range of TDS values (from 540 to 5776 mg/l), but generally these samples are Ca–SO₄ with higher Na⁺ and Cl[–] concentrations than the

Toyah West zone samples. The Pecos County zone samples are mixed cation–SO₄ and Ca–SO₄ waters with relatively high concentrations of Na⁺ and Cl[–] and tend to have higher TDS values than the other sulfate zones. In the Rustler Hills, Toyah West, and Toyah East zones, sulfate increases linearly at a rate of 0.62 to 0.74 meq/l per meq/l of major anions (Fig. 11). Chloride also increases as the sum of the major anions increases in these zones (Fig. 12). The data contain a fair amount of scatter, however, and the relation may not be linear.

In the Rustler Hills, the distinct Ca–SO₄ signature of the water and an average Ca–SO₄ mole ratio of 1.03 indicate that gypsum or anhydrite dissolution is controlling the water chemistry. The Toyah West and Toyah East zones have average Ca–SO₄ mole ratios of 0.71 and 0.83, respectively, suggesting that additional processes are removing calcium ions from solution or adding sulfate ions to the groundwater (Table 3). Calcite saturation indices of 75% of the samples (182 out of 243 samples) in the Toyah West and Toyah East zones are greater than zero, suggesting that precipitation of calcite is removing calcium ions from solution. Cation exchange is another likely processes that could deplete calcium ions.

The plot of TDS versus Na–Cl (Fig. 13) indicates that most of the sulfate zone samples do not lie near the halite dissolution line and suggest that halite dissolution is not a significant process in those zones. However, Na–Cl values approach the halite dissolution line at high TDS and suggest that either halite dissolution or mixing with Na–Cl waters generated by halite dissolution are significant at higher TDS.

5.3.3. *Predominantly chloride facies*

Chloride zones occur along the northwest boundary of the Davis Mountains, in the middle of the Toyah Basin, and along the Pecos River in Pecos County. TDS values in the chloride zone samples are generally 1000–10,000 mg/l with some samples greater than 10,000 mg/l TDS, and these samples also tend to have high SO₄^{2–} values. The NW Davis zone samples are Na–Cl waters with relatively low TDS values (~ 1000–3000 mg/l). The Toyah Middle zone samples have higher TDS values (~ 1200–7000 mg/l) and are generally mixed cation–Cl waters with Na–Cl waters near San Solomon Springs. The Pecos River zone samples are Na–Cl waters

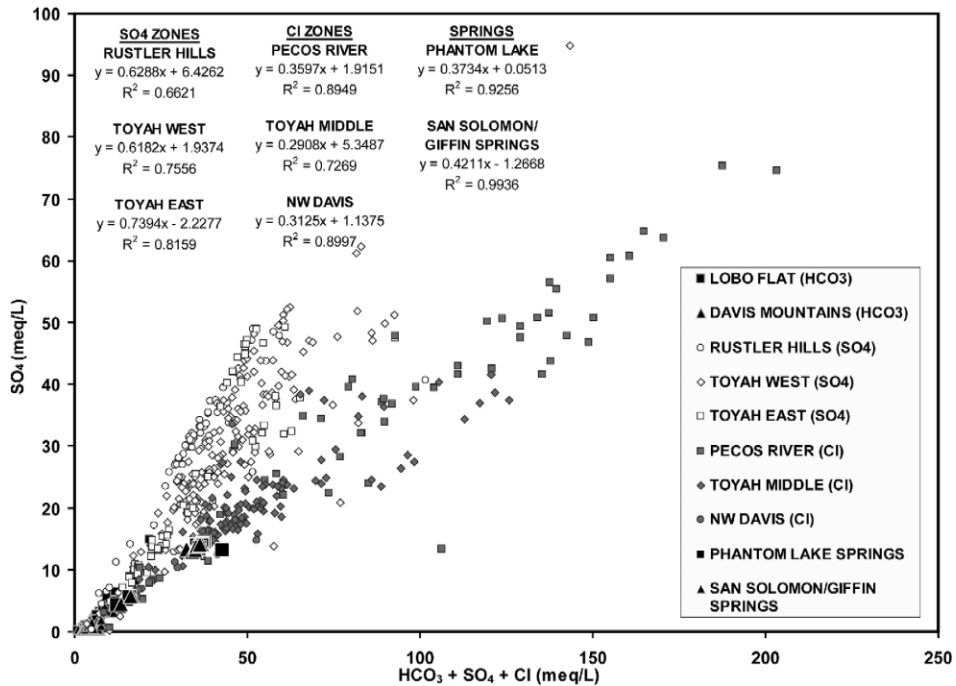


Fig. 11. Plot of the sum of the major anions versus SO₄. Regression equations and r^2 values for data from each SO₄ and Cl zone are included. Spring samples are also included.

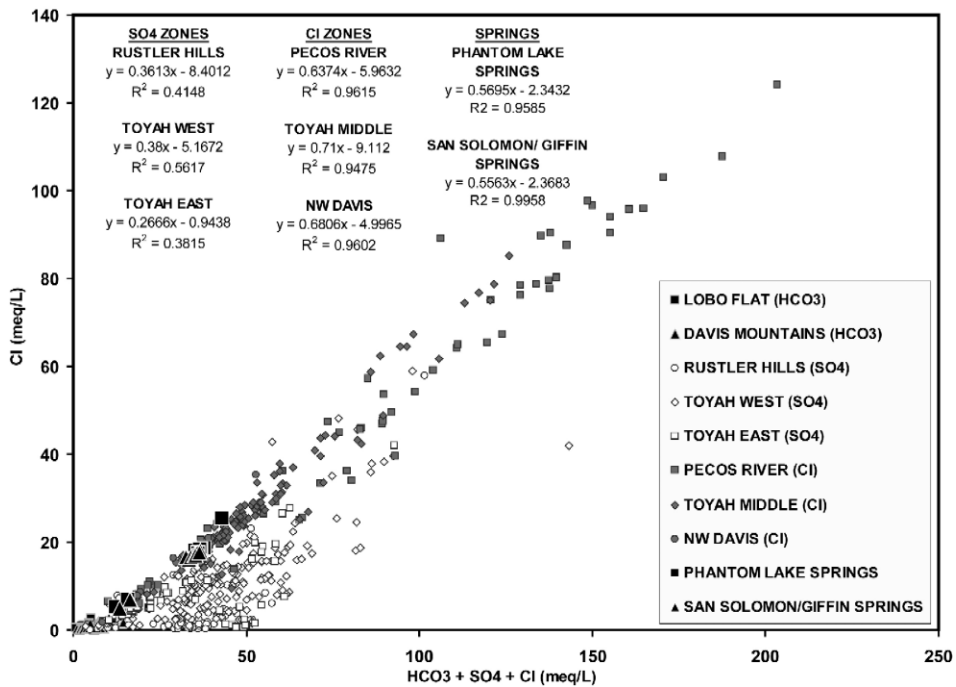


Fig. 12. Plot of the sum of the major anions versus Cl. Regression equations and r^2 values for data from each SO₄ and Cl zone are included. Spring samples are also included.

Table 3

Average ion concentrations, ion ratios, temperature, pH, and TDS for each of the predominant anion zones

All in mg/l unless otherwise noted.

	Ca	Mg	Na	K	Sr	HCO ₃	SO ₄	Cl	F	NO ₃	Temperature (°C)	pH	TDS	Na–Cl (meq/l)	Na–Cl (meq/l)	Ca–SO ₄ (meq/l)	Ca–SO ₄ (meq/l)
<i>Sulfate zones</i>																	
Rustler Hills	479	83	126	8.3	7.9	142	1376	155	1.68	36.0	21.0	7.3	2346	1.48	2.28	0.43	1.03
Toyah West	377	105	395	13.0	7.1	202	1410	414	2.0	14.3	24.3	7.3	2839	1.20	1.85	0.29	0.71
Toyah East	361	89	224	12.8	7.8	181	1137	298	1.5	31.8	24.8	7.3	2257	0.97	1.50	0.35	0.83
Pecos County	528	165	375	16.2	10.0	246	1728	589	2.2	11.7	25.0	7.2	3540	0.83	1.28	0.31	0.75
<i>Bicarbonate zones</i>																	
Davis Mountains	52	7	29	3.9	0.39	202	27	17	1.2	4.5	21.6	7.6	273	2.29	3.53	3.46	8.30
Lobo Flat	22	5	97	4.8	0.33	197	78	27	1.7	7.8	24.3	7.9	383	5.12	7.89	0.37	0.88
Carrizo	79	33	79	3.1	0.96	344	134	40	1.3	46.6	21.3	7.4	602	2.43	3.74	1.09	2.60
Edwards Trinity	67	18	24	2.7	1.73	238	44	31	1.0	6.7	22.4	7.5	322	0.87	1.34	2.07	4.96
<i>Chloride zones</i>																	
Toyah Middle	345	118	550	21	6.8	227	968	958	1.4	27.7	24.6	7.2	3115	0.61	0.94	0.35	0.85
NW Davis	146	72	442	21	3.8	250	549	612	2.3	1.9	24.5	7.7	1969	0.74	1.13	0.27	0.65
Pecos River	508	243	1147	28	9.5	264	1745	1951	1.9	27.3	22.8	7.3	5775	0.60	0.93	0.36	0.87

with the highest TDS values (~ 1200 – $12,000$ mg/l) of the chloride zones.

The chloride zone samples, like the sulfate zone samples, show a linear relationship between the sum

of major anions and SO_4^{2-} . Chloride zone samples show a strong linear relationship ($R^2 > 0.93$) between the sum of major anions and Cl^- with slopes of 0.63–0.71 meq/l Cl^- per meq/l of major anions

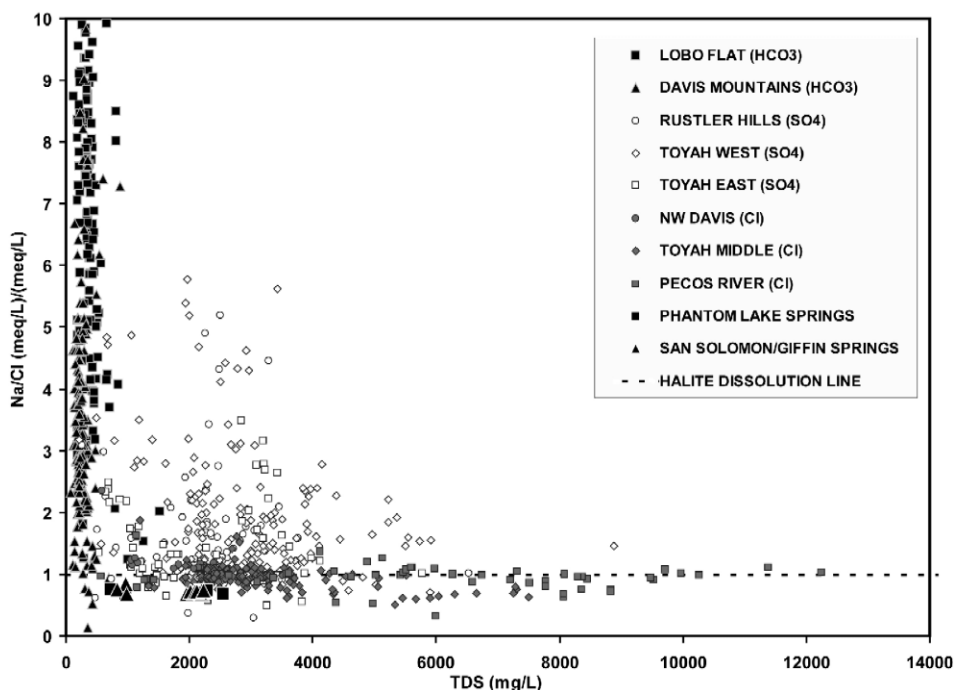


Fig. 13. Plot of TDS versus Na–Cl relative to the halite dissolution line. Spring samples are included.

(Fig. 12). SO_4^{2-} increases at a rate of 0.29 to 0.36 meq/l per meq/l of major anions (Fig. 11).

The plot of TDS versus Na–Cl (Fig. 13) indicates that the chloride zone samples cluster around the halite dissolution line and suggest that halite dissolution controls chloride zone chemistry. However, Na–Cl mole ratios in the NW Davis zone average 1.13. This is higher than expected for halite dissolution and we infer that another mechanism is either adding Na^+ ions to the groundwater or removing Cl^- ions from solution. Cation exchange could result in increased Na^+ concentrations and higher Na–Cl mole ratios, but a corresponding decrease in Ca^{2+} and Mg^{2+} does not occur in NW Davis waters (Fig. 10). The chemistry of the water in the NW Davis chloride zone is likely caused by mixing of halite dissolution-derived brines from depth with shallow, relatively high Na^+ waters from Lobo Flat and Wildhorse Flat.

The Toyah Middle and Pecos River chloride zones have average Na–Cl mole ratios of 0.94 and 0.93, respectively. This suggests that halite dissolution is a probable source of sodium and chloride ions. These

zones also have high NO_3^- concentrations (Fig. 14). This suggests that irrigation return flow may be a source of salinity. In the Toyah Basin, irrigation return flow as a source of high chloride concentrations in groundwaters has been documented by LaFave (1987), and Ashworth (1990) demonstrated that the source of high nitrate concentrations is from application of ammonia-based fertilizers to irrigated crops.

5.4. Comparison of spring chemistry to the hydrochemical facies

Spring discharge water quality data are plotted on Figs. 11–13 for comparison to the data from the hydrochemical facies. Spring samples plot in the same region as the chloride zone samples; spring discharge chemistry is more similar to the chloride zone waters than to the other waters. Samples of baseflow discharge from San Solomon and Phantom Lake Springs are Na–Cl waters with relatively high SO_4^{2-} concentrations (Table 1). The baseflow samples from Phantom Lake Springs and San Solomon

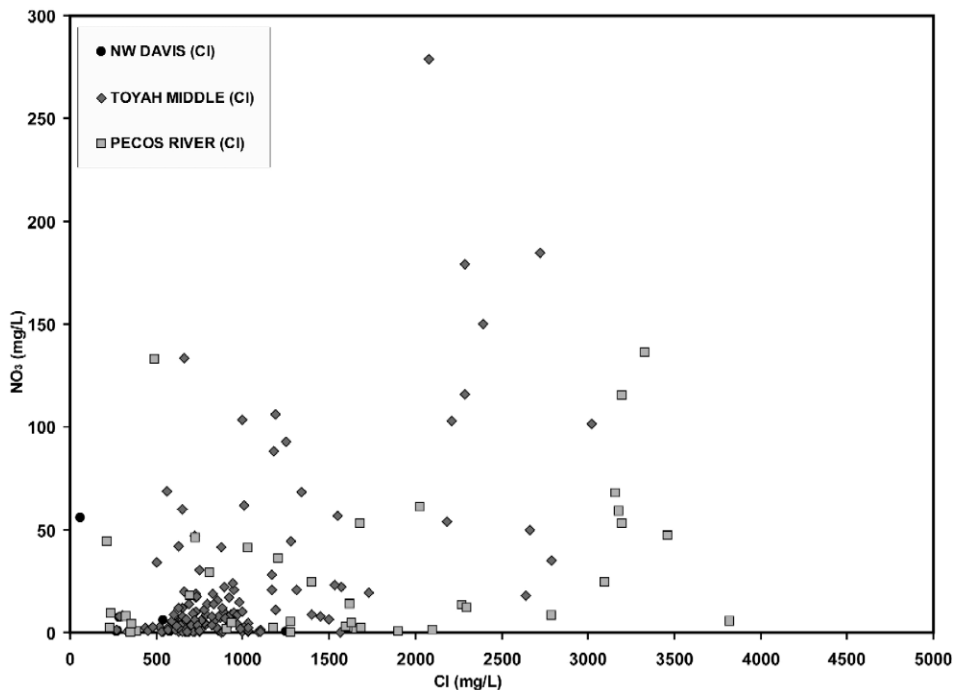


Fig. 14. Plot of Cl versus NO_3 for all predominantly chloride facies.

Springs have average Na–Cl mole ratios of 1.10 and 1.09, respectively, and average Ca–SO₄ mole ratios of 0.67 and 0.69, respectively.

Samples representing stormflow conditions are mixed cation–mixed anion with SO₄²⁻ comprising a higher percentage of the total anions than the baseflow samples. Stormflow spring discharge samples from Phantom Lake Springs and San Solomon Springs taken on October 31, 1990, and November 1, 1990, have Na–Cl mole ratios of 1.02 and 1.15, respectively, and Ca–SO₄ mole ratios of 0.94 and 1.11, respectively.

Data suggest that the baseflow component of spring discharge is derived from the same source as the NW Davis zone water, and that the stormflow component represents an influx of water from a different source.

6. Geochemical models

The geochemical modeling program PHREEQC (Parkhurst, 1995; Parkhurst et al., 1980) simulated water mixing and mineral/water reactions that could explain the chemistry of the water discharging from San Solomon Springs. The modeling objectives were to: (1) determine mineral phase reactions that may be occurring along the regional flow path and controlling the chemistry of baseflow discharge from the springs; and (2) use a set of samples taken at a single moment during a storm event to estimate a momentary percentage of local versus regional recharge to the springs under storm flow conditions.

6.1. Inverse models

The inverse modeling routine in PHREEQC generated possible scenarios to explain water chemistries observed at San Solomon Springs. Inverse models used San Solomon Springs discharge as a target solution, three hydraulically upgradient samples as input solutions, and halite, calcite, dolomite, gypsum, anhydrite, and CO₂ (g) as phase constraints. Scenarios calculated by the inverse modeling routine were then input to PHREEQC and run as forward models. The results of the forward models were compared to the target solution chemistry using the square of the Pearson product moment correlation coefficient (r^2) (Adler and Roessler, 1972) to quantify the similarity between the model results and the target solution. Model results that are identical to the target solution would result in an r^2 value of 1; greater variation between the model results and the target solution produces lower r^2 values.

Individual (not composite) records from three groundwater samples in the TWDB database were chosen as input solutions for the models (Fig. 1). These samples were chosen because we felt that they are representative of the zones from which they were taken. Solution 1 is from a well in the NW Davis chloride facies that represents the upgradient end of the flow system. Solution 2 is a mixed-anion sample from a well located near the eastern edge of the Apache Mountains and represents an intermediate point along the hypothesized flow path. Solution 3 is from a well in the Tertiary volcanics in the Davis Mountains bicarbonate facies. This sample represents

Table 4

End-member solutions used in the geochemical models; sample locations are shown in Fig. 1

Solution key: (1) NW Davis CL zone upgradient of springs; (2) sample near Stocks Ranch; intermediate along flow path; and (3) recent meteoric recharge from Davis Mountains.

All in mg/l unless otherwise noted.

Solution ID	State Well #	Date	Temperature (°C)	Ca	Mg	Na	K	Sr	HCO ₃	SO ₄	Cl	F	NO ₃	pH	TDS	Calcite SI
Solution 1	47-61-403	6/27/85	23.0	101	39	226	13.0	251	325	278	2.3	1.1	7.90	1126	0.63	
Solution 2	47-64-401	3/13/70		156	59	296		270	483	407	1.90	0.4	7.40	1550	0.33	
Solution 3	52-09-501	4/15/90	21.0	34	3	17	2.5	0.2	136	8	7	1.48	2.2	7.44	179	-0.35
SS Base Flow	52-02-611	4/14/90	26.0	185	75	440	24.0	4.3	284	650	628	1.7	1.2	7.29	2169	0.28
SS Storm Flow	52-02-611	11/1/90	21.0	99	23	133	12.0	1.4	247	213	178	1.1	7.3	7.20	827	-0.05

SS = San Solomon Springs.

Table 5
Summary of model results from the best models.

Element	Target solution (mmol/l)	Model results (mmol/l)	Mineral phase exchange			
			Phase	Moles	% Total	
<i>(A) Evolution along flow path</i>						
Ca	3.89	3.79	Calcite	0.00145	22%	Precipitate Calcite
Mg	2.43	2.49	CO ₂ (g)	-0.00059	9%	Dissolve CO ₂ (g)
Na	12.88	13.23	Dolomite	-0.00089	13%	Dissolve Dolomite
C	4.42	5.07	Gypsum	-0.00183	27%	Dissolve Gypsum
S	5.03	5.21	Halite	-0.00339	51%	Dissolve Halite
Cl	11.48	11.24	Results correlation (r^2): 0.995			
<i>(B) Base flow spring discharge (solution 3)</i>						
Ca	4.62	4.93	Calcite	0.00583	16%	Precipitate Calcite
Mg	3.09	3.74	CO ₂ (g)	-0.00169	5%	Dissolve CO ₂ (g)
Na	19.14	18.69	Dolomite	-0.00362	10%	Dissolve Dolomite
C	4.65	5.49	Gypsum	-0.00629	18%	Dissolve Gypsum
S	6.77	6.37	Halite	-0.01795	51%	Dissolve Halite
Cl	17.72	18.15	Results correlation (r^2): 0.995			
<i>Base flow spring discharge (solution 2)</i>						
Ca	4.62	4.77	Calcite	0.00153	15%	Precipitate Calcite
Mg	3.09	3.26	CO ₂ (g)	-0.00023	2%	Dissolve CO ₂ (g)
Na	19.14	19.13	Dolomite	-0.00083	8%	Dissolve Dolomite
C	4.65	5.08	Gypsum	-0.00158	15%	Dissolve Gypsum
S	6.77	6.62	Halite	-0.00623	60%	Dissolve Halite
Cl	17.72	17.73	Results correlation (r^2): 0.999			
<i>Base flow spring discharge (solution 1)</i>						
Ca	4.62	4.63	Calcite	0.00303	16%	Precipitate Calcite
Mg	3.09	3.33	CO ₂ (g)	-0.00082	4%	Dissolve CO ₂ (g)
Na	19.14	19.44	Dolomite	-0.00173	9%	Dissolve Dolomite
C	4.65	5.41	Gypsum	-0.00340	18%	Dissolve Gypsum
S	6.77	6.79	Halite	-0.00960	52%	Dissolve Halite
Cl	17.72	17.45	Results correlation (r^2): 0.998			
<i>(C) Storm flow spring discharge (solution 2)</i>						
Ca	2.47	2.51	Calcite	-0.03612	37%	Dissolve Calcite
Mg	0.95	1.11	CO ₂ (g)	-0.06255	63%	Dissolve CO ₂ (g)
Na	5.79	5.93				
C	4.05	4.38				
S	2.22	2.20				
Cl	5.02	5.03	Results correlation (r^2): 0.995			
<i>Storm flow spring discharge (baseflow spring discharge)</i>						
Ca	2.47	2.57	Calcite	-0.04763	34%	Dissolve Calcite
Mg	0.95	0.95	CO ₂ (g)	-0.07353	53%	Dissolve CO ₂ (g)
Na	5.79	5.90	Gypsum	-0.01806	13%	Dissolve Gypsum
C	4.05	4.36				
S	2.22	2.14				
Cl	5.02	5.12	Results correlation (r^2): 0.997			

“Mineral Phase Exchange” values represent moles of each mineral or gas phase exchanged with solution (for example, in model A, 0.00145 mol of calcite precipitate from solution; 0.00089 mol of dolomite dissolve into solution, etc.) “% total” represents the amount exchanged for each phase divided by the total amount exchanged (i.e., the sum of the absolute values of all phases) expressed as a percentage; all percentages should add up to 100%.

recent meteoric recharge to the local flow system originating in the Davis Mountains. San Solomon Springs stormflow and baseflow target solutions were also taken from the TWDB database. Well numbers, sample dates, and sample data used in the modeling are presented in Table 4.

6.2. Forward models

The evolution of water chemistry from solutions 1 to 2 was simulated by reacting solution 1 with mineral and gas phases. Results indicate that dissolution of halite, gypsum, dolomite, and CO_2 (g) and precipitation of calcite generates a solution with the closest match to the chemistry of solution 2 (Table 5A).

Inverse modeling of baseflow chemistry at San Solomon Springs did not suggest any scenario that incorporate mixing of the input solutions. Baseflow chemistry from San Solomon Springs was modeled using only mineral phase reactions. The results indicate that, with any of the three input solutions as the initial solution, dissolution of halite, gypsum, dolomite, and CO_2 (g) and precipitation of calcite generates a solution with a general match to the chemistry of the San Solomon Springs baseflow discharge sample. The model that reacts solution 2 (from near the Apache Mountains) with the mineral and gas phases resulted in the highest degree of similarity to the baseflow discharge sample (Table 5B).

Stormflow spring discharge was simulated by mixing solutions 2 (from near the Apache Mountains) and 3 (local meteoric recharge from the Davis Mountains) and reacting the mixture with mineral phases. Model results indicate that a mixture of 43% of solution 2 and 57% of solution 3, along with dissolution of calcite and CO_2 (g), generates a solution with a close match to the November 1, 1990, San Solomon Springs stormflow discharge sample (Table 5C). Stormflow discharge was also simulated by mixing baseflow spring discharge with solution 3 and reacting the mixture with mineral phases. Model results indicate that a mixture of 28% baseflow discharge and 72% solution 3, along with dissolution of calcite, gypsum, and CO_2 (g), generates a solution with a close match to the chemistry of the same stormflow discharge sample (Table 5C).

7. Discussion of data analysis and model results

Mineral phase exchange values in model results suggest that dissolution of halite is the primary mineral reaction occurring along the regional flow path (Table 5A). Model results also suggest that dissolution of gypsum and precipitation of calcite are significant and roughly equal in magnitude along the flow path. Saturation indices for samples from the regional flow path indicate that these waters are under-saturated with respect to gypsum and super-saturated with respect to calcite, which is consistent with model results. Dolomite and CO_2 (g) dissolution also contribute to groundwater chemistry. This dedolomitization reaction has also been observed by Plummer et al. (1990) in the Madison aquifer in Montana, Wyoming, and South Dakota. Halite dissolution should result in Na–Cl mole ratios near 1. The plot of Na–Cl values along the regional flow path (Fig. 9F) indicates that Na–Cl values approach the halite dissolution line along the regional flow path. In addition, the plot of TDS versus Na–Cl (Fig. 13) shows that groundwaters approach the halite dissolution line with increasing TDS.

Gypsum dissolution should result in Ca– SO_4 mole ratios approaching 1 along the flow path. Samples in the Rustler Hills sulfate zone have Ca– SO_4 mole ratios that average 1.03. This indicates that gypsum dissolution dominates water chemistry here. However, waters from the other sulfate zones, from the chloride zones, and from the flow path samples used in the geochemical models have average Ca– SO_4 mole ratios that range from 0.65 to 0.87. Calcite precipitation, as suggested by the model results, would remove calcium ions from solution and cause Ca– SO_4 mole ratios to drop below 1. Dolomite dissolution would add calcium ions back into solution. However, the mineral phase exchange values (Table 5A) indicate that the relative number of ions added by dolomite dissolution is much less than the number removed by calcite precipitation.

Model-calculated moles of calcium added to solution by gypsum and dolomite dissolution, minus moles of calcium removed by calcite precipitation, would result in a net increase in calcium ions along the flow path (Table 5A). Fig. 9B indicates that calcium concentration is increasing along the regional flow path. Moreover, dissolution of dolomite

should result in an increasing concentration of magnesium along the flow path. Fig. 9C indicates that magnesium concentration is increasing along the flow path.

The three models that simulate spring chemistry suggest that baseflow discharge from San Solomon Springs is derived from water flowing along the regional flow path and reacting with the mineral phases discussed above (Table 5B). These models also suggest that reacting recent meteoric recharge in the Davis Mountains with the same mineral phases also results in a solution that is similar to baseflow discharge from the springs. However, the mineral phase exchange values indicate that an exchange of three times more ions are required to evolve the Davis Mountains water to a solution similar to baseflow spring discharge than are required to evolve Apache Mountains water to match spring chemistry. This does not mean that some baseflow spring discharge cannot be derived from the Davis Mountains, but the fact that the regional flow path model results in a closer match and requires less ion exchange over a much longer flow path demonstrates that it is a more plausible model. Other phenomena (water temperature, consistency of spring discharge, and isotopic data (Uliana and Sharp, 1999; LaFave and Sharp, 1987)) agree with the regional hypothesis according to the principles elucidated by Mifflin (1968).

The spring discharge models suggest that stormflow discharge from San Solomon Springs during the 1990 sampling event is derived from a mixture of 28% baseflow discharge and 72% locally derived recent meteoric recharge from the Davis Mountains that is further modified by dissolution of calcite, gypsum, and CO₂ (g). LaFave (1987) calculated a similar value of 73% local recharge for a sample taken during the storm event of September 12, 1932. Our calculated percentages of local versus regional flow represent the distribution of recharge at a point in time during a storm event, and should not be taken to represent the overall contribution of local recharge during storm events. The relative contributions of local and regional flow during any storm event will vary throughout the event.

Calcite saturation indices for baseflow discharge from San Solomon, Giffin, and Phantom Lake Springs (Table 1) are generally near or above zero;

these waters are saturated to supersaturated with respect to calcite. There is some uncertainty about the early data because of differences in analytical methods. Model input solutions 1 and 2 are also supersaturated with respect to calcite (Table 4). These saturation indices, and the model results from the base flow models (Table 5A and B), suggest that calcite is either near equilibrium or is precipitating throughout the regional flow system. This is contradicted by the presence of large karst features dominating groundwater flow in the system (Davis and Leggat, 1965; LaFave, 1987; Tucker, 2000) and the almost complete absence of speleothems in caves below the water table (Tucker, personal communication). Storm flow discharge models, which incorporate mixing of low-TDS local recharge with more saline (~2000 mg/l TDS) waters from the regional flow system, result in calcite dissolution. This is consistent with the work of Back et al. (1986), who observed that mixing of low-TDS/bicarbonate waters and saline waters in the subsurface along carbonate coastlines lowered the calcite saturation index and resulted in extensive cave formation. This suggests that cave formation in this system, and possibly karst systems in other arid regions as well, is only occurring during large storm events.

8. Summary and conclusions

The chemistry of spring discharge and its correlation with local precipitation events indicate that San Solomon, Giffin, and Phantom Lake Springs have both a regional baseflow component and a local stormflow component. The regional groundwater system that supplies baseflow to the springs originates in the Salt Basin and flows through the Apache Mountains towards the springs.

Historical geochemistry data identified flow paths in the regional system. Sampling records obtained from the Texas Water Development Board were reduced to 295 composite records. Maps of stiff diagrams and predominant ionic constituents were used to identify predominant anion (sulfate, bicarbonate, or chloride) zones that were further refined to 11 hydrochemical facies. The bicarbonate zones are low-TDS waters that represent recent recharge. Sulfate zones are intermediate to high-TDS waters

controlled by gypsum dissolution and either halite dissolution or mixing with high Na–Cl waters. Chloride zones are intermediate to high-TDS waters controlled by halite dissolution and probably influenced by irrigation return flow and mixing with brines from deeper in the subsurface. Mixed-anion waters dominate samples along the regional flow path.

Plots of spring discharge and groundwater chemistry indicate that spring discharge is most similar to the chloride zone waters. Spring discharge Na–Cl and Ca–SO₄ mole ratios indicate that baseflow spring discharge is derived from the same source as the chloride facies located upgradient along the regional flow path.

Geochemical data along the flow path indicate a trend of increasing dissolved solids and increasing Cl–HCO₃ along the flow path. High Na–Cl values at the upgradient end decrease steadily along the flow path and approach the halite dissolution line. These trends are consistent with the evolution of groundwater in an unconfined regional system dominated by geochemical reactions with carbonates and evaporites.

PHREEQC was used to model groundwater evolution along the flow path and spring discharge under both baseflow and stormflow conditions. Output indicates that water chemistry along the regional flow path is controlled by dissolution of halite, gypsum, and dolomite, and precipitation of calcite. Model simulations incorporating baseflow spring discharge indicate that baseflow discharge is derived from the regional flow path modified by dissolution of halite, gypsum, dolomite, and CO₂ (g), and precipitation of calcite. Model simulations of stormflow spring discharge based on a single sample taken during a storm event indicate that the sample of stormflow discharge was a mixture of 28% baseflow discharge and 72% locally derived water, with the mixture further modified by dissolution of calcite, gypsum, and CO₂ (g). Model results are consistent with the water chemistry trends identified in the predominant anion zones, and suggest that karstification is only occurring during major storm events.

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All data, model input files, and model results can be obtained on-line at <http://www.geo.utexas.edu/hydro/yools.htm>.

References

- Adler, H.R., Roessler, E.B., 1972. *Introduction to Probability and Statistics*. 5th edn. Freeman, San Francisco, p. 206.
- Ashworth, J.B., 1990. Evaluation of ground-water resources in parts of Loving, Pecos, Reeves, Ward, and Winkler Counties, Texas. Texas Water Development Board, Report 317, 51 pp.
- Back, W., 1961. Techniques for mapping of hydrochemical facies. U.S. Geological Survey Professional Paper 424-D, 380–382.
- Back, W., Hanshaw, B.B., Herman, J.S., van Driel, J.N., 1986. Differential dissolution of a Pleistocene reef in the ground-water mixing zone of coastal Yucatan, Mexico. *Geology* 14, 137–140.
- Barnes, V.E., 1976. *Geologic Atlas of Texas, Pecos Sheet: The University of Texas at Austin Bureau of Economic Geology, map with explanation.*
- Barnes, V.E., 1979. *Geologic Atlas of Texas, Marfa Sheet: The University of Texas at Austin Bureau of Economic Geology, map with explanation.*
- Barnes, V.E., 1995a. *Geologic Atlas of Texas, Fort Stockton Sheet: The University of Texas at Austin Bureau of Economic Geology, map with explanation.*
- Barnes, V.E., 1995b. *Geologic Atlas of Texas, Van Horn–El Paso Sheet: The University of Texas at Austin Bureau of Economic Geology, map with explanation.*
- Brune, G., 1981. *Springs of Texas, vol. I, Branch-Smith, Fort Worth, 566 pp.*
- Cameron, K.L., Parker, D.F., Sampson, D.E., 1996. Testing crustal melting models for the origin of flood rhyolites: a Nd–Pb–Sr isotopic study of the Tertiary Davis Mountains volcanic field, west Texas. *Journal of Geophysical Research* 101 (B9), 20407–20422.
- Chebotarev, I.I., 1955. Metamorphism of natural waters in the crust of weathering. *Geochimica et Cosmochimica Acta*. 65, 22–48, 137–170 and 198–212.
- Davis, M.E., Leggat, E.R., 1965. Reconnaissance investigation of the groundwater resources of the upper Rio Grand Basin, Texas. *Reconnaissance Investigation of the Groundwater Resources of the Rio Grand Basin, Texas. Texas Water Commission Bulletin, vol. 6502, pp. U1–U199.*

- Gates, J.S., White, D.E., Stanley, W.D., Ackerman, H.D., 1980. Availability of fresh and slightly saline ground water in the basins of westernmost Texas. Texas Department of Water Resources, Report 256, 108 pp.
- LaFave, J.I., 1987. Groundwater flow delineation in the Toyah Basin of Trans-Pecos Texas: unpublished MA thesis, The University of Texas at Austin, 160 pp.
- LaFave, J.I., Sharp Jr., J.M., 1987. Origins of groundwater discharging at the springs of Balmorhea, West Texas. *Geological Society Bulletin* 26, 5–14.
- Larkin, T.J., Bomar, G.W., 1983. Climatic Atlas of Texas. Texas Department of Water Resources Publication LP-192, Austin, TX, 151 pp.
- Mifflin, M.D., 1968. Delineation of ground-water flow systems in Nevada: University of Nevada at Reno, Center for Water Resources Research and Desert Research Institute Technical Report Series H-W, No. 4, 112 pp.
- Neilson, P.D., Sharp, J.M., 1985. Tectonic controls on the hydrogeology of the Salt Basin, Trans-Pecos Texas. In: Muehlberger, W.R., Dickerson, P.W. (Eds.), *Structure and Tectonics of Trans-Pecos Texas*, vols. 85–81, West Texas Geological Society Publication, Midland, TX, pp. 231–234.
- Parkhurst, D.L., 1995. User's guide to PHREEQC—a computer program for speciation, reaction-path, advective-transport, and inverse geochemical calculations: United States Geological Survey Water Resources Investigations Report 95-4227, 143 pp.
- Parkhurst, D.L., Thorstenson, D.C., Plummer, N.L., 1980. PHREEQE—a computer program for geochemical calculation: United States Geological Survey Water Resource Investigation Report 80-96.
- Plummer, L.N., Busby, J.F., Lee, R.W., Hanshaw, B.B., 1990. Geochemical modeling of the Madison aquifer in parts of Montana, Wyoming and South Dakota. *Water Resources Research* 26, 1981–2014.
- Schuster, S.K., 1996. Water resource and planning assessment in San Solomon Springs and associated spring systems surrounding Balmorhea, Texas: unpublished MS thesis, The University of Texas at Austin, 102 pp.
- Sharp, J.M., 1989. Regional ground-water systems in northern Trans-Pecos Texas. In: Muehlberger, W.R., Dickerson, P.W. (Eds.), *Structure and Stratigraphy of Trans-Pecos Texas*. American Geophysical Union Field Trip Guidebook T317, pp. 123–130.
- Sharp Jr., J.M., Uliana, M.M., Bogichi, R., 1999. Fracture controls on regional groundwater flow in a semiarid environment and implications for long-term maintenance of spring flows. Water 99 Joint Congress, Inst. of Engineers, vol. 2, International Association of Hydrogeologists (IAH), Brisbane, Australia, pp. 1212–1217.
- Tucker, A.W., 2000. Phantom Lake Cave. The Texas Caver. Texas Speleological Association, pp. 4–7.
- Uliana, M.M., Sharp Jr., J.M., 1999. Tracing regional flow paths to major springs in Trans-Pecos Texas using naturally occurring geochemical and isotopic species. Abs. and Presentation, Geological Society of America National Meeting, Oct. 24–28.