

2008-01-01

A Multi-Tracer Study of Saltwater Origin, Cross-Formational Flow, and the Geochemical Evolution of Groundwater in the Southern High Plains Aquifer along the Western Caprock Escarpment, East-Central New Mexico

Jeff Langman

University of Texas at El Paso, jblangman@miners.utep.edu

Follow this and additional works at: https://digitalcommons.utep.edu/open_etd



Part of the [Geochemistry Commons](#), [Geology Commons](#), and the [Hydrology Commons](#)

Recommended Citation

Langman, Jeff, "A Multi-Tracer Study of Saltwater Origin, Cross-Formational Flow, and the Geochemical Evolution of Groundwater in the Southern High Plains Aquifer along the Western Caprock Escarpment, East-Central New Mexico" (2008). *Open Access Theses & Dissertations*. 298.

https://digitalcommons.utep.edu/open_etd/298

This is brought to you for free and open access by DigitalCommons@UTEP. It has been accepted for inclusion in Open Access Theses & Dissertations by an authorized administrator of DigitalCommons@UTEP. For more information, please contact lweber@utep.edu.

A MULTI-TRACER STUDY OF SALTWATER ORIGIN, CROSS-
FORMATIONAL FLOW, AND THE GEOCHEMICAL EVOLUTION OF
GROUNDWATER IN THE SOUTHERN HIGH PLAINS AQUIFER ALONG
THE WESTERN CAPROCK ESCARPMENT, EAST-CENTRAL NEW MEXICO

JEFF B. LANGMAN

Department of Geological Sciences

APPROVED:

Andre S. Ellis, Ph.D., Chair

Elizabeth Y. Anthony, Ph.D.

Diane I. Doser, Ph.D.

Thomas E. Gill, Ph.D.

John C. Walton, Ph.D.

Patricia D. Witherspoon, Ph.D.
Dean of the Graduate School

Copyright
by
Jeff B. Langman
2008

A MULTI-TRACER STUDY OF SALTWATER ORIGIN, CROSS-
FORMATIONAL FLOW, AND THE GEOCHEMICAL EVOLUTION OF
GROUNDWATER IN THE SOUTHERN HIGH PLAINS AQUIFER ALONG
THE WESTERN CAPROCK ESCARPMENT, EAST-CENTRAL NEW MEXICO

By

JEFF B. LANGMAN, M.S.

DISSERTATION

Presented to the Faculty of the Graduate School of

The University of Texas at El Paso

in Partial Fulfillment

of the Requirements

for the Degree of

DOCTOR OF PHILOSOPHY

Department of Geological Sciences

THE UNIVERSITY OF TEXAS AT EL PASO

December 2008

Acknowledgements

A special thanks to my advisor, Dr. Andre S. Ellis for his advice and patience. I would like to thank my committee members Dr. Anthony, Dr. Doser, Dr. Gill, and Dr. Walton for their support. I also wish to thank Fredrick Gebhardt, Andrew Robertson, and Ralph Wilcox of the U.S. Geological Survey for their help in implementing this study. Most importantly, I never would have been able to complete this study without the love and understanding of my wife, Chantal.

Abstract

Sustainable management of groundwater resources requires sufficient knowledge of the distribution of fresh and saline groundwater and the processes affecting saltwater intrusion that may influence the beneficial use of groundwater. A hydrogeologic investigation that coupled various chemical and isotopic tracers, including $^3\text{H}/^3\text{He}$, ^{14}C , δD , $\delta^{18}\text{O}$, $^{87}\text{Sr}/^{86}\text{Sr}$, and $\delta^{11}\text{B}$, with the physical characteristics of the aquifer was conducted to determine source waters, the origin of saltwater and its influence through cross-formational flow, and water-rock interactions in the Southern High Plains aquifer along the Western Caprock Escarpment. Sub-aquifers or local flow systems are present along the Western Caprock Escarpment, and the study site's local flow system drains a Na-Cl, high dissolved solids (2,000 to 9,500 mg/L) groundwater from the escarpment until it mixes with a regional aquifer or regional flow system that is more oxygenated and a mixed cation- HCO_3^- water type with low dissolved solids (390 to 520 mg/L). The local flow system contains old water (5,500 to 21,000 years) that is similar in age and composition to the underlying, upper Dockum aquifer (Na-Cl water type, 970 to 13,000 mg/L dissolved solids, 12,000 to 27,000 years). The δD and $\delta^{18}\text{O}$ values for the local flow system (-71.74 to -47.96‰ and -9.95 to -6.52‰, respectively) and upper Dockum aquifer (-67.20 to -51.70‰ and -9.11 to -6.93‰) were lower and more variable compared to the regional flow system (-45.97 to -43.29‰ and -6.30 to -6.09‰). Groundwater δD and $\delta^{18}\text{O}$ values in the mixing zone (-45.19 to -43.90‰ and -6.14 to -5.85‰) indicated an additional water source or further evaporation.

To resolve the groundwater evolution along the Western Caprock Escarpment, $^{87}\text{Sr}/^{86}\text{Sr}$ and $\delta^{11}\text{B}$ values were coupled with major ion, trace element, age, and δD and $\delta^{18}\text{O}$ values. The $^{87}\text{Sr}/^{86}\text{Sr}$ range of 0.70845 to 0.70906 and Sr concentrations of 0.90 to 31 mg/L were sufficient to estimate source-water fractions and contributions from chemical weathering through inverse

calculations. Boron concentrations (59 to 1,740 mg/L) and $\delta^{11}\text{B}$ values (+6.0 to +46.0‰) were used to resolve the influence of agricultural recharge in the mixing zone that was ambiguously identified with other tracers. Alteration of B and $\delta^{11}\text{B}$ values in the mixing zone indicated the loss of B and decrease in $\delta^{11}\text{B}$ values likely from plant uptake, adsorption, and weathering contributions in the soil/vadose zone prior to recharge beneath or near agricultural fields. With confirmation of this additional influence in the mixing zone, results from the Sr inverse calculations were used to reinterpret δD and $\delta^{18}\text{O}$ values to account for agricultural recharge.

Geochemical tracer analysis allowed the formation of a conceptual flow model. Groundwater interaction with Permian bedded salts and Dockum Group shales produces a high dissolved-solids groundwater with a strong halite signal that can strongly influence groundwater composition in the Southern High Plains aquifer through cross-formational flow. Cross-formational flow from the Permian bedded salts into the Dockum Group provides a water source where none was expected because of the hydrologic divide of the escarpment, and this water likely originates in the Pecos River Basin and crosses beneath the hydrologic divide through the Permian bedded salts. The mixing of young (less than 100 years), local recharge from surface pathways at the Western Caprock Escarpment and much older (greater than 20,000 years) saltwater from the Permian bedded salts and Dockum Group is spatially variable and dependent on available flowpaths created by fracturing of the Dockum Group shales from Permian bedded-salt subsidence. Groundwater flow in local systems of the Southern High Plains aquifer along the Western Caprock Escarpment mixes with regional flow systems of larger saturated thickness where the geochemical signal of the halite-influenced saltwater is substantially reduced but visible in a thin mixing zone. Alteration of geochemical signals from groundwater flow through Dockum Group shales and the effect of agricultural recharge limited the effectiveness of certain tracers for identifying source waters, mixing patterns, and water-rock interactions.

Table of Contents

Acknowledgements	iv
Abstract	v
List of Tables	viii
List of Figures	ix
Chapter 1: Introduction	1
Geologic and Hydrologic Setting	7
Structural Framework and Landscape Evolution	7
Stratigraphy	9
Hydrogeology	11
Previous Studies	14
Chapter 2: Study Methods	16
Quality Assurance and Quality Control	19
Data Analysis and Tracer Application	20
Chapter 3: Saltwater Origin and Cross-Formational Flow in the Southern High Plains	
Aquifer	26
Formation Properties	27
Groundwater Flow and Potentiometric Surfaces	29
Groundwater Composition	34
Groundwater Age	45
Water Stable Isotopes, Recharge, and Mixing	48
Chapter 4: Geochemical Evolution of Groundwater in the Southern High Plains and	
Upper Dockum Group Aquifers	53
⁸⁷ Sr/ ⁸⁶ Sr and Chemical Weathering	53
δ ¹¹ B, Water-Rock Interactions, and Adsorption	58
Agriculture and Groundwater Geochemistry	62
Chapter 5: Flowpaths in the Southern High Plains Aquifer Along the Western Caprock	
Escarpment	67
Chapter 6: Conclusions and Summary	71
References	75
Curriculum Vita	87

List of Tables

Table 1. Lithology and stratigraphy of geologic formations in the Southern High Plains and at the study site.....	11
Table 2. Sample analytes and laboratory analysis methods.....	17
Table 3. Study site monitoring-well and soil/rock sample location information.....	18
Table 4. Physical and chemical properties of groundwater collected at the study site, June 2006.	37
Table 5. Chemical properties of acid digestion and leachate of soil/rock samples collected at the study site, December 2006.....	38
Table 6. Results of least-squares regression of δD and $\delta^{18}O$ values for the three aquifer systems at the study site.	50
Table 7. Approximate source-water mixing fractions determined by δD and $\delta^{18}O$ for the local flow system at the study site.	51
Table 8. Fractional contributions of strontium from possible source waters comprising the groundwater mixtures and likely chemical weathering inputs from water-rock interactions at each well site as determined by inverse calculations.	56
Table 9. Comparison of actual boron concentrations and isotope ratios in the mixing zone with calculated values estimated from the likely source-water mixing fractions determined by Sr concentration and $^{87}Sr/^{86}Sr$ inverse calculations.	62
Table 10. Inverse calculation of δD and $\delta^{18}O$ values using mixing fractions determined by Sr concentrations and $^{87}Sr/^{86}Sr$ ratios to examine evaporation from application of mixing-zone water to agricultural fields in the Southern High Plains aquifer at the study site.	63

List of Figures

Figure 1. Effect of groundwater mining on the High Plains aquifers.....	2
Figure 2. Location of study site.	5
Figure 3. Study site well locations.....	6
Figure 4. Peripheral salt dissolution zone in the northern part of the Southern High Plains.....	9
Figure 5. Hypothetical model of possible groundwater flowpaths and geologic relations at the study site.....	27
Figure 6. Lithology, geophysical logs, saturated intervals, and potentiometric surfaces for the Ogallala Formation and Dockum Group at paired well locations.....	28
Figure 7. Groundwater altitudes and flowpaths in the Southern High Plains aquifer and the upper Dockum aquifer at the study site.	30
Figure 8. Land surface and Ogallala Formation-Dockum Group contact topography at the study site.	31
Figure 9. Water-level recovery at well 15 following a well purge in 2006.....	32
Figure 10. Temperature profile of water column in well 15, June 2006.	33
Figure 11. Major-ion relations in groundwater at the study site, June 2006.	35
Figure 12. Major-ion distribution and relative dissolved-solids concentrations at the study site, June 2006.....	36
Figure 13. Molar ratios of sodium and calcium to chloride in groundwater at the study site, June 2006.....	42
Figure 14. Dissolved-oxygen and manganese concentrations in groundwater at the study site, June 2006.....	43
Figure 15. Lithium and strontium concentrations in groundwater at the study site, June 2006.....	44
Figure 16. Helium concentrations in groundwater at the study site, June 2006.....	46
Figure 17. Groundwater δD and $\delta^{18}O$ values at the study site, June 2006.	49
Figure 18. Groundwater δD and $\delta^{18}O$ values for the Permian salts, Dockum Group, and Ogallala Formation in the Southern High Plains.	52

Figure 19. Strontium concentrations and $^{87}\text{Sr}/^{86}\text{Sr}$ ratios in groundwater at the study site, June 2006.....	55
Figure 20. Ratios of $^{87}\text{Sr}/^{86}\text{Sr}$ and fractional contribution of strontium from source waters and chemical weathering in the different groundwater systems at the study site, June 2006.....	57
Figure 21. Chloride/boron molar ratios and $\delta^{11}\text{B}$ values in groundwater and rock samples at the study site in relation to possible boron sources.....	60
Figure 22. Boron concentrations and $\delta^{11}\text{B}$ values for groundwater at the study site, June 2006.....	61
Figure 23. Groundwater δD and $\delta^{18}\text{O}$ values at the study site and calculated isotope ratios for the mixed zone wells from inverse calculations using water source fractions as determined by strontium concentration and $^{87}\text{Sr}/^{86}\text{Sr}$ ratios.....	64
Figure 24. Likely source-water origins and cross-formational flow in the Southern High Plains aquifer.	69
Figure 25. Study-supported conceptual model of groundwater flowpaths in the Southern High Plains along the Western Caprock Escarpment.....	70

Chapter 1: Introduction

The saturated Ogallala Formation in eastern, central New Mexico is within the western boundary of the Southern High Plains aquifer (Hart and McAda, 1985), which is part of the larger High Plains aquifer system extending from Texas to South Dakota (fig. 1). The Southern High Plains aquifer is the principal source for agricultural and drinking water in one of the Nation's major agricultural areas. Farmers began using the Southern High Plains aquifer in the 1940s for irrigation, and about 94% of the water pumped from the entire High Plains aquifer system in 1995 was used for irrigation (McGuire et al., 2003). Heavy reliance on groundwater for agriculture has substantially decreased groundwater levels throughout much of the Southern High Plains aquifer since the mid-1940s (McGuire et al., 2003) (fig. 1).

Declining water levels in the Southern High Plains aquifer (fig. 1) have led water managers to examine other possible source waters including deeper aquifers. Aquifers underlying the Southern High Plains aquifer are known to be of different chemical compositions and poorer quality (Nativ and Smith, 1987). Distinct hydrochemical facies in the Southern High Plains aquifer have been attributed to recharge by cross-formational flow from underlying aquifers (Nativ, 1992; Nativ and Smith, 1987; McMahon and Böhlke, 2007). Existing and future water-level declines in the Southern High Plains aquifer have and will likely affect interaction with underlying aquifers, and further groundwater mining will likely exacerbate this alteration. The relation between the Southern High Plains aquifer and underlying aquifers is unclear and has generally been inferred from large, regional data sets that do not address specific source waters and the geochemical processes that cause the changes in hydrochemical facies.

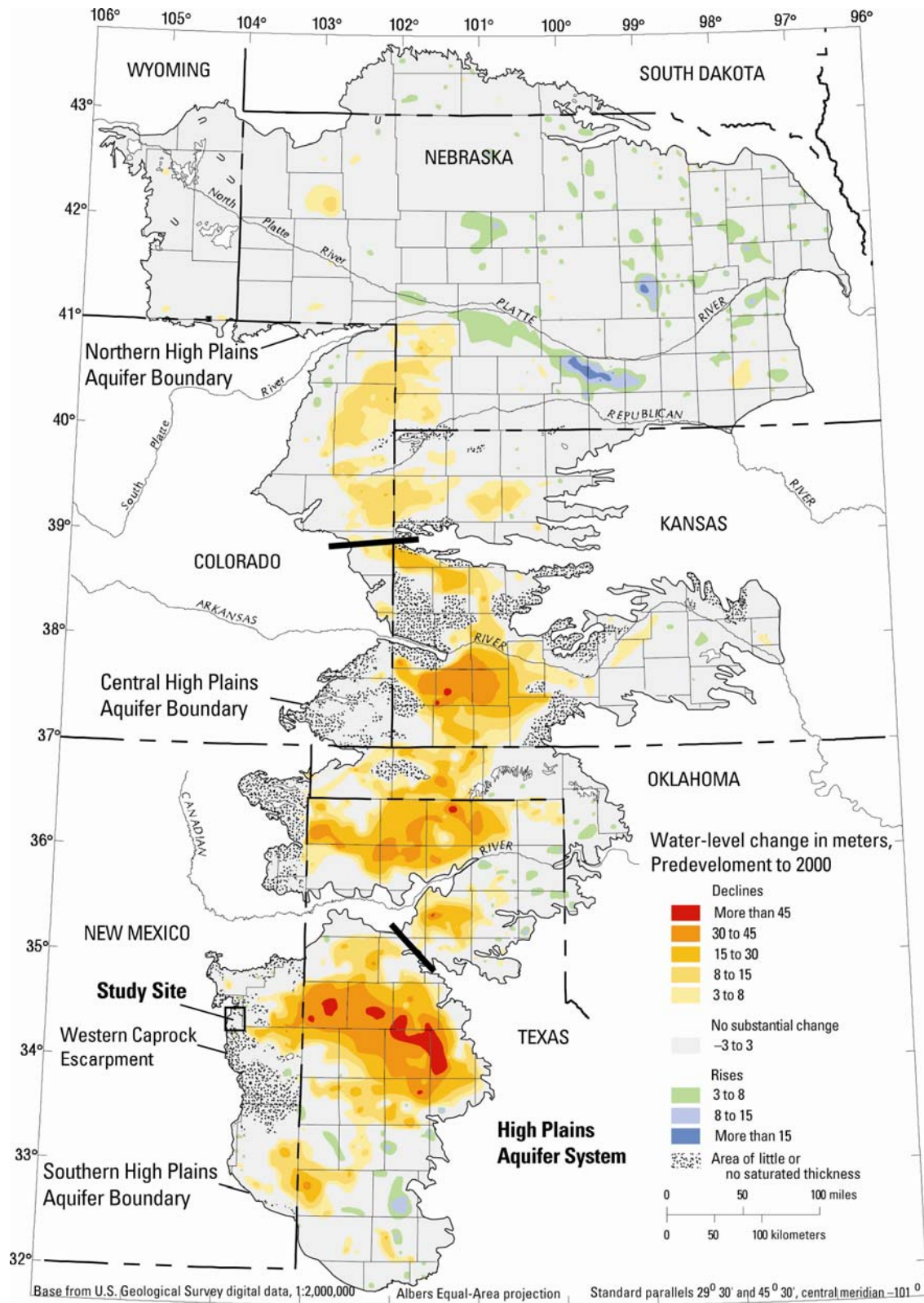


Figure 1. Effect of groundwater mining on the High Plains aquifers (modified from McGuire et al., 2003; courtesy of the U.S. Geological Survey).

The Texas Bureau of Economic Geology and the U.S. Geological Survey have regionally examined flow patterns, groundwater management, and hydrochemical facies in the Southern High Plains aquifer and have included data from underlying aquifers when available. Current issues and understanding of hydrologic properties of the Southern High Plains aquifer can be found in Nativ (1992), Dutton (1995), Scanlon and Goldsmith (1997), McGuire et al. (2003), and McMahon et al. (2007). Previous studies have used traditional geochemical tracers, such as major ions and the isotopic composition of water, to suggest the hydrochemical facies in the Southern High Plains are an effect of saltwater cross-formation flow where available flowpaths are present and underlying aquifers have higher potentiometric surfaces (e.g., Nativ, 1992, Dutton, 1987 and 1995, McMahon et al., 2007). These previous studies have been insufficient for resolving contributions from cross-formational flow and the origin and evolution of aquifer source waters. The goal of this paper is to determine the saltwater origin, identify cross-formational flow between the Southern High Plains aquifer and an underlying aquifer, and examine the geochemical evolution of the local, mixed waters in the Southern High Plains aquifer along the Western Caprock Escarpment by coupling traditional tracers of major ion and trace element concentrations, tritium-helium ($^3\text{H}/^3\text{He}$) and 14-carbon (^{14}C) dating, δD , and $\delta^{18}\text{O}$ with nontraditional tracers of $^{87}\text{Sr}/^{86}\text{Sr}$ and $\delta^{11}\text{B}$. Results of the study will be beneficial to future studies for evaluation of water-quality changes related to groundwater mining.

The study site was chosen because of the limited groundwater use in the area and previously identified spatial differences in hydrochemical facies that indicate strong variability in source-water contributions across the study site (Langman et al., 2004). The site is located in Curry and Roosevelt Counties, New Mexico (fig. 2) along the Western Caprock Escarpment that forms the western boundary of the Southern High Plains and includes lands managed by the U.S. Air Force (fig. 3). A small part of the study site has been actively used by the U.S. Air Force for

non-live-fire training since the 1960s. The land surrounding the training area is managed by the U.S. Air Force as a buffer zone and consists of agricultural land, rangeland, and natural grassland. The study site represents a small area (about 15 kilometers by 10 kilometers) where sufficient well density is present for examining groundwater flow in the Southern High Plains aquifer and its underlying upper Dockum aquifer. To reduce possible human or animal interference in U.S. Air Force operations, groundwater use at the study site has been limited, which has helped to preserve natural flow patterns. Other studies have found that groundwater flow patterns can be highly altered in the Southern High Plains aquifer because of large anthropogenic withdrawals (Langman et al., 2006; McMahon and Böhlke, 2007). The study site includes a part of the Western Caprock Escarpment known locally as “the Mesa” with the remainder of the study site consisting of grasslands, rangeland, and agricultural fields typical of the Southern High Plains (fig. 3). Selected wells from an existing monitoring-well network were used for groundwater sampling and measurement of the potentiometric surfaces of the Southern High Plains aquifer in the Ogallala Formation and the underlying, confined aquifer in the upper Dockum Group. Soil or rock samples were collected from formation exposures along the Mesa in the southwest part of the study site for correlation of groundwater composition and aquifer matrices. Geophysical logs were available from the installation of monitoring wells in 2002 and 2004 for evaluating local characteristics of the aquifer formations.

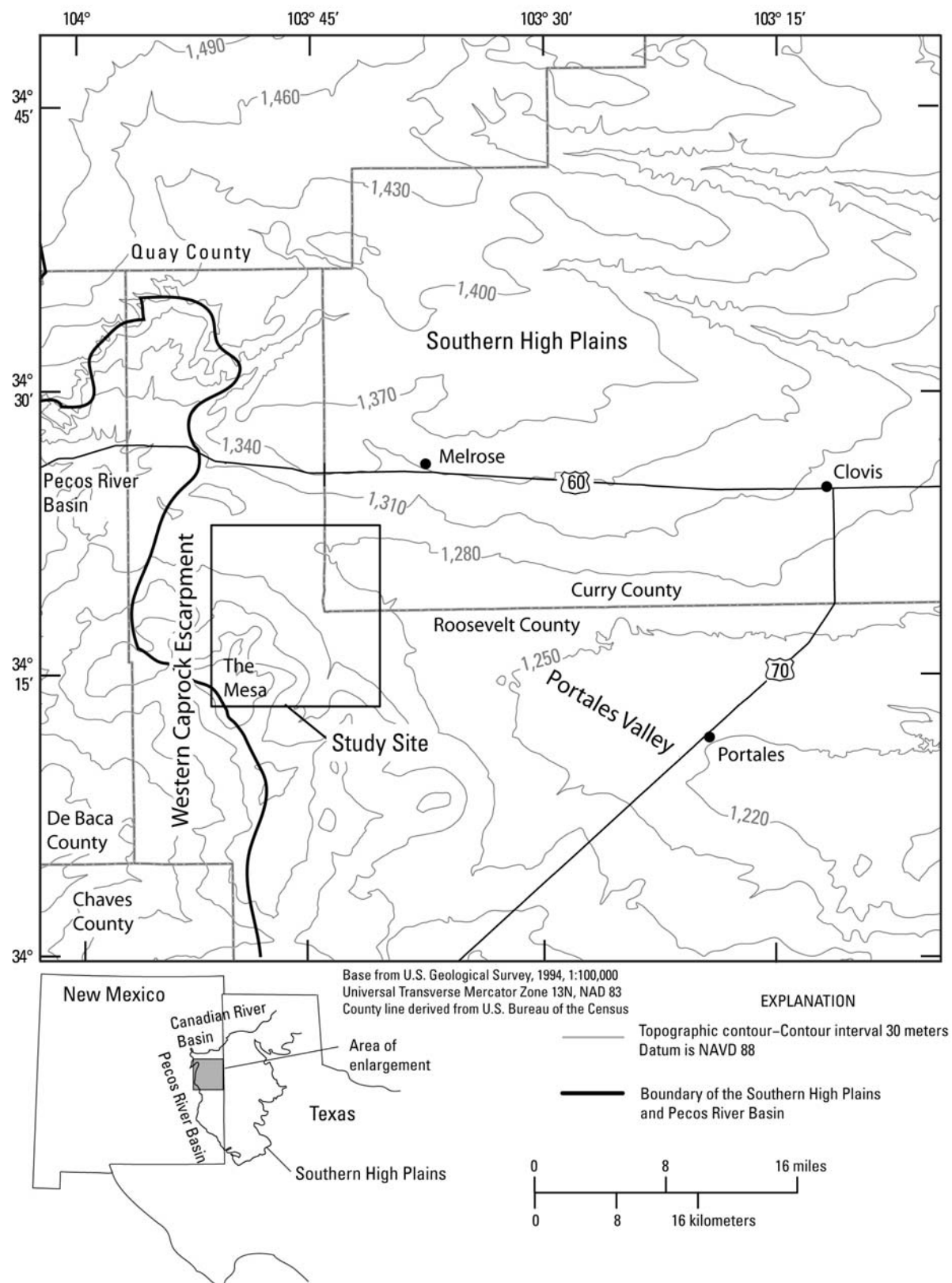
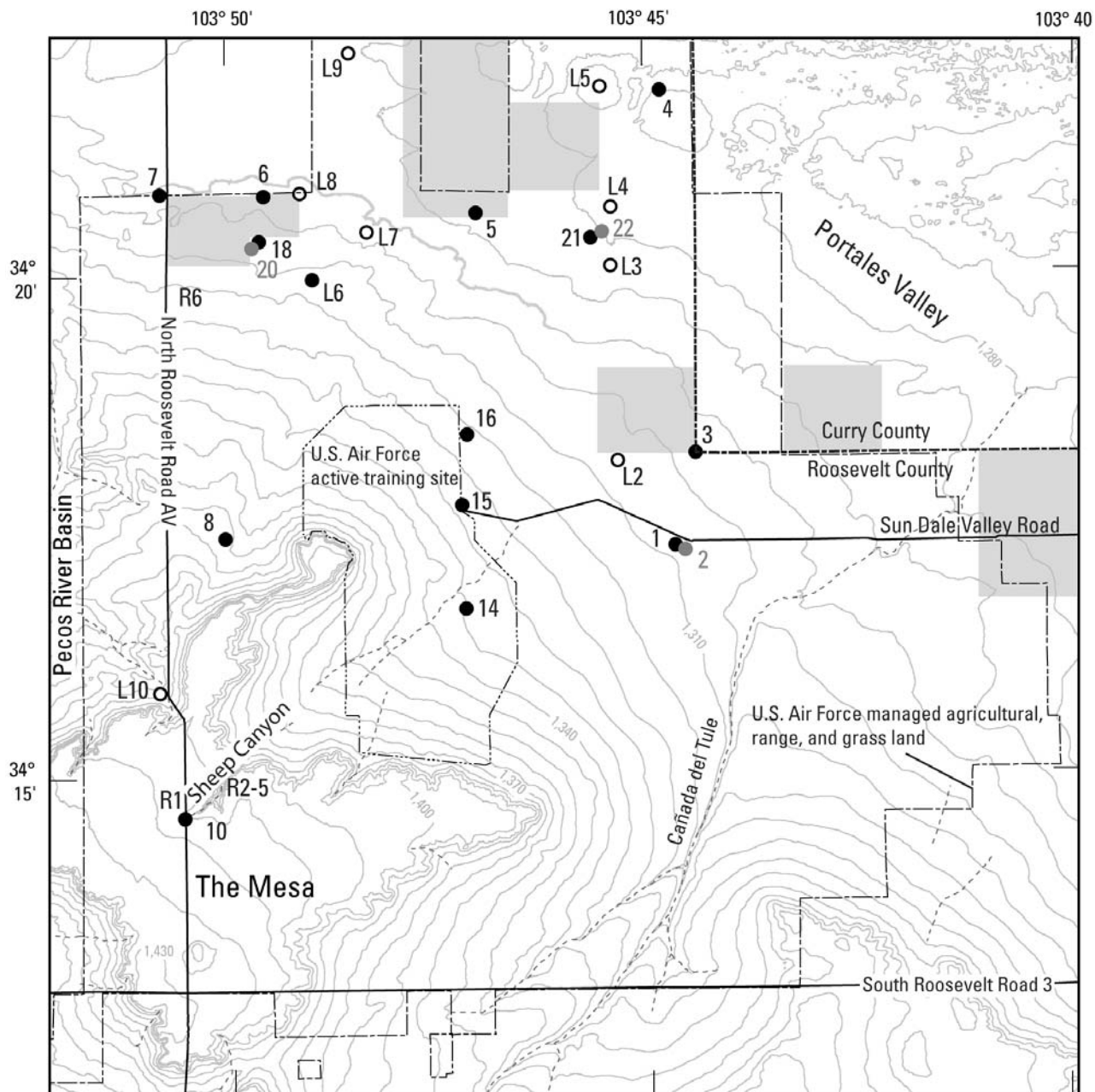


Figure 2. Location of study site.



Base from U.S. Geological Survey digital data, 1994, 1:100,000
Universal Transverse Mercator Zone 13N, NAD 83

County line derived from U.S. Bureau of Census

EXPLANATION

- | | |
|------|---|
| — | Topographic contour—Contour interval is 6 meters. Vertical coordinate information is referenced to NAVD 88. |
| ● 10 | Water-quality and water-level monitoring well and well identifier—well completed in the Ogallala Formation. |
| ○ L1 | Water-level monitoring well and well identifier—well completed in the Ogallala Formation. |
| ● 2 | Water-quality and water-level monitoring well and well identifier—well completed in the Dockum Group. |
| R1 | Soil/rock sample location—samples collected from soil and study site geologic formations. |
| ■ | Active or recently active agricultural fields. Remainder of area is rangeland for cattle or is natural grassland. |

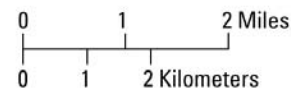


Figure 3. Study site well locations.

GEOLOGIC AND HYDROLOGIC SETTING

The study site is located in the Southern High Plains physiographic region (Fenneman and Johnson, 1946), in the Plains-Mesa Grassland vegetation unit (Dick-Peddie, 1993), atop the Southern High Plains plateau that slopes gently to the east-southeast from eastern New Mexico into west Texas (Fahlquist, 2003). Topography (excluding the caprock escarpment) is open and mostly flat and generally slopes to the east-southeast. The study site is located within a semiarid region (Tuan et al., 1969), and no perennial or intermittent waterbodies are present. The Mesa dominating the southwest part of the study site is a topographic high and is part of the Western Caprock Escarpment that defines the western boundary of the Southern High Plains and its aquifer (Nativ, 1988) (fig. 3).

Structural Framework and Landscape Evolution

The study site is located along the boundary of two related Precambrian basement-rock basins—Tucumcari and Palo Duro (Gustavson, 1996). During the late Paleozoic, the Wichita igneous province and the Red River mobile terrane were faulted and uplifted to form the Amarillo Uplift and the Matador Arch, which produced the Palo Duro Basin (Birsa, 1977). The Tucumcari Basin was formed by the Sierra Grande Uplift, the Pedernal Uplift, Frio Uplift, and the Bravo Dome during the same period (Broadhead and King, 1988). Marine carbonates were deposited in these basins during the Mississippian followed by granitic wash during the Pennsylvanian and early Permian (Gustavson and Finley, 1985). A shallow seaway extended into west Texas and eastern New Mexico during the late Permian that produced halite, anhydrite, dolomite, limestone, and clay-dominated sediments that become the Permian bedded salts (Dutton et al., 1979; Gustavson et al., 1980; Johns, 1989; Baker and Leonard, 1995). The Dockum Group was deposited upon the Permian salts during the Triassic when fluvial, deltaic,

and lacustrine environments were present (Dubiel, 1989). The Laramide Orogeny resulted in the uplift of the southern Rocky Mountains, eastward tilting of strata, receding of the Cretaceous seas, and development of southeasterly-flowing drainage systems that heavily eroded exposed strata including the Dockum (Brand, 1952; Walker, 1978). Erosion of Jurassic, Cretaceous, and Paleogene deposits by river systems allowed the deposition of the Neogene Ogallala (alluvial sediments derived from the tectonically-active Southern Rocky Mountains) atop the eroded Dockum in the region (Gustavson et al., 1980; Knowles et al. 1984).

The regional topography is a result of erosion by paleodrainage systems and subsidence caused by salt dissolution. Formation of the southeasterly-flowing drainage systems following draining of the Cretaceous seas cut channels and valleys up to 45 meters (m) deep in the Triassic deposits (Seni, 1980). The Portales Valley (figs. 2 and 3) is characterized by a northwest-southeast paleochannel (ancient Portales River) eroded into the Dockum that may have been part of the ancestral Brazos River in Texas (Gustavson and Finley, 1985). Such paleodrainage systems were cut off when subsidence of lands around the Southern High Plains formed the table-like structure and ended major fluvial erosion and deposition. The Southern High Plains and the surrounding basins of the Pecos River and Canadian River formed because of Permian-salt dissolution and subsidence in the peripheral salt dissolution zones (younger, higher stratigraphic salt units along the margins of the Southern High Plains) that have undergone greater dissolution than the salt units near the center of the Palo Duro Basin (fig. 4) (Gustavson et al., 1980; Seni, 1980; Simpkins et al., 1981; Gustavson and Finley, 1985; Gustavson, 1986; Dutton, 1987).

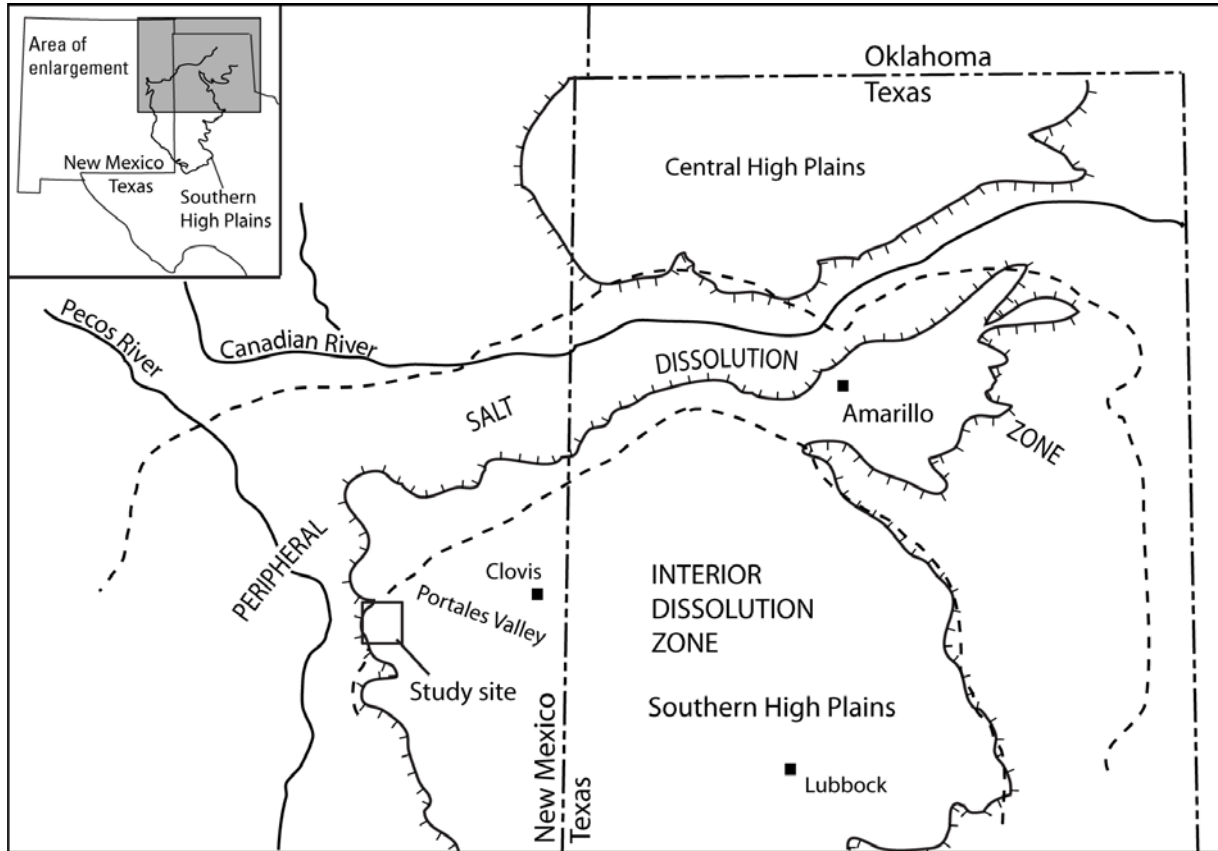


Figure 4. Peripheral salt dissolution zone in the northern part of the Southern High Plains (modified from Gustavson and Finley, 1985; courtesy of the Texas Economic Bureau of Geology).

Stratigraphy

The stratigraphy of the Southern High Plains aquifer at the study site includes the Dockum Group and Ogallala and Blackwater Draw formations (table 1). The Dockum forms the base of the unconfined Southern High Plains aquifer at the study site, consists mostly of shale with some intermixed sandstone and siltstone lenses, and ranges in thickness from about 300 to 370 m (Gustavson and Finley, 1985). The Dockum has informally been divided into upper and lower units based on lithologic characteristics that reflect environmental differences of fluvial, deltaic, and lacustrine deposition (Granata, 1981; Dutton and Simpkins, 1986; Johns, 1989). The lower unit is composed of mudstones and mud-rich sandstones (McGowen et al., 1979). The

upper unit is mud-rich with discontinuous sand deposits and is identified by the reddish-brown, horizontally-bedded or structureless mudstones, siltstones, and sandstones known as “redbeds” (Dutton and Simpkins, 1986).

The Ogallala Formation is the uppermost formation of the central and southern parts of the study site and lies unconformably atop the upper unit of the eastward-dipping Dockum (Dutton et al., 2001). The Ogallala consists of deposits of eolian sand and silt and fluvial and lacustrine sand, silt, clay, and gravel (McLemore, 2001), and ranges in thickness from 10 to 55 m at the study site (Langman et al., 2004). The eolian sand deposits of the late Neogene and Quaternary Blackwater Draw Formation generally overly the Ogallala in the northern part of the study site and can range in thickness from 0 to 25 m in eastern New Mexico (McLemore, 2001). The Blackwater Draw is the primary surface deposit of most of the Southern High Plains and is composed of aggradational sequences of eolian sand, silt, and clay derived from reworked Ogallala and Dockum deposits (Holliday, 1990).

Caliche is typically present in the unsaturated zone of the Blackwater Draw or Ogallala formations in eastern New Mexico (Hart and McAda, 1985). Observations during drilling at the study site have indicated that the caliche is laterally discontinuous, of variable thickness, and typically found within 15 m of the surface. A one-meter thick outcrop of caliche is present near the surface of the Mesa and is exposed along the Mesa rim. Gustavson (1996) indicated that the caliche within the Western Caprock Escarpment (fig. 2) is pedogenic carbonate that accumulated locally during the Neogene.

Table 1. Lithology and stratigraphy of geologic formations in the Southern High Plains and at the study site.

Era	System	Series	Stratigraphic Unit	Lithology	Hydrologic Unit	Study Site
Cenozoic	Quaternary	Holocene, Pleistocene	Site-specific	Windblown sand and silt, fluvial flood plain deposits, playa silt and clay		Blackwater Draw Formation
	Neogene	Miocene	Ogallala	Silty to coarse sand mixed with silty clay and gravel. Caliche common near surface	Southern High Plains aquifer	Ogallala Formation
Mesozoic	Cretaceous	Lower Cretaceous	Site-specific	Fine to medium, thin to thick-bedded sandstone, shale, and limestone		
	Jurassic, Triassic		Site-specific	Shale interbedded with fine to coarse sandstone		Dockum Group (Triassic)
Paleozoic	Permian		Site-specific	Interbedded shale, siltstone, sandstone, gypsum, anhydrite, dolomite, and limestone		Artesia Group San Andres Formation Glorieta Formation (all upper Permian salts)

Hydrogeology

Aquifers underlying the Southern High Plains aquifer have not been as thoroughly investigated and are not currently used as principal source waters (Bradley and Kalaswad, 2003). Groundwater upwelling and flowpaths in and from the Permian salts is poorly understood and likely complex (Dutton, 1989), but high chloride concentrations in the Pecos and Canadian River basins and continued sinkhole formation in the Southern High Plains indicate that salt dissolution and subsidence is still active (Simpkins et al., 1981; Gustavson and Finley, 1985). Dockum aquifers are contained within thin sand deposits embedded in shale layers and typically produce only 4-8 liters per minute (lpm) of water (Trauger, 1972), but may range from 2 to 8,700 lpm (Bradley and Kalaswad, 2003). The surrounding Dockum shale layers are considered impermeable unless fractured (U.S. Nuclear Regulatory Commission, 2005). The source of Dockum water is likely site specific and has been attributed to recharge at basin-margin outcrops and contributions from overlying and underlying formations, in addition to water recharged

during previous climates or emplaced during deposition (Dutton, 1995; Bradley and Kalaswad, 2003). Dutton and Simpkins (1989) and Senger (1987) indicated that the location of groundwater divides in the Dockum would inhibit any substantial recharge from a Dockum aquifer into the Southern High Plains aquifer along the Western Caprock Escarpment. From δD and $\delta^{18}O$ values, Dutton (1995) indicated that Dockum water might have been recharged during the Middle to Late Wisconsinian time (15,000 to 35,000 years before present).

The unconfined Southern High Plains aquifer is highly productive and is the part of the most intensively used aquifer system of the United States (Maupin and Barber, 2005). Hydraulic conductivities in the Southern High Plains aquifer generally range from 3 to 70 m per day, and the saturated thickness in the region generally ranges from 5 to 30 m (Knowles et al., 1984; Hart and McAda, 1985). The variability of saturated thickness was attributed to the erosional contact between the Ogallala and Dockum with thinner thicknesses located at paleouplands and thicker sequences in paleovalleys or paleochannels. The eroded base layer causes the aquifer to be discontinuous near the Western Caprock Escarpment where no saturated thickness may be found along parts of the basin margin (Hart and McAda, 1985). A majority of the annual precipitation falls during summer and early fall, and much of the 46 centimeters (cm) of annual precipitation (Clovis weather station) likely is lost to evapotranspiration (average of 221 cm of annual pan evaporation) (Western Regional Climate Center, 2007a and 2007b). The current view of recharge in the Southern High Plains is that most surface recharge occurs through playa areas and drainage channels and that interplaya areas contribute little recharge (Gustavson et al., 1995; Scanlon and Goldsmith, 1997; Scanlon et al., 2003).

Cross-formational flow from underlying aquifers into the Southern High Plains aquifer likely produces the distinct differences in water composition throughout the Southern High Plains (Nativ, 1992; Nativ and Smith, 1987; McMahon and Böhlke, 2007). Nativ and Smith

(1987) and Nativ (1988) found that different geologic provinces in the Southern High Plains produced different hydrochemical facies in the aquifer. Nativ (1992) indicated that Ogallala water changes from the typical mixed-cation- HCO_3^- facies to Na-HCO_3^- water in local areas of the western Southern High Plains aquifer where the potentiometric surface of the Dockum aquifer(s) is equal to or above the potentiometric surface of Ogallala water. Groundwater in the Southern High Plains aquifer where the aquifer is underlain by Triassic or Permian rocks also contains lower (depleted) $\delta^{18}\text{O}$ values than where the aquifer is underlain by Cretaceous rocks (Nativ and Smith 1987). Dutton and Simpkins (1989) suggested that the depleted isotopic composition of water stored in the Dockum aquifer reflects the influence of Pleistocene climatic variations and the altitude effect of the previous recharge zone of the aquifer in eastern New Mexico, before it was cut off by the incising Pecos and Canadian Rivers.

Previous studies (Nativ and Smith, 1987; Dutton and Simpkins, 1989; Nativ, 1992; and McMahon et al., 2007) have indicated that cross-formational flow of water from the underlying aquifer(s) in the Dockum Group into the Southern High Plains aquifer is probable and likely a local effect. In areas of limited groundwater pumping, McMahon and Böhlke (2007) and McMahon et al. (2004) found strong vertical age gradients in the Southern High Plains aquifer with younger water near the surface of the aquifer and older water near the base of the aquifer. Younger water near the surface was sometimes less than 50 years old indicating young recharge, and deeper water was up to 9,000 years old indicating possible recharge from the early Holocene or late Pleistocene (McMahon et al., 2004). The oldest water at the base of the aquifer also was brackish in composition, which was attributed to the poorer quality of water in underlying aquifers (McMahon and Böhlke, 2007). Results from McMahon and Böhlke (2007) and McMahon et al. (2004) agree with Dutton's (1995) suggestion that Dockum water was recharged during the Middle to Late Wisconsinian time (15,000 to 35,000 years before present) as

estimated from δD and $\delta^{18}O$ values, and that poorer-quality Dockum water is migrating into the Southern High Plains aquifer through cross-formational flow in certain locations.

In addition to changes in water composition from possible cross-formation flow, there is the possible alteration of Southern High Plains groundwater from irrigation (agricultural recharge). Agriculture is the dominant land use in the Southern High Plains and the source of irrigation water is the Southern High Plains aquifer. McMahon et al. (2004) and McMahon and Böhlke (2007) found vertically-stratified water quality in the Southern High Plains aquifer in parts of Texas underlying agricultural areas. Upper stratified layers of different water composition were attributed to recharge facilitated by irrigation that carried larger concentrations of major ions to the top of the water table.

PREVIOUS STUDIES

Regionally, the Texas Bureau of Economic Geology produced a number of reports described above that identified the variability of hydrochemical facies in the Southern High Plains aquifer. In particular, the work of Nativ and others (1992; 1988; Nativ and Gutierrez, 1988; Nativ and Riggio, 1989; Nativ and Smith, 1987) and Dutton and others (1987; 1989; 1995; Dutton and Simpkins, 1986 and 1989; Dutton et al., 1979 and 2001) identified many of the likely source waters and ongoing geologic processes that have and continue to shape the Southern High Plains and its major aquifer. The U.S. Geological Survey has more recently examined groundwater characteristics of the Southern High Plains (in particular, the work of McMahon and others described above (McMahon et al., 2004; McMahon and Böhlke, 2007; and McMahon et al., 2007)) that identified many of the same attributes found by the Texas Bureau of Economic Geology while also more closely examining the effects of agriculture. Both sets of studies were conducted because of the heavy use of groundwater by agriculture in the Southern High Plains

that has substantially increased depth to water (fig. 1) and raised concerns about the long-term viability of the aquifer as the sole source for agriculture in the region.

Locally, the western Southern High Plains aquifer is poorly described because of limited data from the lower density of wells as a result of the reduced aquifer thickness along the Western Caprock Escarpment. Many of the regional studies did not extend across the Texas-New Mexico border because of a lack of data on the New Mexico part of the Southern High Plains. A study by Langman et al. (2006) at a nearby site located between the current study site and Clovis, New Mexico, found overall water-level declines since measurements began in 1954, alteration of groundwater flow patterns, and variable groundwater composition that suggested that the aquifer was likely a mixture of multiple sources from different formations or recharge areas. An examination of groundwater composition and groundwater age at this same site by Falk (2005) found the presence of modern water recharged since the mid-1940s mixed with older water, and it was suggested that different mixtures of these waters produced differences in water composition in the Southern High Plains aquifer at this site.

Langman et al. (2004) examined the Southern High Plains aquifer at the study site in 2002 and 2003. Results of the study indicated declines in water levels of up to 6 m between 1960 and 2003. Groundwater flows northeastward away from the Mesa in a sub-aquifer (local flow system) and into the Portales Valley regional aquifer (regional flow system) where groundwater then flows southeast and east (Langman et al., 2004). A thin (0.5 m), confined aquifer was found in the upper unit of the Dockum about 70 m below land surface during exploratory drilling in the eastern part of the study site. Groundwater composition in the Southern High Plains aquifer was substantially different across the study site, and certain areas indicated some similarity to groundwater composition in the underlying Dockum aquifer (Langman et al., 2004).

Chapter 2: Study Methods

Data collection for this study was implemented with assistance from the U.S. Geological Survey and the U.S. Air Force, but data analysis and interpretation were completed without additional funding or their assistance. The contents of this paper do not reflect views or policies of the U.S. Government. All groundwater data were collected in June 2006 as part of a long-term monitoring project by the U.S. Geological Survey for the U.S. Air Force, and all data are publicly available through the U.S. Geological Survey's NWISWeb website. To characterize inputs to the Southern High Plains aquifer, groundwater samples were collected from the saturated deposits of the Ogallala and Dockum, and soil/rock samples were collected from exposures of the Blackwater Draw, Ogallala, and Dockum. Groundwater and soil/rock samples were analyzed by various laboratories for the constituents listed in table 2. Additionally, geophysical logs were available for select wells installed in 2002 and 2004 to examine the Ogallala and Dockum lithology.

Sixteen wells were selected from the existing U.S. Geological Survey monitoring network for groundwater-sample collection and water-level measurement (table 3 and fig. 3). Thirteen of the wells had a single screen set in the Ogallala. Three wells had screens in the confined aquifer of the upper unit of the Dockum (upper Dockum aquifer). The three Dockum wells were part of three well nests that paired a shallow Ogallala well with a Dockum well at each location (wells 1/2, 18/20, and 21/22). An additional 11 wells set in the Ogallala were selected for water-level measurement only (table 3 and fig. 3). Water levels were measured below a known, fixed altitude prior to well purging using either an electric tape or steel tape. Groundwater samples were collected as 0.45 μm -filtered water.

Table 2. Sample analytes and laboratory analysis methods.

[°C, degrees Celsius; µS/cm, microsiemens per centimeter at 25 degrees Celsius; mg/L, milligrams per liter; µg/L, micrograms per liter; USGS, U.S. Geological Survey; mmol/L, millimoles per liter; δ^X (‰) = (Ratio_{sample}/Ratio_{standard} • 1) x 1000 of specified isotope ratio; ‰, per mil]

Constituent	Description	Method/Lab code	Medium	Laboratory	Analytical precision
Field values	Water temperature, pH, conductance	Orion 130A, Orion 250A+	Water	Field collection	±0.1 °C, ±0.02 pH, ±0.5% µS/cm
Alkalinity	Alkalinity as CaCO ₃	MCAWW 310.1 ²	Water, rock ³	TestAmerica, Denver	1.1 mg/L
Major anions	Br, Cl, F, SO ₄	MCAWW 300.0A ²	Water, rock ³	TestAmerica, Denver	0.06 to 1.2 mg/L
Major cations	Ca, Mg, Na, K	SW846 6010B ⁴	Water, rock ³	TestAmerica, Denver	0.034 to 1.1 mg/L
Trace elements	24 trace elements ⁵	SW846 6010B ⁴ , SW846 6020 ⁴	Water, rock ³	TestAmerica, Denver	0.01 to 2 µg/L
Tritium-helium dating	³ H/ ³ He	USGS 1033 (Schlosser et al., 1989)	Water	Lamont-Doherty Earth Observatory Noble Gas Laboratory	±0.5 years ¹
Dissolved gases	He and O ₂	Gas chromatography with thermal conductivity detector	Water	USGS Reston Chlorofluorocarbon Laboratory	±0.0001 mmol/L
Carbon dating	¹⁴ C, conventional age (Mook and Van der Plicht, 1999)	USGS 3169 (accelerator mass spectrometry)	Water	University of Arizona Accelerator Mass Spectrometry Laboratory	±0.4% of ¹⁴ C content
Water isotopes	² H/ ¹ H, ¹⁸ O/ ¹⁶ O	USGS 1142 (Coplen et al., 1991; Epstein and Mayeda, 1953)	Water	USGS Reston Stable Isotope Laboratory	±2‰ as δD and ±0.2‰ δ ¹⁸ O
Strontium isotopes	⁸⁷ Sr/ ⁸⁶ Sr	Positive thermal ionization mass spectrometry	Water, rock ⁶	USGS Menlo Park Regional Research Laboratory	±0.00002 as ⁸⁷ Sr/ ⁸⁶ Sr
Boron isotopes	¹¹ B/ ¹⁰ B	Negative thermal ionization mass spectrometry	Water, rock ⁶	USGS Menlo Park Regional Research Laboratory	±0.5 ‰ as δ ¹¹ B

¹ Larger uncertainties in age result from corrections in defining the tritogenic ³He (U.S. Geological Survey, 2006).

² U.S. Environmental Protection Agency, 1983.

³ Acid digestate preparation for analysis.

⁴ U.S. Environmental Protection Agency, 1986.

⁵ Ag, Al, As, B, Ba, Be, Cd, Co, Cr, Cu, Fe, Li, Mn, Mo, Ni, Pb, Sb, Se, Si, Sr, Ti, U, V, Zn.

⁶ Leachate: 50 grams of solid and 100 milliliters of deionized water in a 125-ml nalgene bottle. Samples were shaken for 1 hour on a wrist action shaker and then allowed to settle for about 20 hours. Leachate was removed by syringe and filtered through a 0.45-µm syringe filter.

Table 3. Study site monitoring-well and soil/rock sample location information.

[m bls, meters below land surface; nest, well is part of a well nest that pairs a well in the Ogallala Formation with a well in the Dockum Group; -----, not applicable]

Sample type	Site number	Latitude (NAD 83)	Longitude (NAD 83)	Land-surface altitude (NAVD 88)	Well depth (m bls)	Casing material	Pump	Formation
Water-composition and water-level wells	1 (nest)	34° 17' 14"	103° 44' 25"	1,307.2	41	PVC	No	Ogallala
	2 (nest)	34° 17' 14"	103° 44' 25"	1,307.2	73	PVC	No	Dockum
	3	34° 18' 20"	103° 44' 26"	1,300.4	50	Steel	Yes	Ogallala
	4	34° 21' 52"	103° 44' 42"	1,280.2	19	PVC	Yes	Ogallala
	5	34° 20' 31"	103° 46' 47"	1,289.2	31	Steel	Yes	Ogallala
	6	34° 20' 48"	103° 49' 27"	1,301.1	35	Steel	Yes	Ogallala
	7	34° 20' 46"	103° 50' 35"	1,297.9	30	Steel	Yes	Ogallala
	8	34° 17' 20"	103° 49' 47"	1,361.4	34	Steel	No	Ogallala
	10	34° 19' 54"	103° 50' 31"	1,413.6	18	Steel	Yes	Ogallala
	14	34° 16' 40"	103° 47' 05"	1,334.6	37	PVC	No	Ogallala
	15	34° 17' 43"	103° 47' 08"	1,327.2	56	PVC	No	Ogallala
	16	34° 18' 25"	103° 47' 03"	1,317.1	55	PVC	No	Ogallala
	18 (nest)	34° 20' 23"	103° 49' 34"	1,307.8	45	PVC	No	Ogallala
	20 (nest)	34° 20' 23"	103° 49' 34"	1,307.7	91	PVC	No	Dockum
	21 (nest)	34° 20' 45"	103° 44' 26"	1,283.1	20	PVC	No	Ogallala
	22 (nest)	34° 20' 45"	103° 44' 26"	1,283.1	47	PVC	No	Dockum
Water-level wells only	L6	34° 19' 58"	103° 48' 54"	1,311.0	40	Steel	No	Ogallala
	L1	34° 16' 58"	103° 41' 19"	1,291.6	37	Steel	No	Ogallala
	L2	34° 17' 58"	103° 45' 04"	1,307.4	42	Steel	No	Ogallala
	L3	34° 19' 56"	103° 45' 22"	1,287.0	23	Steel	No	Ogallala
	L4	34° 20' 44"	103° 45' 14"	1,285.0	17	Steel	No	Ogallala
	L5	34° 21' 55"	103° 45' 31"	1,277.9	10	PVC	No	Ogallala
	L 6	34° 19' 58"	103° 48' 54"	1,311.0	40	Steel	No	Ogallala
	L7	34° 20' 26"	103° 47' 51"	1,296.6	34	Steel	No	Ogallala
	L 8	34° 20' 50"	103° 48' 51"	1,297.7	35	Steel	No	Ogallala
	L9	34° 22' 00"	103° 47' 55"	1,291.9	15	Steel	No	Ogallala
Soil/rock samples	L10	34° 15' 42"	103° 50' 29"	1,394.5	16	Steel	No	Ogallala
	R1	34° 14' 39"	10350' 32"	1,414	<i>Description:</i> Soil supporting grasses and small shrubs			----
	R2	34° 14' 60"	10350' 00"	1,404				----
	R3	34° 15' 01"	10350' 02"	1,390	Caliche			Ogallala
	R4	34° 14' 60"	10350' 00"	1,399	Brown, silty sand			Ogallala
	R5	34° 15' 04"	10349' 58"	1,387	Reddish conglomerate of silt, sand, and pebbles			Ogallala
	R6	34° 19' 54"	10350' 40"	1,318	Green shale			Dockum
					Red, silty sand			Blackwater

For comparison of formation chemical properties with groundwater solute properties, soil/rock samples were collected at six locations at the study site (table 3 and fig. 3)—one sample from the uppermost soil layer atop the Mesa (R1) near well 10, one sample of the Mesa caliche (R2), two samples of the Ogallala in Sheep Canyon (R3 and 4), one sample of the Dockum in Sheep Canyon (R5), and one sample of the Blackwater Draw along North Roosevelt Road (R6). Two samples were collected from the Ogallala because of variability in the composition of the formation exposure at the Mesa. All soil samples were collected from a horizontal or vertical depth of approximately 0.5 to 1 m into the formation. Additionally, natural gamma and resistivity (lateral) logs were available from the geophysical logging of boreholes for wells 1/2, 18/20, and 21/22 (paired shallow and deep wells).

QUALITY ASSURANCE AND QUALITY CONTROL

To ensure an accurate water-level measurement and that water levels were stable, water level was repeatedly measured prior to purging. During purging, field values of specific conductance, water temperature, dissolved oxygen, and pH were monitored in a flowthrough chamber and allowed to stabilize prior to sample collection. Following a purge of at least one well volume, field measurements were deemed stable if a minimum of three or more sequential measurements during a minimum 10-minute period were within the following parameter ranges: specific conductance, $\pm 0.3\%$; temperature, $\pm 0.2^{\circ}\text{C}$; dissolved oxygen, $\pm 0.3\text{ mg/L}$; and pH, ± 0.1 standard unit (Wilde and Radtke, 2005). Sequential replicate samples were collected at randomly selected wells to evaluate laboratory precision. Matrix-spike and matrix-spike duplicate samples were collected to ascertain matrix interference. One field-equipment blank was collected to determine the adequacy of cleaning procedures of the portable submersible pump.

Analysis of the strontium (Sr) and boron (B) isotopes was conducted at Tom Bullen's U.S. Geological Survey research laboratory in Menlo Park, California by John Patrick. Due to the lack of a standardized method for referencing these analyses, analytical procedures are presented below. Strontium purification was conducted using eichrome Sr-spec resin. The resin was cleaned thoroughly by warming on a hotplate for a week. The resin was transferred to Teflon 50ul micro columns. A sample volume was loaded to typically obtain 250 nanograms (ng) Sr and eluted with 4M nitric acid. Ratios of $^{87}\text{Sr}/^{86}\text{Sr}$ ratios were measured on a Finnigan Mat 261 thermal ionization mass spectrometer (TIMS). The Sr is mixed with phosphoric acid and loaded on degassed zone refined Ta filaments, and the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios are normalized to $^{86}\text{Sr}/^{88}\text{Sr}$ of 0.1194. Long-term precision on the NIST Sr 987 is better than 0.00003 (2 sigma, 95% confidence level). The $^{11}\text{B}/^{10}\text{B}$ ratios were measured by negative TIMS on the same instrument used for Sr isotope analysis. Sufficient water to supply 2 ng of B was loaded directly onto degassed, zone refined Re filaments. The boron isotopes were measured as the BO_2 species at masses 42 and 43. A NIST 951 boric acid and seawater were measured on each sample turret. The long-term $^{11}\text{B}/^{10}\text{B}$ ratio for seawater relative to NIST 951 is +39.5‰. The typical agreement of replicate analyses of a sample is with 1‰.

DATA ANALYSIS AND TRACER APPLICATION

It was expected that the Permian salts, clay-dominated Dockum, and mixed alluvium of the Ogallala would impart different concentration and isotopic signatures, and the longer recharge pathways associated with the Permian salts and Dockum would produce older groundwater ages. Initial data exploration consisted of graphical (matrix plots) and multivariate statistical analysis of the major ion and trace element data groups. Principal component analysis, PCA (S-PLUS 7.0, Insightful Corporation, 2005), was used as a screening tool to identify linear

combinations of data (mole units) that largely explain groundwater-composition variation amongst the data groups (loading values are presented where appropriate). Major ion and trace element concentrations were used as indicators of water-rock interactions and reduction-oxidation conditions (Hem, 1989). The isotopic composition of water ($^2\text{H}/^1\text{H}$ as δD and $^{18}\text{O}/^{16}\text{O}$ as $\delta^{18}\text{O}$) was analyzed to constrain hydrologic flowpaths because of the variation in isotopic composition of precipitation that may discriminate recharge areas or recharge during different climates (Genereux and Hooper, 1998; Ingraham, 1998). The water isotopes were used to estimate fractional contributions of source waters by inserting δD and $\delta^{18}\text{O}$ values into a binary, isotope-mixing equation (Eby, 2004):

$$R_M = R_A f_A + R_B (1-f_A), \quad (1)$$

R = isotopic ratio, M = mixture, A = component 1, B = component 2, f = compositional fraction of mixture.

Groundwater samples were dated using tritium (^3H) and the helium-3 isotope (^3He) and ^{14}C that are incorporated into precipitation and carried to an aquifer through recharge. The $^3\text{H}/^3\text{He}$ method was used for suspected young waters (less than 100 years old). This method mass balances the helium isotopes to determine the amount of ^3He derived from radioactive decay of ^3H in the water sample (Schlosser et al., 1989). The $^3\text{H}/^3\text{He}$ method is not affected by reducing conditions that were known to exist in the Dockum aquifer. For wells where excess helium concentrations were present (excess helium may indicate old water), groundwater ages were calculated using the conventional ^{14}C age determination as described by Mook and van der Plicht (1999). In the conventional age determination, the ^{13}C isotopic fractionation is taken into account by normalizing to -25‰ with respect to the Pee Dee Belemite standard, and the radiocarbon age is determined by measuring the $^{14}\text{C}/^{13}\text{C}$ ratio in a sample and comparing that ratio with a similar one measured for known standards (Mook and Van der Plicht, 1999). The final carbon activity percent modern carbon (pmC) values were used to determine unadjusted ages before present (set

to 1950), which do not account for any geochemical reactions or incorporation of additional carbon during infiltration and recharge to or within the aquifer.

Because major ion and δD and $\delta^{18}O$ values have shown to be highly variable in the Southern High Plains and Dockum aquifers (Nativ, 1988; Dutton, 1995), Sr concentrations and the isotope ratio of radiogenic ^{87}Sr and stable ^{86}Sr ($^{87}Sr/^{86}Sr$) were used to examine water-rock interactions and further constrain likely source waters. Strontium is a prevalent trace element; is a divalent cation that will substitute for calcium in carbonates, sulphates, feldspars and other rock minerals; has four stable isotopes (^{84}Sr , 0.56%; ^{86}Sr , 9.87%; ^{87}Sr , 7.04%; and ^{88}Sr , 82.53%); and is a useful geochemical tracer for chemical weathering such as water-rock interactions in aquifers (Stewart et al., 1998; Bullen and Kendall, 1998). Mass fractionation of Sr is relatively small compared to traditional isotope tracers such as H, C, O, and S, and fractionation of Sr isotopes from biogeochemical processes and instrument analysis is corrected for by normalizing to a standard $^{88}Sr/^{86}Sr$ ratio (Capo et al., 1998). With this fractionation removed, the measured $^{87}Sr/^{86}Sr$ ratio reflects only variations derived from the source such as dissolution of Sr-bearing minerals or labile Sr that represents the exchangeable Sr adsorbed to mineral or organic matter surfaces (Capo et al., 1998).

Precipitation can provide some input of Sr, but the main factor controlling the Sr concentration and $^{87}Sr/^{86}Sr$ ratio is the availability of the element in the aquifer matrix (Sr pool). The Sr pool is all available matrix sources, which are predominantly labile Sr from exchangeable sites or the dissolution of Sr-bearing minerals where more soluble minerals will have a greater influence (Johnson and Depaolo, 1994; Bullen et al., 1997). Various rock types develop different $^{87}Sr/^{86}Sr$ ratios because of the chemical fractionation of Sr during mineral formation and the influence of mineral age where radiogenic ^{87}Sr increases from the β -decay of ^{87}Rb (Nimz, 1998). With a difference between the $^{87}Sr/^{86}Sr$ ratio of waters entering an aquifer and that of the aquifer

matrix, it is possible to quantitatively assess water–rock interactions (e.g., Banner et al., 1989, 1994; Johnson and DePaolo, 1994; Bullen et al., 1996; Johnson and DePaolo, 1997; Naftz et al., 1997). Inverse mass-balance calculations of the Sr results were used to quantify chemical weathering contributions. Modifying the isotope-mixing equation (1) with associated concentrations and an additional variable for Sr-mineral dissolution/labile Sr (total chemical weathering from water-rock interaction), the mixing equation (2) was used to calculate an estimated contribution from chemical weathering and fractional contribution of each water source to the mixture:

$$R_M M = R_A f_A A + R_B f_B B + R_C f_C C + R_D f_D D \quad (2)$$

R = isotopic ratio, f = compositional fraction of component,

A–D, M = mixture, source water, or chemical weathering component, subscript indicates source and capital letter indicates concentration of the component.

Microsoft Excel Solver (what-if-analysis tool) was used to perform the inverse calculations (precision equal to 0.00001, convergence set at 0.0001). Each component fraction was adjusted along with the chemical-weathering variable that represented the Sr mass and isotopic contribution from water-rock interactions. Each well was individually analyzed (as opposed to a model fit of well groups) because of the likely difference in Sr contribution from water-rock interactions from differences in groundwater ages (time of mineral dissolution or contribution of labile Sr). The inverse calculator varied the possible chemical weathering input and the fractional contribution of each likely water source that had a known Sr signal (concentration and isotopic ratio) to minimize the sum of the square of the residuals of the Sr calculated output for each well site and the known Sr concentration and $^{87}\text{Sr}/^{86}\text{Sr}$ ratio. Additionally, a sensitivity analysis was performed to examine the precision uncertainty of the strontium analyses. The inverse calculations were run with possible larger and smaller values for the each input data given the $\pm 3\%$ precision for the strontium concentrations and ± 0.00002

precision for the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios. The total possible range of outputted values is presented. The outputted ranges did not indicate significant differences given the variable inputs, which indicate sufficient analytical precision to analyze differences amongst the laboratory values.

Boron concentrations and stable isotope ratios ($^{11}\text{B}/^{10}\text{B}$ as $\delta^{11}\text{B}$) were analyzed to refine the influence of water-rock interactions because of the possible limited range of $^{87}\text{Sr}/^{86}\text{Sr}$ from the predominance of siliciclastic sediments that comprise the Ogallala and Dockum. Boron is an abundant element in the earth's crust and is highly mobile in natural waters where it exists in only one oxidation state but forms two major oxides—borate ion ($\text{B}(\text{OH})_4^-$) and boric acid ($\text{B}(\text{OH})_3$) (Bullen and Kendall, 1998; Nimz, 1998). Boron speciation is a function of pH, the heavier B isotope is the dominant species (80.18%), and $\delta^{11}\text{B}$ values can indicate differences in flowpaths and formation interaction through different mineral assemblages and changes in pH (Bullen and Kendall, 1998). At a pH of 7, boron in solution is predominantly boric acid, and the borate anion is the principal form in solutions with a pH greater than 8 (Kakihana et al., 1977; Hershey et al., 1986). Boron is highly sensitive to water-rock interactions, its concentration can span over 4 orders of magnitude, and $\delta^{11}\text{B}$ can range from -30‰ up to +60‰ (Leeman and Sisson, 1996; Palmer and Swihart, 1996). Boron will fractionate during mineral crystallization (Oi et al., 1989), biological activity and changes in pH conditions (Vengosh et al., 1994; Eisenhut et al., 1996), and clay mineral adsorption (Schwarcz et al., 1969). Adsorption of B onto solid surfaces preferentially removes ^{10}B (Lemarchand et al., 2005; Palmer et al., 1987), and the fractionation of boron isotopes due to adsorption is apparent in the enrichment of ^{11}B in seawater (average $\delta^{11}\text{B}$ value of +40‰), which is typically 40 to 50‰ greater than average continental crust values (Barth, 2000). Precipitation $\delta^{11}\text{B}$ values generally are lighter than seawater (Rose-Koga et al., 2006). Silicate rocks generally have negative isotopic compositions (typically -10‰ to 0‰), are lighter than any other rock source, and isotopic fractionation from dissolution of

these rocks is none to very small (Spivack et al., 1987; Arnorsson and Andresdottir, 1995).

Shales usually are enriched in B compared to igneous rocks because of adsorption, and ^{11}B is preferentially incorporated into boric acid in solution while ^{10}B is preferentially incorporated into the borate ion in the solid/sorbed phase (Kakihana et al., 1977; Spivack et al., 1987).

Chapter 3: Saltwater Origin and Cross-Formational Flow in the Southern High Plains Aquifer

From previous studies, it is possible to create a hypothetical model of potential flowpaths at the study site (fig. 5). The presence of groundwater atop the Western Caprock Escarpment (Langman et al., 2004) indicates local recharge along the topographic high (the Mesa). Dissolution of Permian salts has occurred, is continuing to occur, and is probably strongest along the caprock escarpment (Gustavson and Finley, 1985; McGookey et al., 1985). Dissolution and subsidence of the Permian salts has likely fractured the Dockum shales (Gustavson and Finley, 1985; Goldstein and Collins, 1984). Recharge to the Permian salts from overlying groundwaters has likely occurred since emplacement of the salts and causes continued dissolution (Gustavson et al., 1980; Gustavson and Finley, 1985; Gustavson, 1986). Cross-formational flow between the Permian salts, Dockum, and Ogallala is possible because of preferential pathways created by fracturing of the Dockum shales from salt subsidence. What remains unanswered is where and to what extent is saltwater moving from the Permian salts and interacting with the waters and rock of the Dockum and Ogallala that subsequently produces the wide variability of groundwater composition at the study site in the Southern High Plains aquifer.

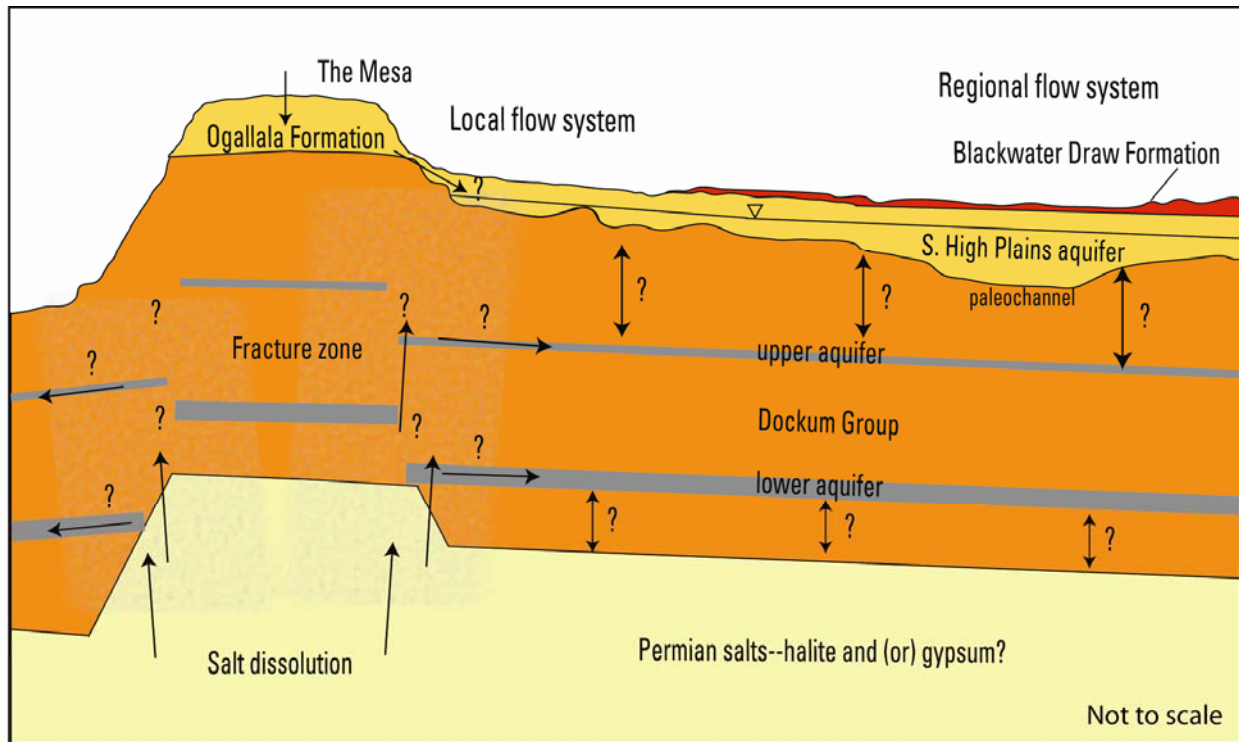


Figure 5. Hypothetical model of possible groundwater flowpaths and geologic relations at the study site.

FORMATION PROPERTIES

Lithologic descriptions and geophysical logs recorded during construction of paired Ogallala/Dockum wells (2, 20, and 22) indicate sharp distinctions in formation composition between the Ogallala (mixed silicate sands) and Dockum (mixed silicate clays) at the study site (fig. 6). No evaporite or limestone deposits were present in any formation except for a thin (<0.5 m) caliche deposit within 5 m of the surface at all three locations. Permeable gravel or mixed-sand deposits were located at or near the Ogallala-Dockum contact. Silt, sand, and sandstone stringers are present in the upper Dockum and compose the permeable sequences of the upper Dockum aquifer.

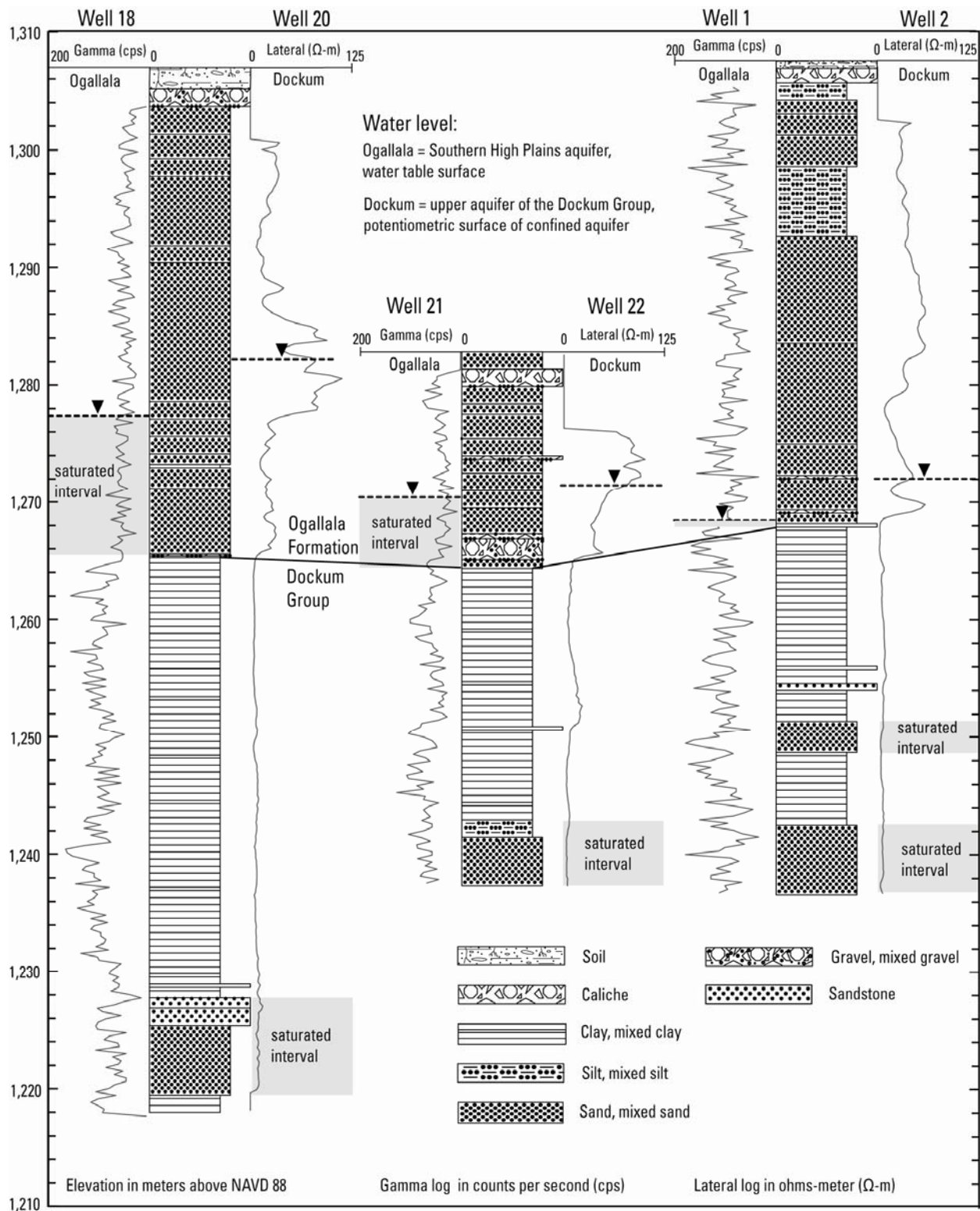
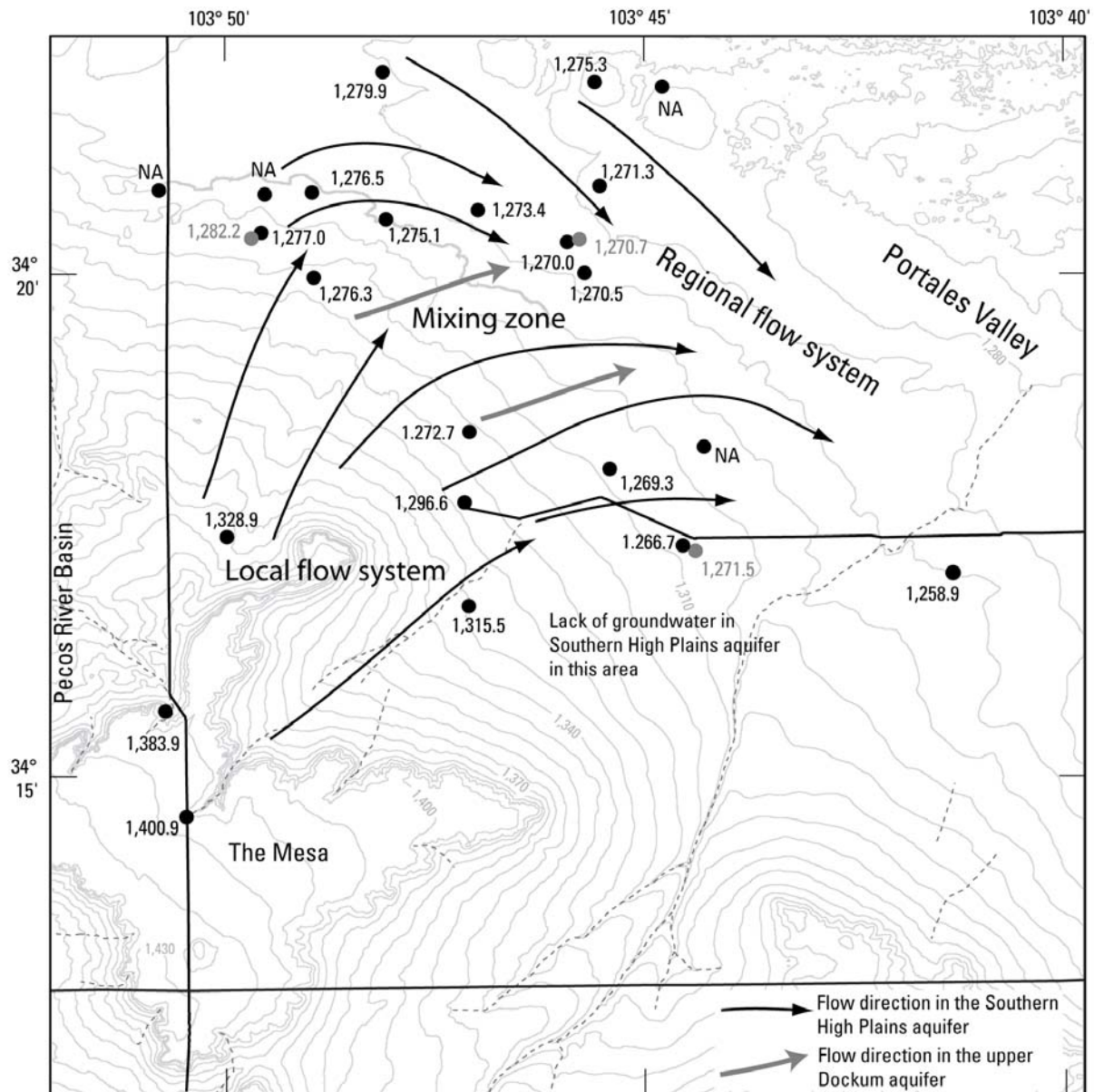


Figure 6. Lithology, geophysical logs, saturated intervals, and potentiometric surfaces for the Ogallala Formation and Dockum Group at paired well locations (water level from June 2006).

GROUNDWATER FLOW AND POTENTIOMETRIC SURFACES

The sub-aquifer (local flow system) of the study site (wells 8, 14–16) originates along the Western Caprock Escarpment within the salt dissolution zone (fig. 4) and drains groundwater from the Mesa (well 10). The local flow system moves groundwater northeastward until this system merges with the regional aquifer (regional flow system) (wells 4–7) that is defined by the paleochannel of the Portales Valley (fig. 7). The area where the two flow systems merge and mix contains wells 3, 18, 21, and L6 and is termed the “mixing zone” for this study. The structural high of the Mesa forms the local flow system at a higher altitude than the surrounding regional flow system and interaction between the systems is limited to the mixing zone in the north and northeastern parts of the study site (fig. 8). Groundwater in the upper Dockum aquifer underlying the local flow system appears to flow easterly to northeasterly. Within the regional flow system of the Southern High Plains, flow is dictated by the Portales Valley paleochannel that is visible in the Ogallala-Dockum contact (fig. 8). The highest elevation of the Ogallala/Dockum contact (fig. 6), a lack of groundwater in well 1 in the Southern High Plains aquifer, and a potentiometric surface in the paired Dockum well (2) higher than the base of the Southern High Plains aquifer indicates a structural high and lack of cross-formational flow in the eastern part of the local flow system. The three boreholes drilled into the Dockum (wells 2, 20, and 22) showed a range of 18 to 38 m between the bottom of the Ogallala and the upper Dockum aquifer, and this interval consisted primarily of redbed shales.



Base from U.S. Geological Survey digital data, 1994, 1:100,000
Universal Transverse Mercator Zone 13N, NAD 83

0 1 2 miles
0 1 2 kilometers

EXPLANATION

- Dirt road — Paved road - - - - - Drainage channel
- 1,430 - Topographic contour—Contour interval is 6 meters. Vertical coordinate datum is NAVD 88.
- 1,400.9 Well location—Altitude of water level in feet above NAVD 88. Well is located in the Southern High Plains aquifer in the Ogallala Formation.
- 1,271.5 Well location—Altitude of water level in feet above NAVD 88. Well is located in the confined aquifer in the upper Dockum Group.
- NA Water-level measurement was unable to be collected because pump was on upon arrival at the well or the measurement was unable to be collected because of other well access issues.

Figure 7. Groundwater altitudes and flowpaths in the Southern High Plains aquifer and the upper Dockum aquifer at the study site.

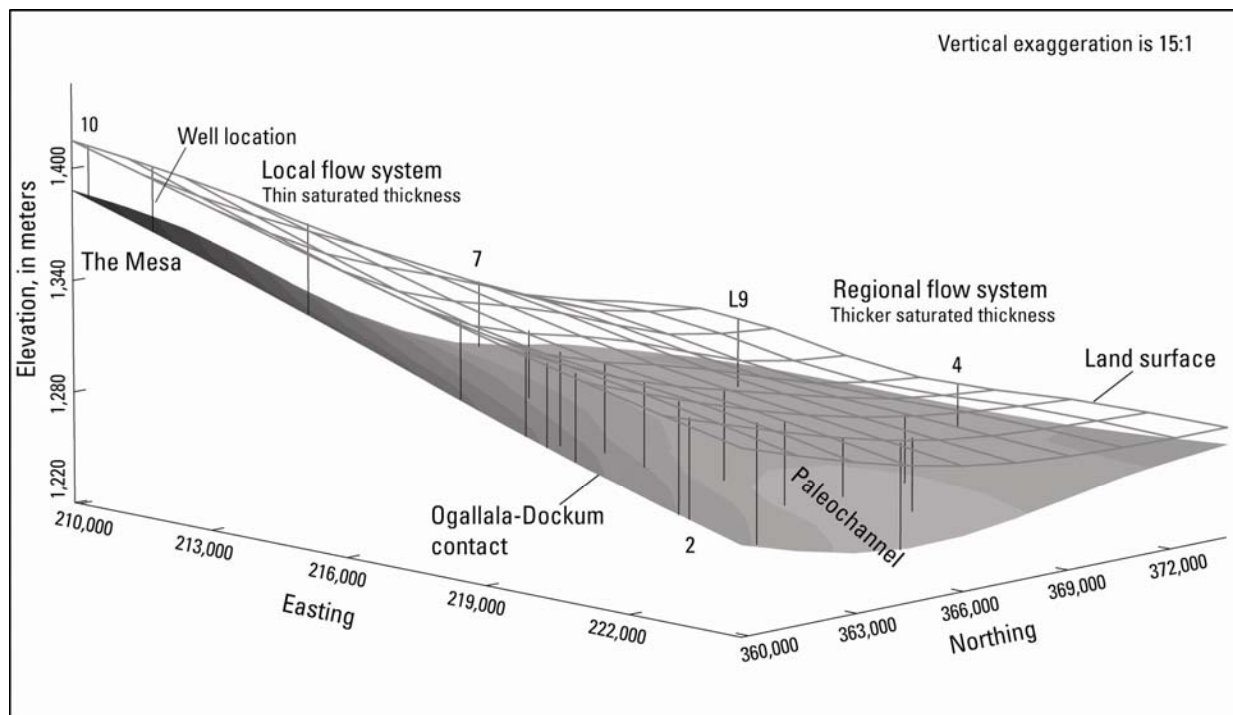


Figure 8. Land surface and Ogallala Formation-Dockum Group contact topography at the study site. Select well names shown for location reference.

Vertical recharge from the surface or from underlying aquifers superimposes upon lateral flow in the Ogallala and Dockum that may produce groundwater mixing of various ages along flowpaths in the Southern High Plains aquifer and the confined aquifer of the upper Dockum. All three wells in the Dockum exhibited a potentiometric surface greater than the potentiometric surface in the Ogallala (fig. 6), suggesting that upward cross-formational flow is possible in the local and regional flow systems. Vertical hydraulic gradients at the paired wells were -0.15 (wells 1/2), -0.11 (wells 18/20), and -0.03 (wells 21/22) and indicate a lessening of the vertical gradient moving away from the Mesa. For cross-formational flow to occur, a permeable pathway also must be present in addition to the higher potentiometric surface in the upper Dockum aquifer. Low permeability is typically associated with the clay-dominated Dockum, but drill cuttings and geophysical logging indicated small, horizontal sand and silt stringers in the upper Dockum (fig. 6). Additionally, sub-horizontal fractures in the Dockum shales around areas of

subsidence in the Southern High Plains, such as the Western Caprock Escarpment, have been reported by Gustavson et al. (1980). A continuous recovery measurement of water level at well 15 in 2006 (dedicated transducer) following a well purge may have recorded cross-formational flow from the Dockum into the Ogallala (fig. 9). The initial recovery was not recorded (3 days passed before water level rose above the transducer), so the initial refilling of the well from the Ogallala Formation was not observed. The small hydraulic conductivities of this late portion of the recovery could represent leakage from the Dockum shales.

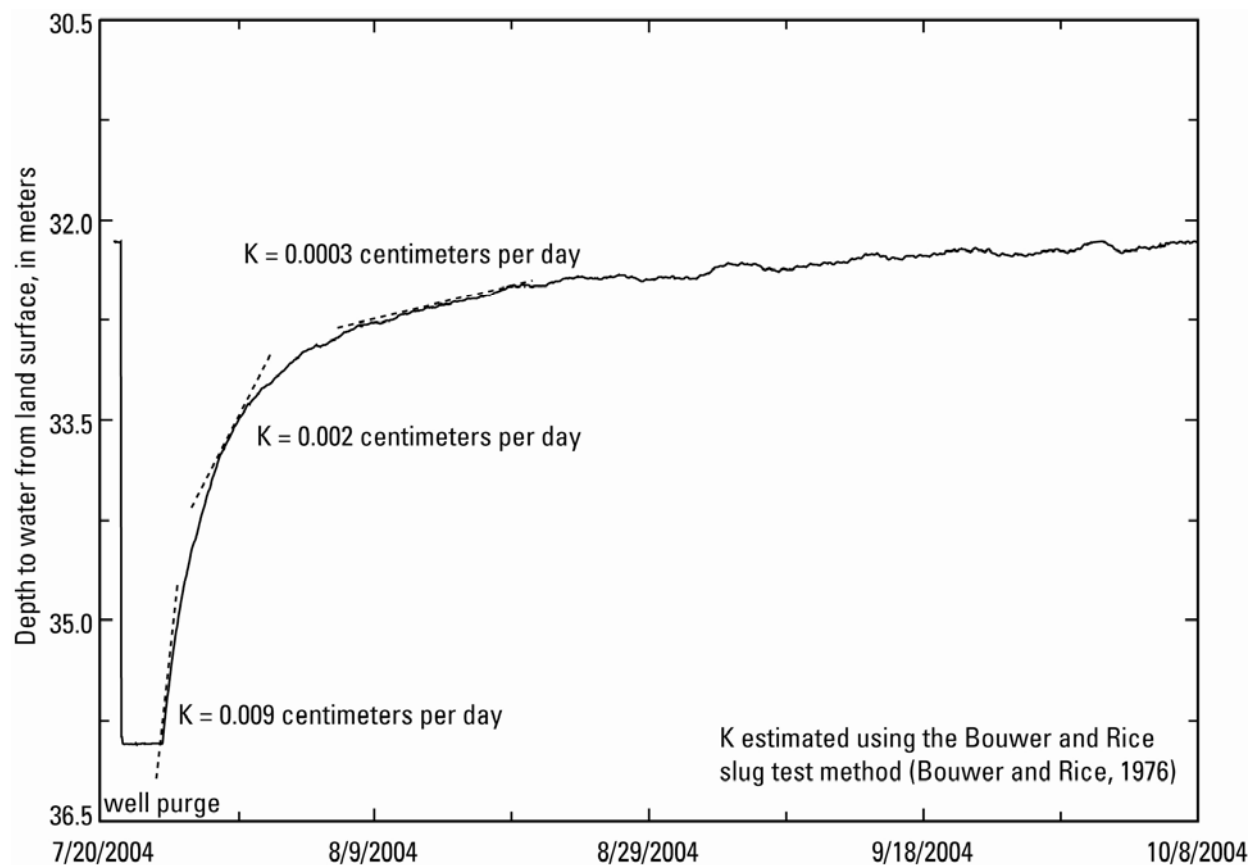


Figure 9. Water-level recovery at well 15 following a well purge in 2006.

A temperature profile of the water column in well 15 was conducted to examine possible temperature stratification that may indicate cross-formational flow from differences in water temperature between Dockum and Ogallala water (fig. 10). The profile indicated a decreasing

temperature from the top of the water table to the middle of the water column where the temperature stabilized then began to increase with depth. Although this increase in temperature was small (about 0.1°C), the slight temperature stratification in the lower part of the water column likely reflects the intrusion of warmer water from the Dockum. The stratification was very limited and was likely minimized because of the small difference in temperatures between the two aquifers and the large hydraulic conductivity of the mixed alluvium of the Ogallala that would quickly mix the two waters in the small saturated interval (10 to 25 m in the local flow system wells).

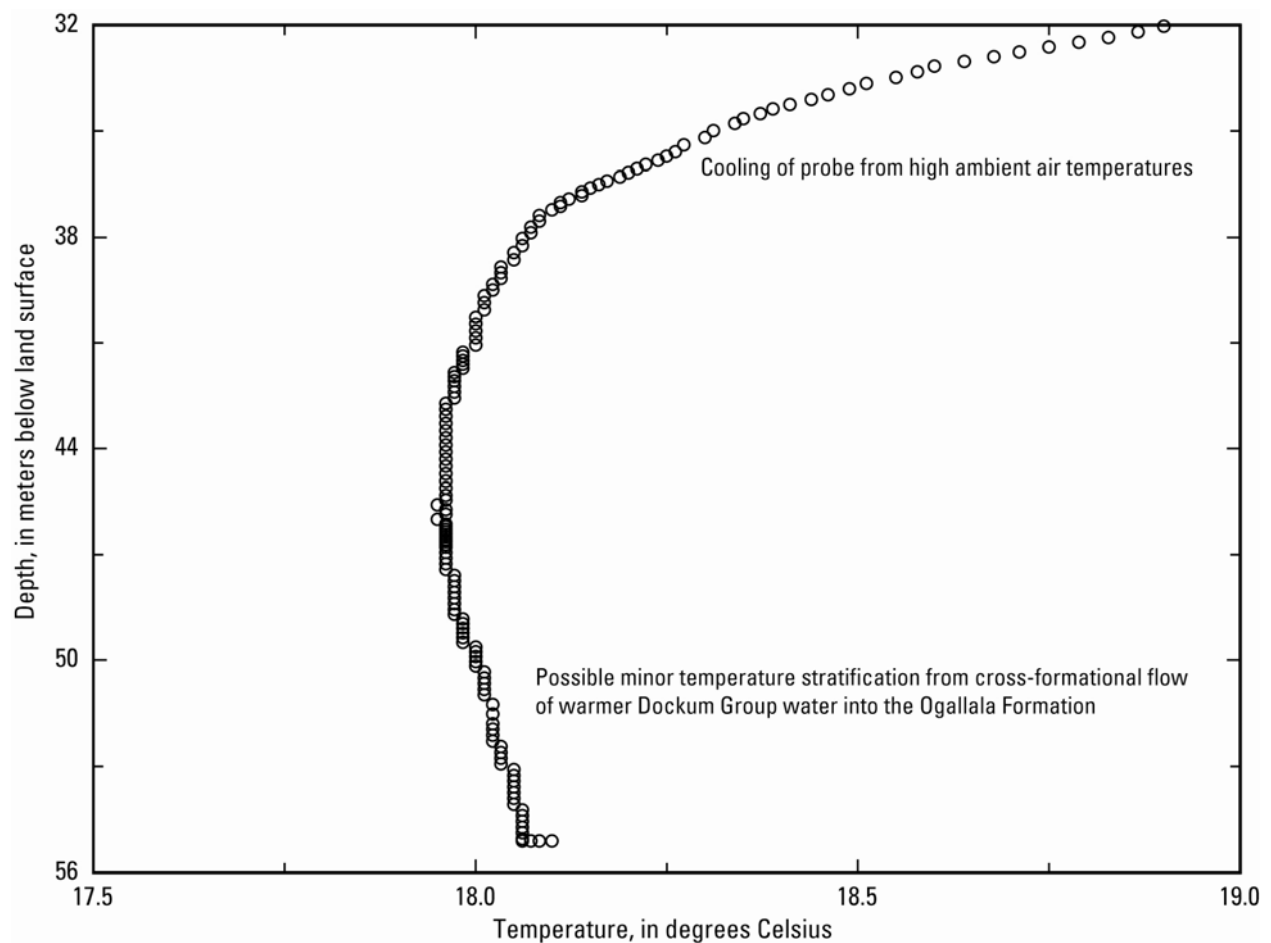


Figure 10. Temperature profile of water column in well 15, June 2006.

GROUNDWATER COMPOSITION

Groundwater hydrochemical facies are representative of atmospheric and anthropogenic inputs and subsequent water-rock interactions, and long water-rock interactions will increase solute concentrations in response to dissolution reactions with formation minerals (Bullen and Kendall, 1998). Groundwater at the study site shows a strong contrast in hydrochemical facies—a mixed cation- HCO_3^- water in the regional flow system and atop the Mesa (well 10), and a Na-Cl or Na-mixed anion water in the local flow system and in the upper Dockum aquifer (figs. 11 and 12 and table 4). Mixed cation-mixed anion water or mixed cation- SO_4^{2-} water is present in the mixing zone. Principal component analysis strongly indicates that Na and Cl are the dominant major ion variables (loading values of -0.64 and -0.76 of the 1st component) affecting changes in water type at the study site. The halite-influenced water of the local flow system becomes a mixed-cation water in the mixing zone because of the dominance of the regional flow system, but water composition differences in the local flow system and upper Dockum aquifer indicate multiple influences affecting these waters prior to mixing with regional water. A detectable but more limited SO_4^{2-} variability identified by PCA (2nd component variable with a loading value smaller than Na and Cl) indicates an additional influence specific to the mixing zone. This SO_4^{2-} source could be dissolution of Permian gypsum and cross-formational flow into the Southern High Plains aquifer that is not spatially consistent with Permian-halite dissolution or a local effect such as agricultural recharge (crop fields are present in this area but not in the local flow system).

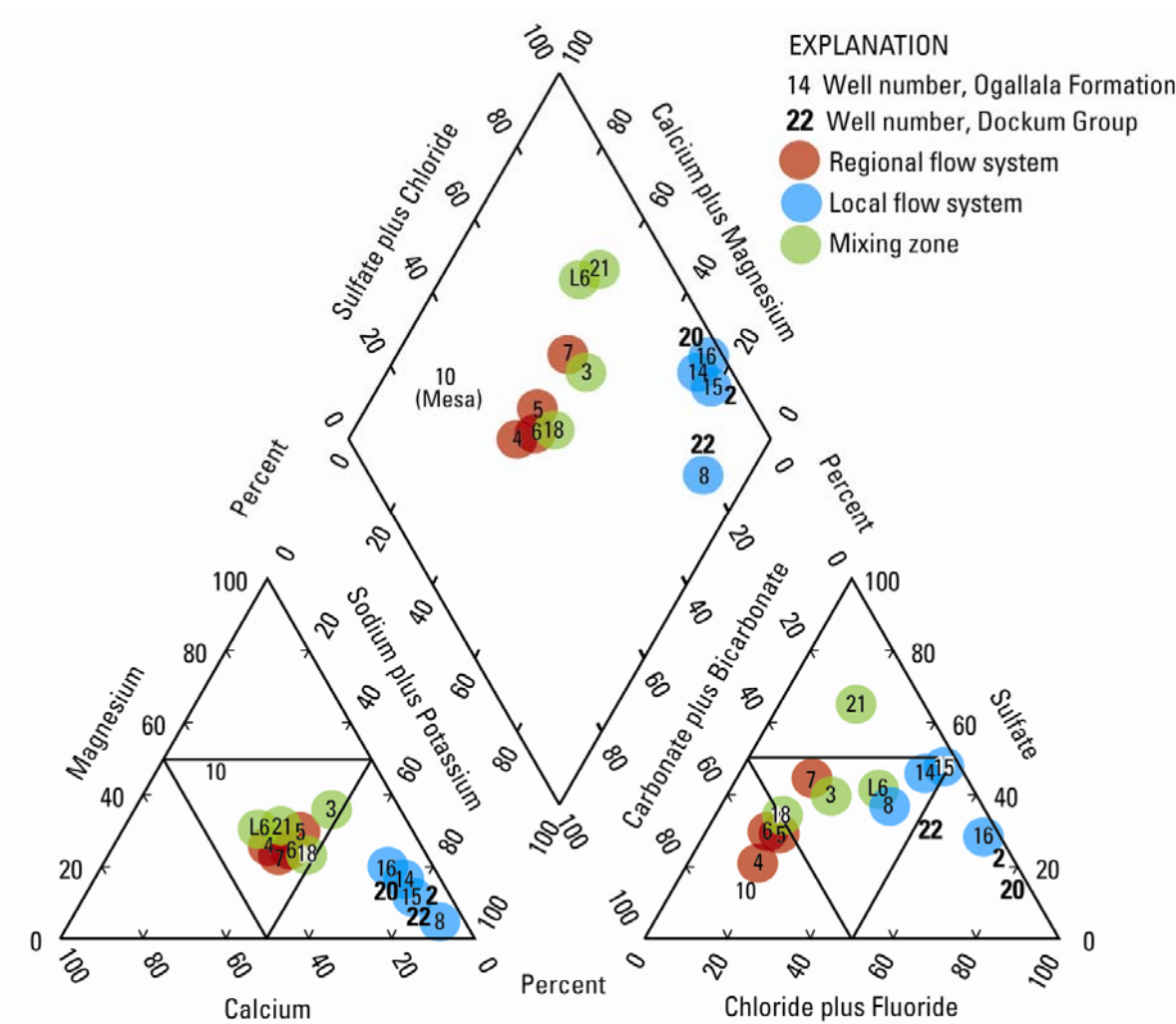


Figure 11. Major-ion relations in groundwater at the study site, June 2006.

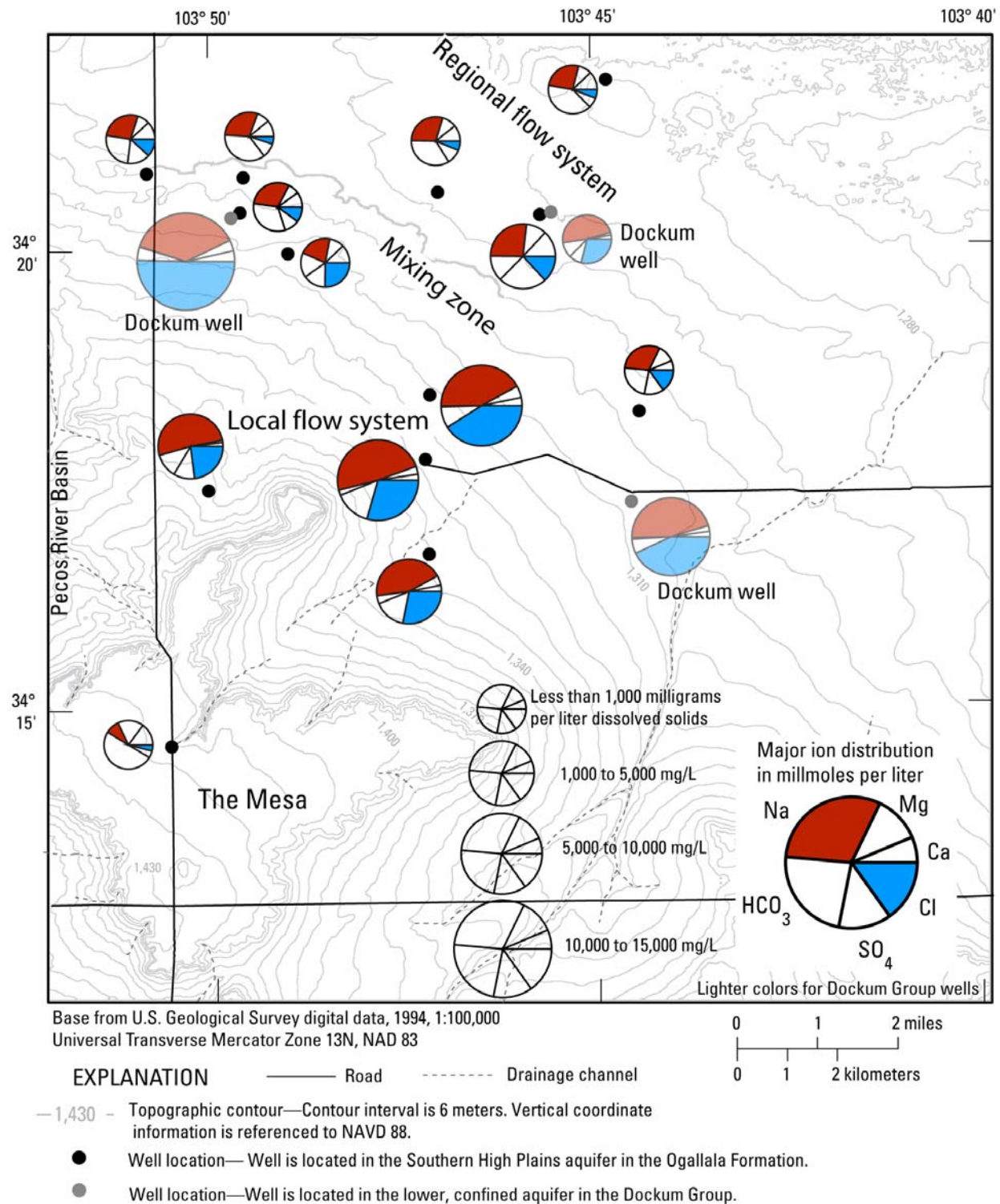


Figure 12. Major-ion distribution and relative dissolved-solids concentrations at the study site, June 2006.

Table 4. Physical and chemical properties of groundwater collected at the study site, June 2006.

[mg/L; milligrams per liter; µg/L, micrograms per liter; -N, as nitrogen; NA, not available; ‰, per mil; TU, tritium units; ND, not detected; ----, not calculated; pmC, percent modern carbon]

		Ogallala Formation													Dockum Group			
		Mesa	Regional flow system					Local flow system				Mixing zone				Upper Dockum aquifer		
Constituent	Units	10	4	5	6	7	8	14	15	16	3	18	21	L6	2	20	22	
Temperature	°C	19.2	18.0	18.1	18.6	18.6	21.3	20.6	23.4	23.5	18.6	21.1	20.0	21.0	25.4	22.6	20.3	
pH		7.23	7.33	7.41	7.40	7.39	7.37	7.90	7.37	7.71	7.59	7.69	7.26	7.42	7.45	7.47	7.94	
Dissolved oxygen	mg/L	7.87	7.4	6.78	5.59	7.84	0.3	3.46	0.94	1.08	6.34	5.77	3.31	5.59	0.25	0.63	0.2	
Organic carbon	mg/L	0.60	0.49	0.64	0.56	0.71	1.8	0.73	6.1	0.42	0.56	0.52	1.9	0.67	0.97	0.66	2.1	
Dissolved solids	mg/L	370	430	510	390	520	2,000	2,600	5,500	9,500	560	440	1,800	690	6,300	13,000	970	
Silica	mg/L	39	40	50	57	55	11	12	15	7.9	34	58	49	48	7.5	9.3	9.7	
Calcium	mg/L	50	46	43	39	56	46	82	140	350	33	42	180	71	170	550	29	
Magnesium	mg/L	35	21	23	18	23	17	76	110	310	36	19	85	35	110	330	12	
Potassium	mg/L	5.6	3.1	3.0	2.6	2.6	4.5	13	12	21	6.4	3.2	12	4.5	9.9	17	3.0	
Sodium	mg/L	18	57	67	60	74	710	650	1,600	2,600	91	73	210	72	2,000	3,300	300	
Alkalinity	mg/L	210	190	170	160	150	360	130	150	56	150	170	220	120	63	52	140	
Sulfate	mg/L	37	62	94	81	170	610	970	2,000	2,200	160	100	800	210	1,100	1,600	220	
Chloride	mg/L	12	20	22	16	49	490	640	1,500	3,900	69	38	160	130	2,900	6,800	280	
Flouride	mg/L	0.98	1.8	2.4	2.7	2.2	2.4	2.8	1.9	0.69	2.0	1.8	2.5	1.4	0.10	0.06	1.1	
Nitrate-N	mg/L	9.3	5.5	6.7	4.9	1.8	0.06	3.1	6.4	0.71	0.99	0.58	1.4	0.62	0.03	0.05	0.56	
Boron	µg/L	59	117	146	110	111	1,320	1,640	1,590	1,740	180	140	300	155	1,230	1,100	640	
Lithium	µg/L	44	42	66	70	76	130	240	470	520	100	78	190	92	420	720	79	
Manganese	µg/L	0.31	0.49	0.38	0.53	0.4	380	2.4	32	46	0.38	0.33	3.3	68	310	870	220	
Strontium	mg/L	2.93	0.99	1.11	0.93	1.11	1.54	4.30	5.80	17.1	2.20	1.08	4.09	1.88	9.69	31	0.90	

Continued on the next page.

Table 4. Physical and chemical properties of groundwater collected at the study site, June 2006—continued.

[mg/L; milligrams per liter; µg/L, micrograms per liter; -N, as nitrogen; NA, not available; ‰, per mil; TU, tritium units; ND, not detected; ----, not calculated; pmC, percent modern carbon]

		Ogallala Formation													Dockum Group		
Constituent	Units	Mesa	Regional flow system				Local flow system				Mixing zone				Upper Dockum aquifer		
		10	4	5	6	7	8	14	15	16	3	18	21	L6	2	20	22
⁴ Helium	µg/L	0.054	NA	0.051	0.135	0.113	NA	NA	NA	NA	0.174	0.132	0.094	0.098	NA	NA	NA
δ ³ He	‰	-59.89	NA	-42.06	-53.56	-54.31	NA	NA	NA	NA	-64.26	-58.43	-45.69	-50.12	NA	NA	NA
Tritium	TU	6.31	0.49	0.14	0.07	0.06	ND	0.02	7.86*	0.12	0.07	0.07	0.40	0.03	ND	0.05	0.05
³ He- ³ H age **	years	25±1	NA	70±25	60±5	65±15	----	----	----	----	105±25	90±20	40±2	>100	----	----	----
¹⁴ C	pmC	NA	NA	NA	NA	NA	32.3	49.6	75.9*	7.2	NA	NA	NA	NA	3.3	8.0	23.3
¹⁴ C age ***	years	NA	NA	NA	NA	NA	9,000	5,500	----	21,000	NA	NA	NA	NA	27,000	20,500	12,000
δD	‰	-45.77	-43.29	-45.97	-45.20	-44.62	-71.74	-62.26	-47.96	-59.37	-44.60	-45.19	-44.59	-43.90	-67.20	-51.70	-57.69
δ ¹⁸ O	‰	-6.73	-6.09	-6.21	-6.30	-6.09	-9.95	-8.39	-6.52	-7.92	-6.09	-6.14	-5.85	-5.86	-9.11	-6.93	-7.96
⁸⁷ Sr/ ⁸⁶ Sr	ratio	0.70883	0.70905	0.70905	0.70904	0.70906	0.70845	0.70864	0.70861	0.70870	0.70903	0.70886	0.70891	0.70893	0.70879	0.70903	0.70894
δ ¹¹ B	‰	15.3	17.6	15.1	14.9	18.6	30.3	32.6	25.2	40.8	6.0	15.7	7.7	16.6	46.0	38.1	34.8

* Likely influence from documented, minor petroleum leak at the site (Cannon Air Force Base, 2002). Petroleum and associated byproducts are not present in the groundwater, but relatively high dissolved organic carbon concentrations have been identified in water from this well.

** Groundwater age determined by ³H/³He method developed by Schlosser et al. (1989). Rounded to five-year intervals.

*** Unadjusted or conventional age as described by Mook and van der Plicht (1999).

Table 5. Chemical properties of acid digestion and leachate of soil/rock samples collected at the study site, December 2006.

[mg/kg, milligrams per kilogram; µg/L, micrograms per liter; ‰, per mil; NA, not available]

		Sample medium	Mesa soil	Sheep Canyon Caliche	Ogallala Formation (upper)	Ogallala Formation (lower)	Dockum Group	Blackwater Draw Formation
Constituent	Units		R1	R2	R3	R4	R5	R6
Chloride	mg/kg	Acid-digested soil/rock	11	140	12	9.5	11	9.1
Strontium	ug/L	Leachate	90	1,010	110	240	380	92
⁸⁷ Sr/ ⁸⁶ Sr	ratio	Leachate	0.70882	0.70873	0.70930	0.70887	0.70909	0.70867
Boron	µg/L	Leachate	31	51	108	8	176	39
δ ¹¹ B	‰	Leachate	NA	+14	+8	+5	+6	NA

Similar groundwater composition in the upper Dockum aquifer and the local flow system (Na-Cl water type) suggests the change in hydrochemical facies within the Southern High Plains aquifer at the study site is a result of cross-formational flow from the upper Dockum aquifer into the local flow system. The change in water type in the local flow system does not appear to be an effect of further evaporation where local recharge is evaporated and recharged away from the Mesa. Precipitation of minerals such as calcite and quartz (both oversaturated in the local flow system wells of 14, 15, and 16) is possible but such a large increase in dissolved solids would imply a substantial loss of solution that would suggest minimal volume remaining for recharge from the surface. This possible influence will be further examined with the age and water isotope results. The variable water type in the Southern High Plains aquifer has been the basis of much of the inference for cross-formational flow between the Dockum aquifers and the Southern High Plains aquifer (Nativ, 1992). The highest dissolved-solids concentration in the local flow system (9,500 mg/L) is furthest from the Mesa (well 16, fig. 12), which suggests longer water-rock interaction at this location or a larger contribution of saltwater from cross-formational flow. Hydrochemical facies in the upper Dockum aquifer indicate larger dissolved-solids contributions closer to the Mesa and a possible mixing of sources in the upper Dockum aquifer underlying the regional flow system (well 22, fig. 12).

High Na and Cl concentrations imply halite dissolution, which indicates water-rock interaction in the Permian salts (no substantial evaporite layers are present in the Ogallala or Dockum). The upper Dockum aquifer underlying the local flow system appears to contain water that has crossed from the Permian salts through the lower Dockum shales into the upper conductive layer(s) of the formation, where it was previously thought that no water would be present because of the hydrologic divide of the caprock escarpment (Dutton and Simpkins, 1989). Groundwater from all Dockum wells suggests some saltwater intrusion, but

concentrations are much smaller in well 22 than for wells 2 and 20 indicating dilution from another source (table 4 and fig. 12). Dilution in well 22 suggests that the upper Dockum aquifer away from the caprock escarpment contains groundwater more similar to the regional flow system in the Southern High Plains aquifer. Just as the local flow system groundwater is diluted by mixing with the regional flow system in the Southern High Plains aquifer, it is likely that the upper Dockum aquifer groundwater is also diluted by a regional inflow with similarities to regional Southern High Plains water. This additional source is likely regional Dockum water coming from the northwest and probably represents recharge to the Dockum from inflows along escarpment exposures or downward flow from the Ogallala where the vertical hydraulic gradient is reversed compared to the study site.

A regional flow of Dockum water similar in composition and concentrations to the Southern High Plains regional flow system in the upper Dockum aquifer away from the caprock escarpment is in agreement with previous studies. Knowles et al. (1984) and Nativ (1992) found the potentiometric surface of the Southern High Plains aquifer is typically greater than in the Dockum, and similarities in groundwater composition between the Southern High Plains aquifer and Dockum aquifers suggest downward cross-formational flow between the two formations. Nativ and Smith (1987) and Dutton and Simpkins (1986) indicated that the downward cross-formational flow is likely insignificant because of light isotopic composition in the Dockum waters (likely late Pleistocene or early Holocene recharge), although these studies did not include the possible effect of upwelling Permian-bed saltwater.

Water-rock interactions that produce mineral dissolution or adsorption can result in non-conservative solute behavior that limits the utility of major ion and trace element concentrations for identifying source waters and flowpaths (Langmuir, 1997). The ion exchange pool at any location in a flowpath exemplifies water-rock interactions and atmospheric inputs, and ions will

exchange at the mineral surfaces at relative constants that reflect clay mineralogy, water pH, and water chemistry (Bullen and Kendall, 1998). Excess Na (>1 molar ratio of Na and Cl) is greatest in the regional flow system and decreases in the mixing zone, local flow system, and is only present in well 22 of the upper Dockum aquifer where a regional Dockum water is dominant (fig. 13). The excess Na in the regional flow system corresponds with high alkalinity (HCO_3^-) concentrations from the weathering of silicates that comprise the Ogallala. The Na/Cl ratio decreases with distance from the Mesa in the local flow system (wells 8 to 14/15 to 16) and is highly variable in the upper Dockum aquifer. The alteration of the Na/Cl ratio in the local flow system and the upper Dockum aquifer is likely an effect of the Dockum shales acting as a geochemical membrane with certain ions, including Na, preferentially adsorbing or exchanging (cation exchange) with other ions on clay surfaces. The likely slow and tortuous flowpath through the Dockum shales would provide ample opportunity for exchange of Na that would reduce the Na/Cl ratio. A decreasing Na/Cl ratio along with an increasing dissolved solids concentration in the local flow system with distance from the Mesa indicates that cross-formational flow from the Dockum into the Ogallala is occurring throughout the local flow system and not just at the Mesa.

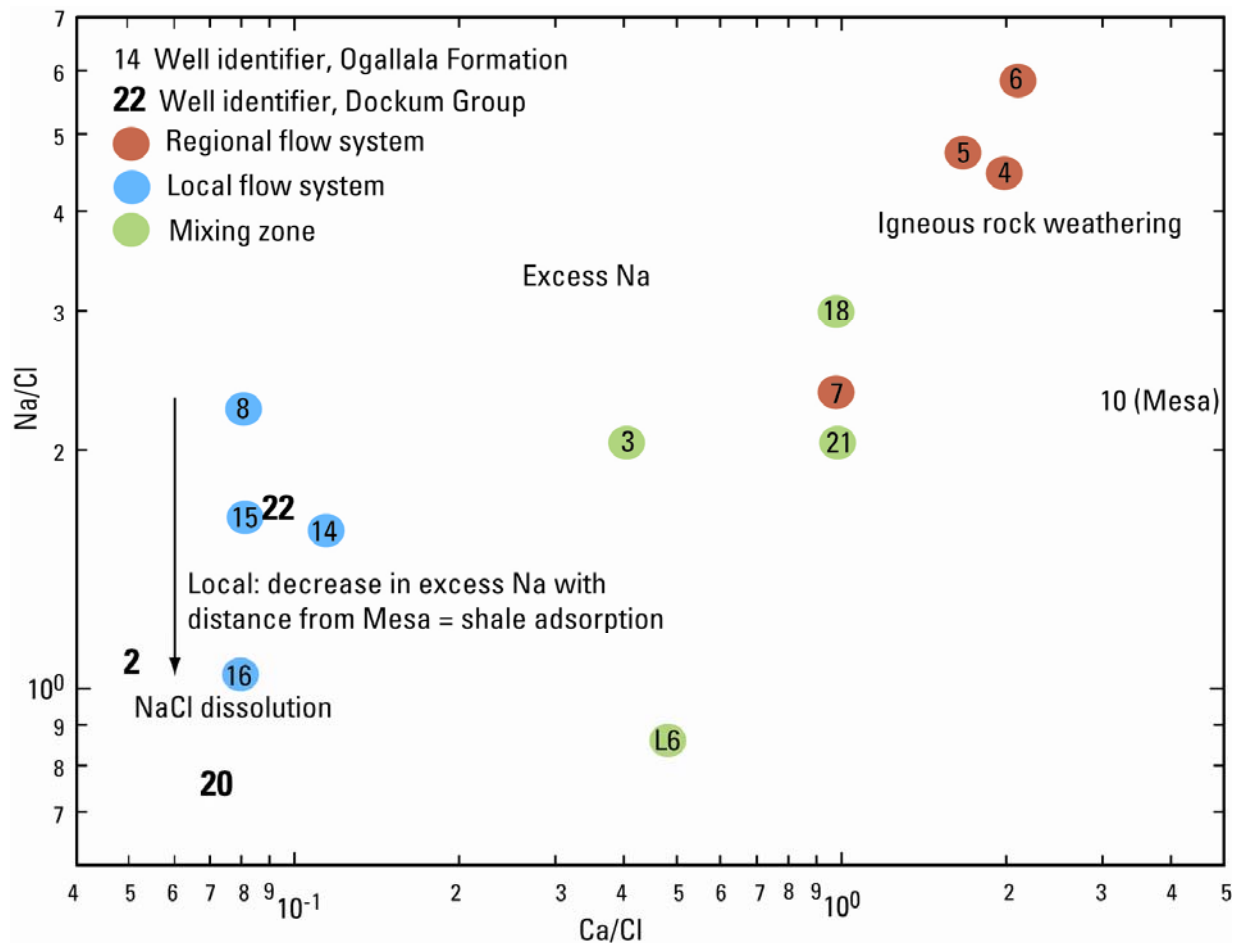


Figure 13. Molar ratios of sodium and calcium to chloride in groundwater at the study site, June 2006.

Trace element concentrations can indicate changes in redox conditions, mineral dissolution, and adsorption/desorption from clay-mineral surfaces (Hem, 1989). Flow of low dissolved oxygen water from underlying formations to the Ogallala may cause various elements to enter the groundwater because of reducing conditions but may also reprecipitate these elements when mixed with oxidized water (redox cycling). Exploratory graphical (matrix plots) and statistical analysis (PCA) suggests trace element compositional differences explained by a few dominant elements (in order of influence with loading values for 1st component): Sr (0.87), B (0.41), and Li (0.28). Manganese (Mn) also was identified as contributing to trace element compositional differences (3rd component), and its concentration variability is a response to

reducing conditions of Permian-bed/Dockum saltwater compared to the well oxidized water in the Ogallala (Mn is more soluble under reducing conditions) (Hem, 1989). Very low Mn concentrations in the local flow system, even though this system likely receives a substantial contribution of low-oxygen saltwater containing soluble Mn, indicates reoxidation and precipitation of Mn with mixing of oxidized, local recharge from the Mesa (fig. 14). The decrease in dissolved oxygen and increase in Mn concentrations from well 14 to well 16 in the local flow system suggests a lessening of the influence of local recharge at the caprock escarpment with distance from the Mesa.

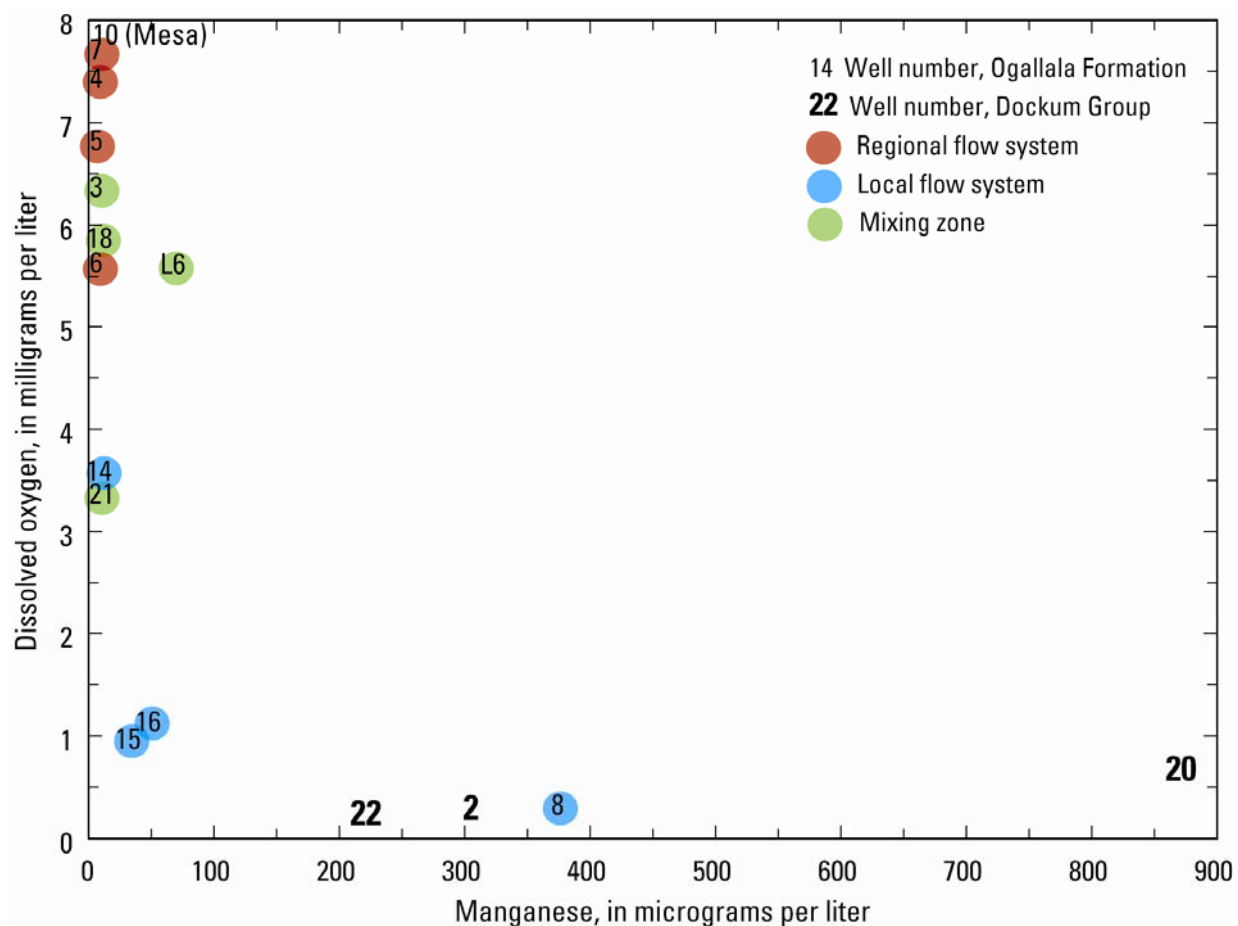


Figure 14. Dissolved-oxygen and manganese concentrations in groundwater at the study site, June 2006.

Strontium and lithium are abundant in the earth's crust and natural waters (Nimz, 1998), and the variability of Sr and Li concentrations at the study site likely reflect varying

contributions from mineral dissolution in the different aquifer matrices. The regional flow system contains the least of both elements (**tables 4**) likely because of the younger age of the water (less water-rock interaction) and less available Sr and Li in the Ogallala alluvium compared to the Dockum shales and Permian salts. Groundwater in the local flow system, mixing zone, and the upper Dockum aquifer all show a linear gradient of Sr and Li concentrations suggestive of a mixing pattern (fig. 15). In the local flow system, concentrations are highest furthest from the Mesa indicating increasing contributions likely from greater mineral dissolution/exchange because of longer water-rock interactions. Concentrations of Sr and Li in Dockum groundwater at well 22 indicate mixing with regional Dockum water that is substantially more dilute than Dockum water present along the caprock escarpment (2 and 20).

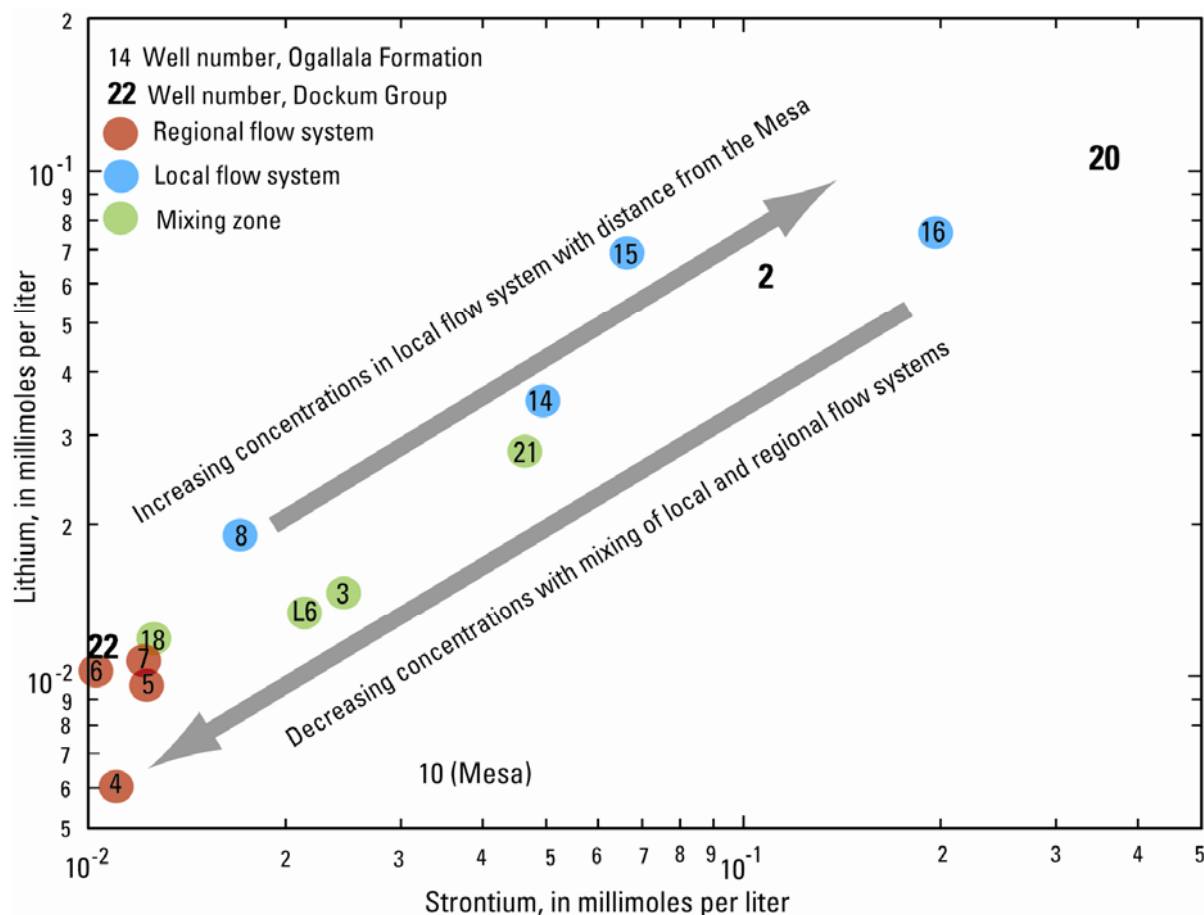


Figure 15. Lithium and strontium concentrations in groundwater at the study site, June 2006.

GROUNDWATER AGE

Dissolved-oxygen, $^3\text{H}/^3\text{He}$, and ^{14}C concentrations all illustrate a large groundwater-age gradient at the study site (table 4). High dissolved-solids groundwater of the upper Dockum aquifer and local flow system contains low dissolved-oxygen concentrations that suggest older water where oxygen is typically consumed during longer transport (Beyerle et al., 1999). Helium was greatest in groundwater from the upper Dockum aquifer and the local flow system (fig. 16) suggesting colder recharge temperatures and (or) the accumulation of radiogenic helium (α -decay of radioactive elements such uranium) (Solomon et al., 1998). From $^3\text{H}/^3\text{He}$ age analysis, young water (less than 100 years old) is present atop the Mesa (well 10), in the mixing zone, and in the regional flow system; from ^{14}C age analysis¹, old water (greater than 5,000 years) is present in the upper Dockum aquifer and local flow system (table 4). The oldest water at the study site was in the upper Dockum aquifer (12,000 to 27,000 years). The mixing zone contained groundwater that was younger than expected, which indicates an additional water source or influence in this area. The old water in the local flow system suggests cross-formational flow and a contribution of old water. This old water contribution indicates that the variable hydrochemical facies in the Southern High Plains aquifer at the study site is not a result of evaporation and precipitation of certain minerals prior to recharge from surface-water sources but an input of water from an underlying formation.

¹ Calculation of ^{14}C ages may overestimate groundwater ages in the local flow system and upper Dockum aquifer because of possible decreases in carbon concentrations from reducing conditions in the upper Dockum aquifer.

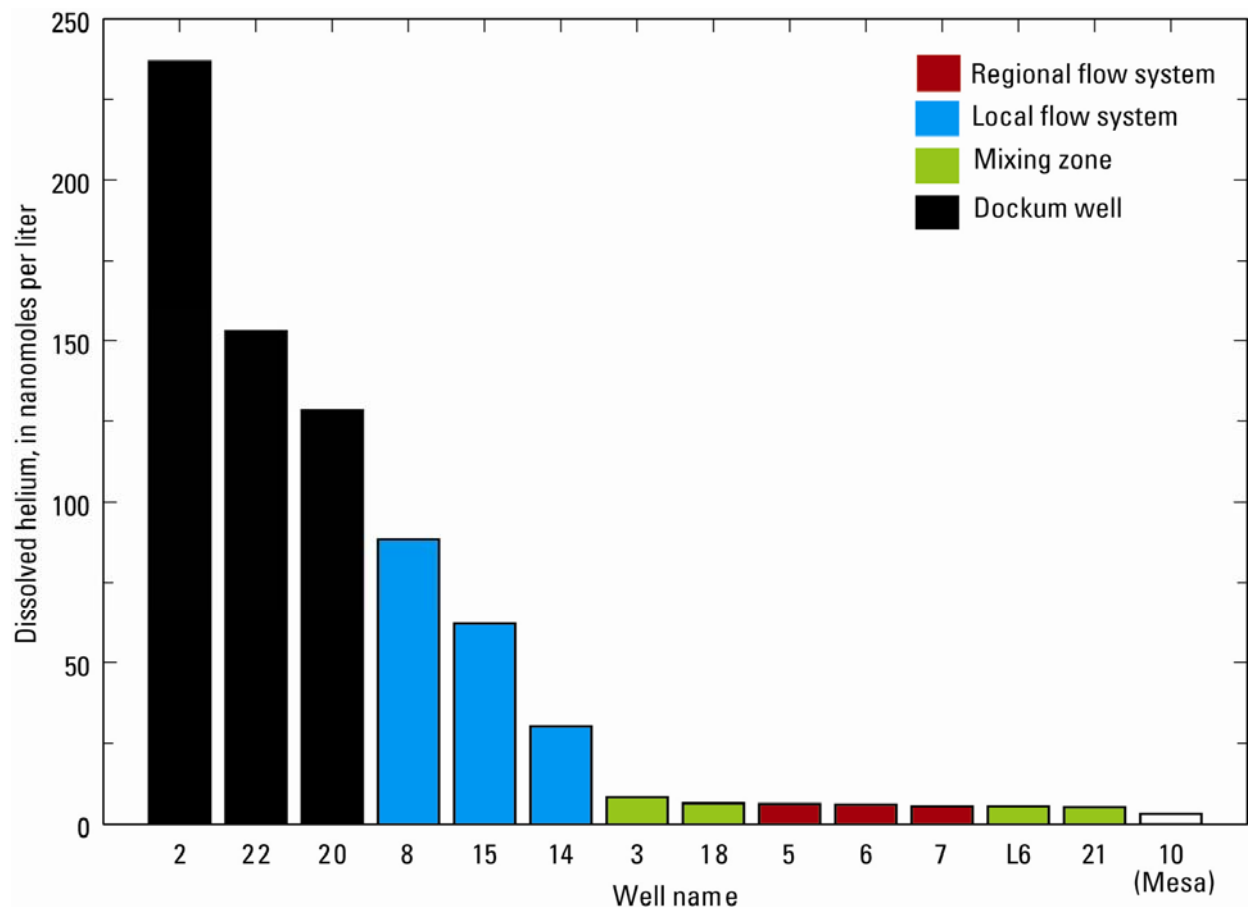


Figure 16. Helium concentrations in groundwater at the study site, June 2006.

Dutton and Simpkins (1989) and Dutton (1995) concluded that the initiation of the hydrologic divide that separated the Pecos River Basin from the Southern High Plains was older than groundwater in the confined Dockum aquifers; therefore, Dockum water likely originates in the Southern High Plains. A substantial contribution of connate water from the Permian salts or the Dockum is unlikely because of the much younger age of groundwater at the study site compared to the Permian and Triassic age of these formations. Groundwater that is dissolving the Permian salts likely enters the Permian formations from downward cross-formational flow of Ogallala/Dockum water followed by upward flow as a result of the change in density from increased water temperature (water temperature was highest in all wells influenced by Permian-bed saltwater). Given the hydraulic heads at the study site, downward cross-formational flow to

the Permian salts is originating at another location. All geologic formations in the region dip eastward, and groundwater in the Permian bedded salts is likely migrating under the hydrologic divide that is present in the Ogallala and Dockum along the Western Caprock Escarpment (fig. 5). The potentiometric gradient within the Permian bedded salts from the Pecos River Basin to the Southern High Plains is from west to east (Bair, 1987); therefore, flow under the hydrologic divide of the Western Caprock Escarpment in the Ogallala and Dockum is possible and likely explains the source of upwelling old saltwater.

Groundwater in the upper Dockum aquifer closer to the Mesa (wells 2 and 20) consists of old water that has interacted with the Permian salts, but the flowpaths from the Permian salts to wells 2 and 20 are likely different as indicated by the large age difference (27,000 and 20,500 years, respectively). This difference may be attributed to tortuous flowpaths through the Dockum shales. The regional Dockum water (well 22) is also old water (12,000 years), but a substantial portion of the groundwater at this location has not similarly interacted with the Permian salts because of its low dissolved-solids concentrations. Permian-bed saltwater has undergone substantial dilution at this location (fig. 12) from mixing with the regional Dockum water that is likely still old water but younger than the water source that has interacted with the Permian salts.

Young water interacting with siliciclastic sediments atop the Mesa (well 10) flows away from the Mesa and mixes in the local flow system with old water upwelling from the Dockum. The contribution of young water in the local flow system is minor compared to the older Permian-bed/Dockum saltwater as indicated by old ages in the local flow system (table 4). This mixing ratio is reversed in the mixing zone, where the young water of the regional flow system is the dominant contributor; although, groundwater ages in the mixing zone are younger than expected. A relatively small contribution of the old Permian-bed/Dockum saltwater would have a substantial impact on groundwater ages because of the large difference in ages between these

two sources (about a 250-fold increase). This lack of older ages in the mixing zone and the presence of younger water in well 21 of the mixing zone compared to the regional flow system suggest another influence on groundwater in this area.

WATER STABLE ISOTOPES, RECHARGE, AND MIXING

Historically, δD and $\delta^{18}O$ values in precipitation across the Southern High Plains have ranged from -162 to +35‰ for δD and -22.7 to -4.7‰ for $\delta^{18}O$ with mean annual weighted values of -48‰ for δD and -7.5‰ for $\delta^{18}O$ (Nativ and Riggio, 1989). Precipitation δD and $\delta^{18}O$ values for the Southern High Plains aquifer generally plot along the global meteoric water line but their overall trend has a reduced slope because of the semiarid climate (Nativ and Riggio, 1989). Values of δD and $\delta^{18}O$ for Dockum water typically are 15 to 25‰ and 2 to 3‰ lighter than Ogallala water, respectively (Dutton and Simpkins, 1986; Dutton, 1995). Lighter δD and $\delta^{18}O$ values have been attributed to lighter isotopic water recharged during the last Pleistocene glaciation (35,000 to 10,000 years ago) (Dutton, 1995). The δD and $\delta^{18}O$ values in groundwater from the study site show a linear relationship with little alteration from water-rock interactions and only a slight change from the global meteoric water line because of evaporation (fig. 17). The limited evaporation signal in the local flow system further disproves the possibility of strong evaporation and mineral precipitation as the reason for the change in hydrochemical facies as might have been inferred from the major ion data. The δD and $\delta^{18}O$ values for the local flow system (-71.74 to -47.96‰ and -9.95 to -6.52‰, respectively) and upper Dockum aquifer (-67.20 to -51.70‰ and -9.11 to -6.93‰) were lower and had a greater range compared to the regional flow system (-45.97 to -43.29‰ and -6.30 to -6.09‰); mixing zone values (-45.19 to -43.90‰ and -6.14 to -5.85‰) indicated an additional water source or further evaporation (table 4).

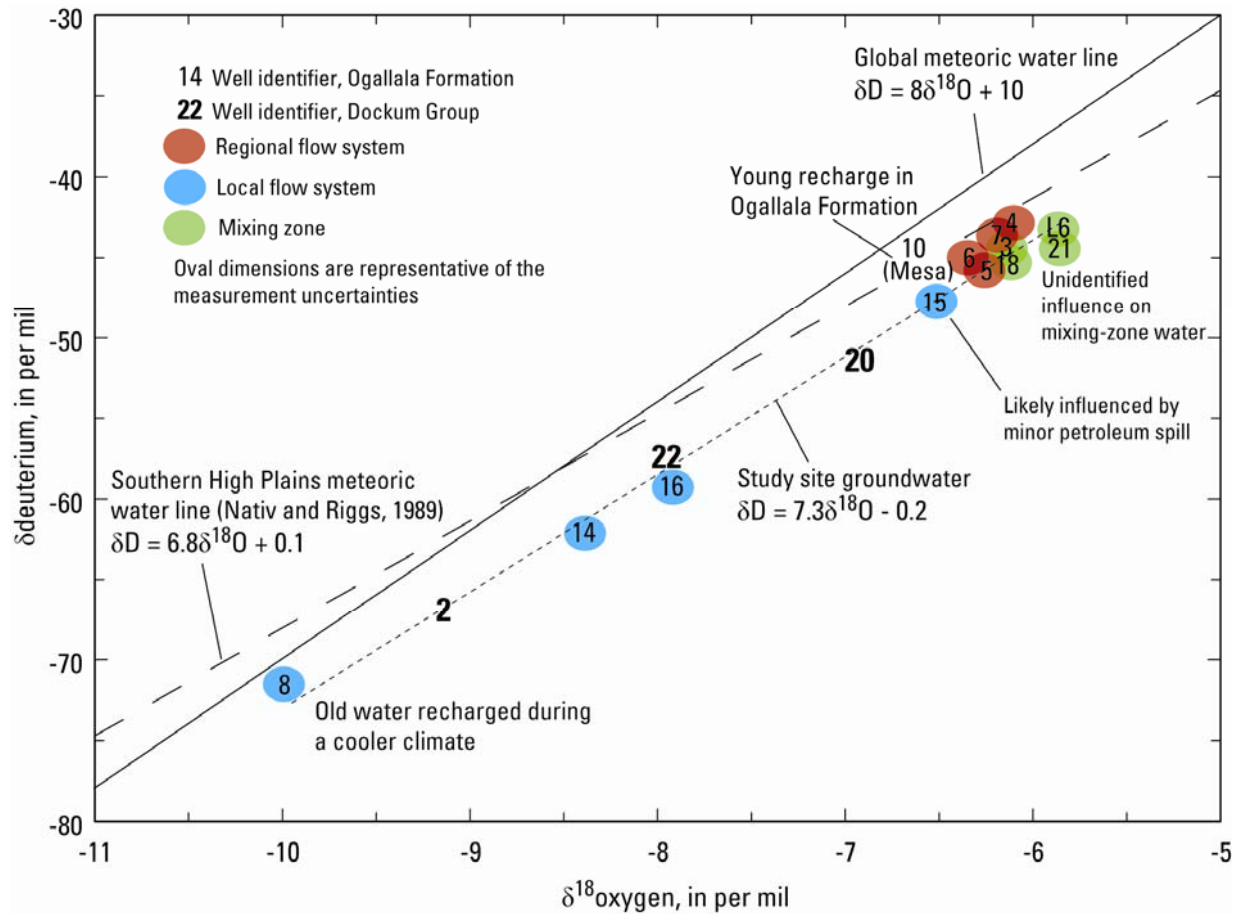


Figure 17. Groundwater δD and $\delta^{18}O$ values at the study site, June 2006.

Examining each system separately through least-squares regression (table 6), the upper Dockum aquifer and local and regional flow systems contain similar water that has been evaporated to varying degrees (similar α and β). The limited relation between δD and $\delta^{18}O$ values in the regional flow system (low R^2 and large p-values) is a result of the close grouping of these sites where analytical uncertainty influences the regression analysis. The δD and $\delta^{18}O$ values in the mixing zone are heavier than expected and suggest a lack of local-flow-system water (fig. 17). The lack of a relation between δD and $\delta^{18}O$ values in the mixing zone (poor R^2 and p-value) indicate that an additional influence is present, spatially variable in this area, and appears to have a stronger effect on hydrogen isotopes compared to oxygen isotopes. The

additional influence appears to be evaporation that would have a greater effect on the lighter hydrogen isotopes. This influence is likely agricultural recharge.

Table 6. Results of least-squares regression of δD and $\delta^{18}O$ values for the three aquifer systems at the study site.

Least-squares regression	Upper Dockum aquifer	Local flow system	Mixing zone	Regional flow system
α (intercept)	-1.8	-3.8	-28.9	1.5
β ($\delta^{18}O$ multiplier)	7.1	6.9	2.6	7.5
R^2	0.99	0.99	0.56	0.46
p-value	0.06	0.00	0.25	0.32

From the age (9,000 years) and δD and $\delta^{18}O$ values of groundwater in well 8 (local flow system adjacent to the Mesa), this water is older water that was likely recharged during a cooler climate and has not mixed with young, local recharge (fig. 17). The lack of young, local recharge at well 8 fits the physical model of surface recharge in the area because of the lack of concentrated surface flow near this well. Additionally, this well recovered very slowly following pumping, suggesting cross-formational flow as the dominant water source. In comparison to old water found in other local flow system wells, water from well 8 represents water that has interacted with the Permian salts and more quickly moved through the Dockum shales (well is closest to the Mesa where shale fracturing is the likely the greatest). Groundwater from the remaining local-flow-system wells indicates more tortuous and longer pathways (older ages) and mixing with local recharge (higher δD and $\delta^{18}O$ values) that is likely represented by groundwater from well 10 atop the Mesa. With identification of groundwater from well 8 as water more representative of Permian-bed saltwater, source-water fractions were estimated for the local flow system using equation 1 and well 8 and well 10 as end members (table 7). Possible source-water mixing fractions indicate a spatially independent influence of Permian-bed saltwater in the local flow system with distance from the Mesa because of the complexity of flowpaths through shale fractures. The saltwater comprises 58% of the groundwater at well 14 and 45% at well 16,

suggesting a lessening of saltwater contribution with distance from the Mesa or additional local recharge away from the Mesa.

Table 7. Approximate source-water mixing fractions determined by δD and $\delta^{18}O$ for the local flow system at the study site.

[NA, not applicable—anthropogenic influence (minor fuel spill) has affected the water isotopes at this location]

Mixing components	δD	$\delta^{18}O$	Permian-bed/Dockum saltwater	Regional water
<i>Local flow system:</i>			<i>Fraction of mixture:</i>	
Permian-bed/Dockum saltwater (well 8)	-71.74	-9.95	1	0
Local Ogallala water (well 10)	-45.77	-6.73	0	1
Well 14	-62.26	-8.39	0.58	0.42
Well 16	-59.37	-7.92	0.45	0.55

Overall, the lower δD and $\delta^{18}O$ values for water in the local flow system and Dockum suggest a source water recharged during a cooler climate that corresponds to the theory of recharge during the last glacial period (Dutton, 1995). Given a general increase in δD and $\delta^{18}O$ values of 5.6 and 0.7 per mil, respectively, with a 1°C increase in temperature (Dansgaard, 1964), the expected recharge temperature of the Permian-bed saltwater in well 8 compared to the regional flow system groundwater would be about 5°C cooler, which corresponds to recharge temperatures during the last glacial maximum (Stute et al., 1992). The large variation of the isotopic values for the other wells is difficult to ascertain but may be a result of climate instability during the last Pleistocene glaciation that has been inferred from analysis of Antarctica ice sheet cores (Dansgaard et al., 1993; Blunier and Brook, 2001; Brook et al., 2005). This large variation in the isotopic composition in Dockum and Ogallala water reduces the effectiveness of this tracer for identifying source waters and flowpaths.

Combining this study's δD and $\delta^{18}O$ values with data from regional studies highlights the variability of water isotopic composition in the Permian salts, Dockum, and Ogallala across the Southern High Plains (fig. 18). Water isotopic values in both the Ogallala and Dockum decrease from north to south in the Southern High Plains (Dutton, 1995), and agricultural recharge likely

enhances the variability of these values. The δD and $\delta^{18}O$ values in the upper Dockum aquifer underlying the local flow system suggest mixing with Ogallala water (fig. 17) that has been suggested as a source of Dockum δD and $\delta^{18}O$ variability (Nativ, 1988; Dutton, 1995), but recharge directly from the Ogallala to the Dockum in this location is unlikely because of the formation elevations and gradients (fig. 8) and the potentiometric surfaces that would suggest an opposing flowpath (fig. 6). This strong δD and $\delta^{18}O$ variation in Dockum water also is visible in the regional data (fig. 18) and indicates that the isotopic composition of water is not a reliable tracer for evaluating the geochemical evolution of groundwater in the Southern High Plains because of climate variability during recharge and the likely influence of agricultural recharge.

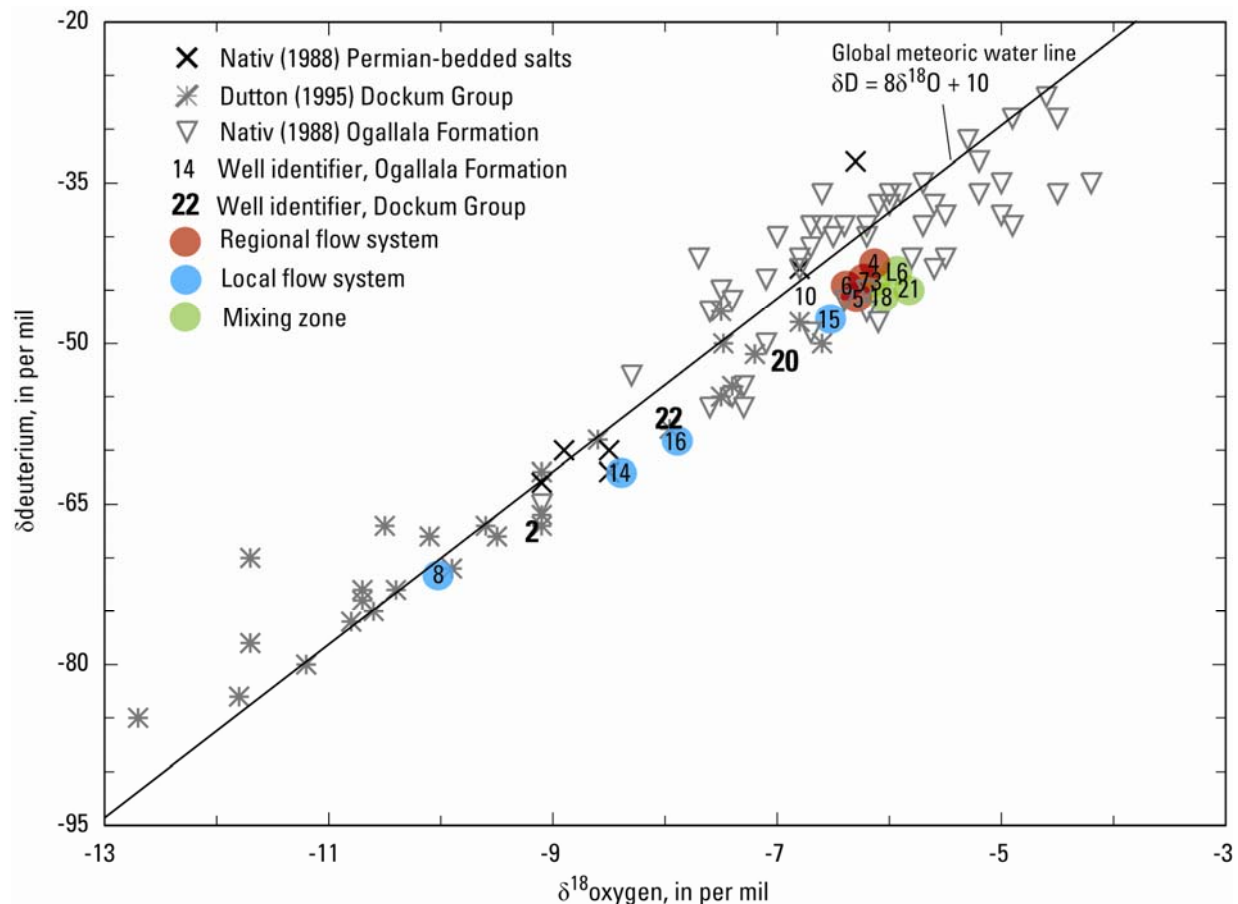


Figure 18. Groundwater δD and $\delta^{18}O$ values for the Permian salts, Dockum Group, and Ogallala Formation in the Southern High Plains.

Chapter 4: Geochemical Evolution of Groundwater in the Southern High Plains and Upper Dockum Group Aquifers

The physical attributes of the aquifers and the chemical composition of groundwater examined in Chapter 3 indicate mixing of various source waters that comprise the three aquifer systems (upper Dockum aquifer, local flow system, and regional flow system), but groundwater evolution is not fully resolved because of large variations in element, age, δD , and $\delta^{18}O$ values within each system. Additional tracers are required to fully identify the source waters, interaction between the aquifer systems, and the effects of water-rock interactions. A mass-transfer model (reaction path model) has limited applicability to the study site because of the division of the wells among the three aquifer systems (limited coverage in each system) and the complexity of flowpaths in and between the aquifers. Instead, the nontraditional aqueous tracers of $^{87}Sr/^{86}Sr$ and $\delta^{11}B$ were used to better resolve source waters and their mixing fractions and water-rock interactions.

$^{87}Sr/^{86}Sr$ AND CHEMICAL WEATHERING

Constraining the possible $^{87}Sr/^{86}Sr$ ratios in groundwater in the three aquifer systems are $^{87}Sr/^{86}Sr$ ratios from the available Sr pools of each aquifer matrix. The $^{87}Sr/^{86}Sr$ ratios for rock samples collected from the Ogallala and Dockum generally were larger than groundwater ratios (0.70845 to 0.70906) and ranged from 0.70887 to 0.70930 (**tables 4 and 5**). Strontium in leachate from the soil/rock samples represents predominantly adsorbed Sr and not mineral-lattice Sr because of the short leachate period (24 hours shaken). The largest ratio was in the upper Ogallala (0.70930), and the smallest ratio was in the Blackwater Draw (0.70867). Available Sr increased with depth in the Ogallala and from the Blackwater to the Ogallala to the Dockum (increased concentrations in leachate) (table 5).

The typical $^{87}\text{Sr}/^{86}\text{Sr}$ ratio in precipitation is similar to modern seawater (about 0.709) but can be influenced by local or regional dust derived from exposed soils and sediments (Capo et al., 1998). Recharge atop the Mesa (well 10) was the youngest and shallowest water sampled and should reflect mostly precipitation and soil Sr inputs without contributions from cross-formational flow or interaction with deeper formations (fig. 19). Groundwater in well 10 contained an $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of 0.70883 (table 4), which is near the likely precipitation value but closer to the Mesa soil value ($^{87}\text{Sr}/^{86}\text{Sr} = 0.70882$, table 5). Weathering of Precambrian granites, or general continental crust, and associated alluvial sediments generally have an $^{87}\text{Sr}/^{86}\text{Sr}$ ratio equal to or greater than 0.71 (Goldstein and Jacobsen, 1988), and younger granites or alluviums may have smaller ratios because of less radiogenic ^{87}Sr (Capo et al., 1998). Groundwater in the regional flow system in the mixed alluvium of the Ogallala had a fairly uniform $^{87}\text{Sr}/^{86}\text{Sr}$ ratio (≈ 0.70905) and contained the largest $^{87}\text{Sr}/^{86}\text{Sr}$ ratios in groundwater at the study site (fig. 19). Burke et al. (1982), Hess et al. (1986), and Brookins (1988) described $^{87}\text{Sr}/^{86}\text{Sr}$ variation during the Phanerozoic and indicate that Permian or Cretaceous marine carbonates and evaporites and derived sediments should have an $^{87}\text{Sr}/^{86}\text{Sr}$ range of 0.7068 to 0.7084. Only groundwater from well 8 had an $^{87}\text{Sr}/^{86}\text{Sr}$ ratio near this range (0.70845, table 4), and this water is likely representative of Permian-bed saltwater, which also was indicated by δD and $\delta^{18}\text{O}$ values in Chapter 3. Dockum shales are probably contributing labile Sr and some Sr from dissolution of the Dockum sediments because of the long residence time (greater than 20,000 years in the local, upper Dockum aquifer represented by wells 2 and 20) (fig. 19). The Dockum Sr pool is isotopically similar to the Ogallala Sr pool as $^{87}\text{Sr}/^{86}\text{Sr}$ ratios increase with greater influence from the Dockum and values approach those seen with the regional flow system (fig. 19).

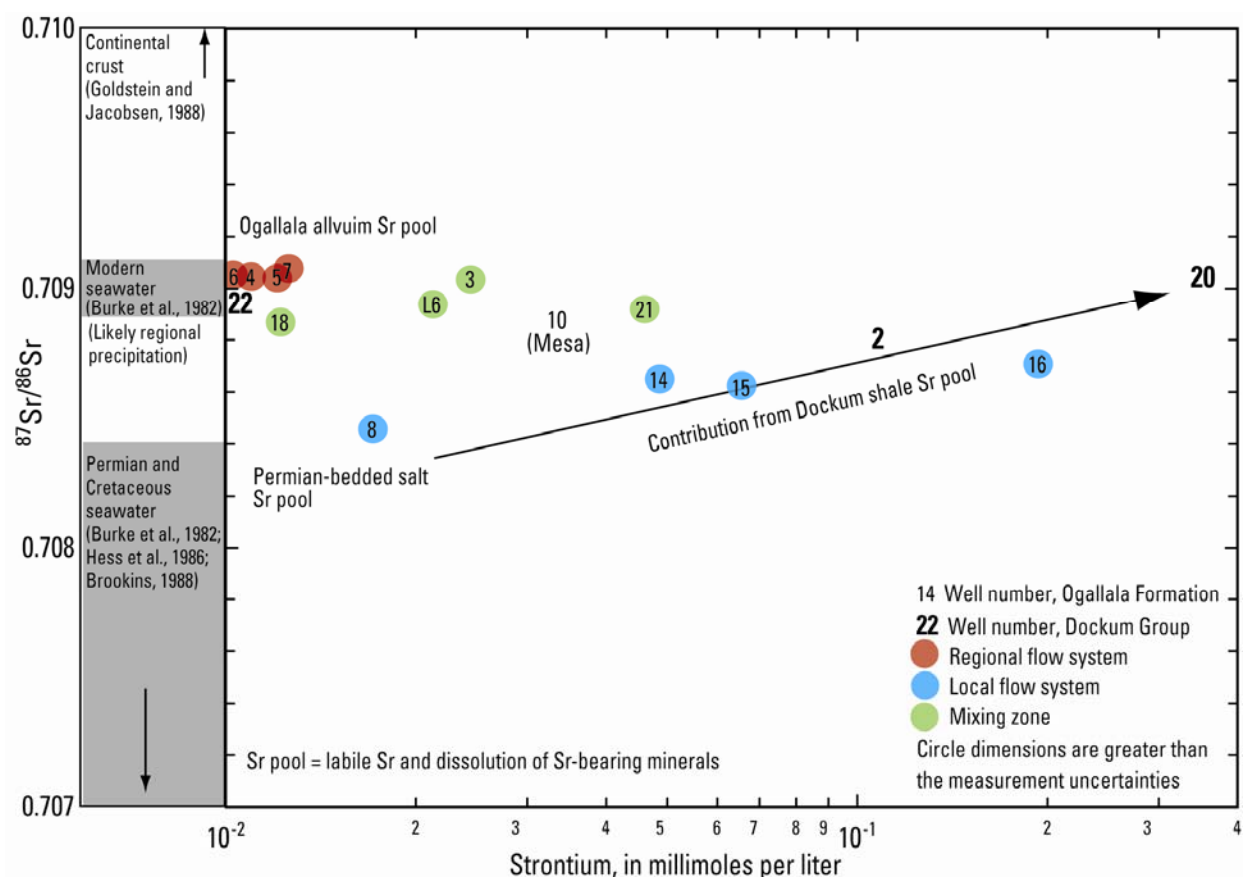


Figure 19. Strontium concentrations and $^{87}\text{Sr}/^{86}\text{Sr}$ ratios in groundwater at the study site, June 2006.

The range of $^{87}\text{Sr}/^{86}\text{Sr}$ ratios was relatively small (0.70845 to 0.70906), but combined with the Sr concentrations (0.90 to 31 mg/L), Sr provides a useful tracer of source waters and water-rock interactions. Building on the source waters and possible flowpaths identified in Chapter 3, Sr was used to quantify source-water fractions for all three systems and estimate contributions from chemical weathering (table 8 and fig. 20). From these results, it can be seen that a relatively low $^{87}\text{Sr}/^{86}\text{Sr}$ Permian-bed saltwater is present in the local, upper Dockum aquifer and local flow system of the Southern High Plains aquifer, but its contribution of Sr is highly variable because of difference in water-rock interaction from the variation in flowpaths through the Dockum shales (table 8 and fig. 20). The larger Sr mass and $^{87}\text{Sr}/^{86}\text{Sr}$ ratio from chemical weathering in the upper Dockum aquifer is a result of the weathering of labile Sr or

siliciclastic Sr-bearing minerals during the longer interval of water-rock interaction. The local flow system receives Permian-bed/Dockum saltwater and local recharge near the Mesa where the chemical weathering contribution is smaller but increases with distance from the Mesa (fig. 20). The regional flow system contribution is dominant in the mixing zone, but a larger contribution of local flow system water is present along the northern part of the mixing zone (wells L6 and 21) compared to the eastern part (well 3) (fig. 20). Minimal water was present in the Southern High Plains aquifer at well 1 about 1.5 kilometers south of well 3. This difference in local flow system contribution is a result of the discontinuous aquifer along the Southern High Plains margin where saturated thickness is highly variable because of the eroded contact with the Dockum.

Table 8. Fractional contributions of strontium from possible source waters comprising the groundwater mixtures and likely chemical weathering inputs from water-rock interactions at each well site as determined by inverse calculations.

[All concentrations (conc.) are in millimoles per liter; NA, not applicable; inverse calculation results are shown as ranges because of the sensitivity analysis that examined precision uncertainty, if no range is shown, the range of inputted values (\pm precision) produced the same results]

Mixing components	Permian-bed saltwater (well 8)	Local Ogallala water (well 10)	Regional Ogallala water (wells 4–7)	Chemical weathering	Calculated weathering Sr concentration	Calculated weathering ⁸⁷ Sr/ ⁸⁶ Sr ratio	Sum of the square of the residuals
Sr conc. (±3%)	0.0176	0.0334	0.0118		Calculation variable		NA
⁸⁷ Sr/ ⁸⁶ Sr (±0.00002)	0.70845	0.70883	0.70905				NA
Fractional component of each source contributing to the strontium signal (concentration and ⁸⁷ Sr/ ⁸⁶ Sr ratio):							
Upper Dockum aquifer (local): Permian-bed saltwater + chemical weathering							
Well 2	0.85–0.86	NA	NA	0.14–0.15	0.6653–0.6664	0.71077–0.71087	0.000
Well 20	0.56–0.58	NA	NA	0.42–0.44	0.7872–0.8441	0.70978–0.70985	0.000–0.058
Local flow system: Permian-bed saltwater + local Ogallala water + chemical weathering							
Well 14	0.47–0.48	0.47	NA	0.05–0.06	0.4490–0.4495	0.70866–0.70867	0.000–0.008
Well 15	0.43–0.45	0.42–0.43	NA	0.13–0.14	0.3192–0.3300	0.70842–0.70847	0.000–0.001
Well 16	0.27–0.30	0.42–0.45	NA	0.27–0.29	0.6231–0.6334	0.70874–0.70879	0.000–0.008
Mixed zone: Permian-bed saltwater + local Ogallala water + regional Ogallala water + chemical weathering							
Well 3	0.10–0.11	0.10–0.11	0.76–0.78	0.02	0.4959–0.4964	0.71193–0.71239	0.000
Well 18	The fractional contributions could not be determined. Additional unidentified influence likely.						
Well 21	0.21	0.26	0.48	0.05	0.5168–0.5238	0.70982–0.70983	0.000
Well L6	0.16–0.17	0.23–0.24	0.59–0.60	0.01	0.4974–0.5029	0.71287–0.71345	0.000

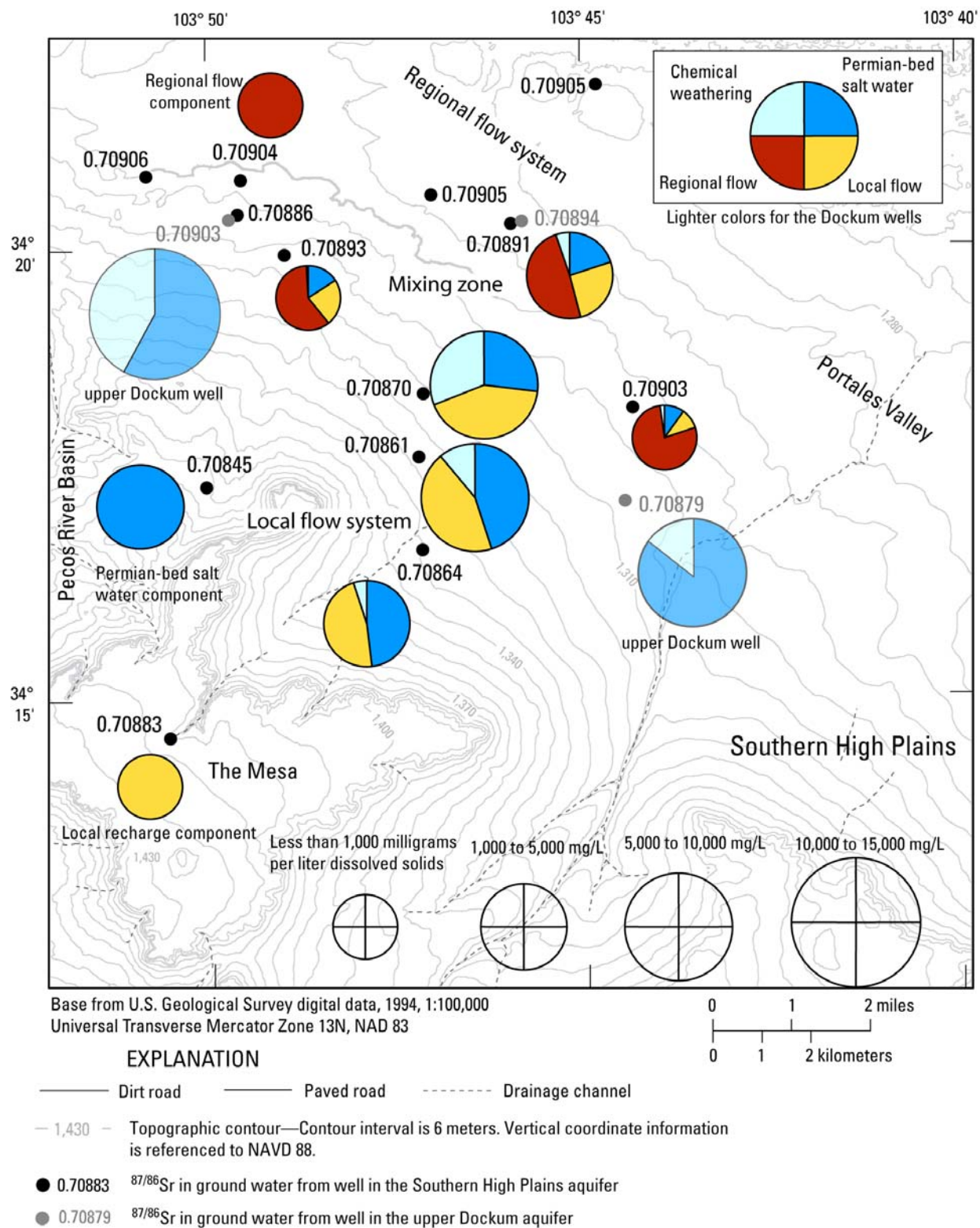


Figure 20. Ratios of $^{87}\text{Sr}/^{86}\text{Sr}$ and fractional contribution of strontium from source waters and chemical weathering in the different groundwater systems at the study site, June 2006.

Large calculated $^{87}\text{Sr}/^{86}\text{Sr}$ ratios for the Sr contributed from chemical weathering suggest this additional Sr is coming from the siliciclastic sediments of the Dockum and Ogallala, but low silica concentrations of groundwater from the upper Dockum aquifer and local flow system (table 4) do not support increased silicate weathering. It is likely that an increase in dissolved silica is inhibited by another control(s) on its solubility. Hem's (1989) review of work done by Hem et al. (1973) and Paces (1978) suggests such an additional control on dissolved silica related to amorphous silicate clay. Silica typically falls within a narrow range of concentrations and does not appear to be a useful indicator of silicate weathering (Hem, 1989). Stumm and Morgan (1996) describe the prevalence of polynuclear amorphous silica species at near neutral pH levels. Although silica is considered uncharged, silica polymorphs tend to form weak acids dependent upon proton, cation, and hydroxyl ion interactions with the silica's oxygen, and the solubility of silica polymorphs decreases with increasing size (Dove and Rimstidt, 1994). Alkali cations and other metals interact with the weakly charged silica polymorphs and may be controlling dissolved silica concentrations in the upper Dockum aquifer and local flow system that produces the low silica concentrations even though $^{87}\text{Sr}/^{86}\text{Sr}$ ratios indicate increased silicate weathering with older groundwater. The "silica problem" or apparent low silica concentrations where kinetic reactions should produce higher concentrations is a known problem and influences on concentrations such as interactions with aluminum, mineral surfaces, iron, and other tri- and divalent metals have been discussed as possible but not fully identified controls on silica solubility (Dove and Rimstidt, 1994).

$\delta^{11}\text{B}$, WATER-ROCK INTERACTIONS, AND ADSORPTION

Boron concentrations (59 to 1,740 mg/L) and $\delta^{11}\text{B}$ values (+6.0 to +46.0‰) were used to further refine geochemical effects of water-rock interactions and resolve the possible influence of

agricultural recharge in the mixing zone that was ambiguously identified with the other tracers. Boron values in groundwater at the study site generally fit the range of $\delta^{11}\text{B}$ values and Cl/B ratios presented in previous studies, and these results fit the conceptual flow model for likely source waters and flowpaths (fig. 21). Similar $\delta^{11}\text{B}$ values for Sheep Canyon caliche and young, local recharge (well 10) suggest a precipitation/soil signal near +15‰ (table 5). Regional flow system $\delta^{11}\text{B}$ values near +15‰ indicate a dominant precipitation/soil signal without substantial alteration from water-rock interaction in the Ogallala. Increased B concentrations and $\delta^{11}\text{B}$ values in the regional flow system indicate some B-mineral dissolution but very limited B exchange with adsorbing surfaces that would increase $\delta^{11}\text{B}$ values. The largest $\delta^{11}\text{B}$ values are in the local flow system and upper Dockum aquifer where groundwater is influenced by the Permian-bed saltwater, which has had long interactions with the Dockum shales where mass fractionation from adsorption is likely.

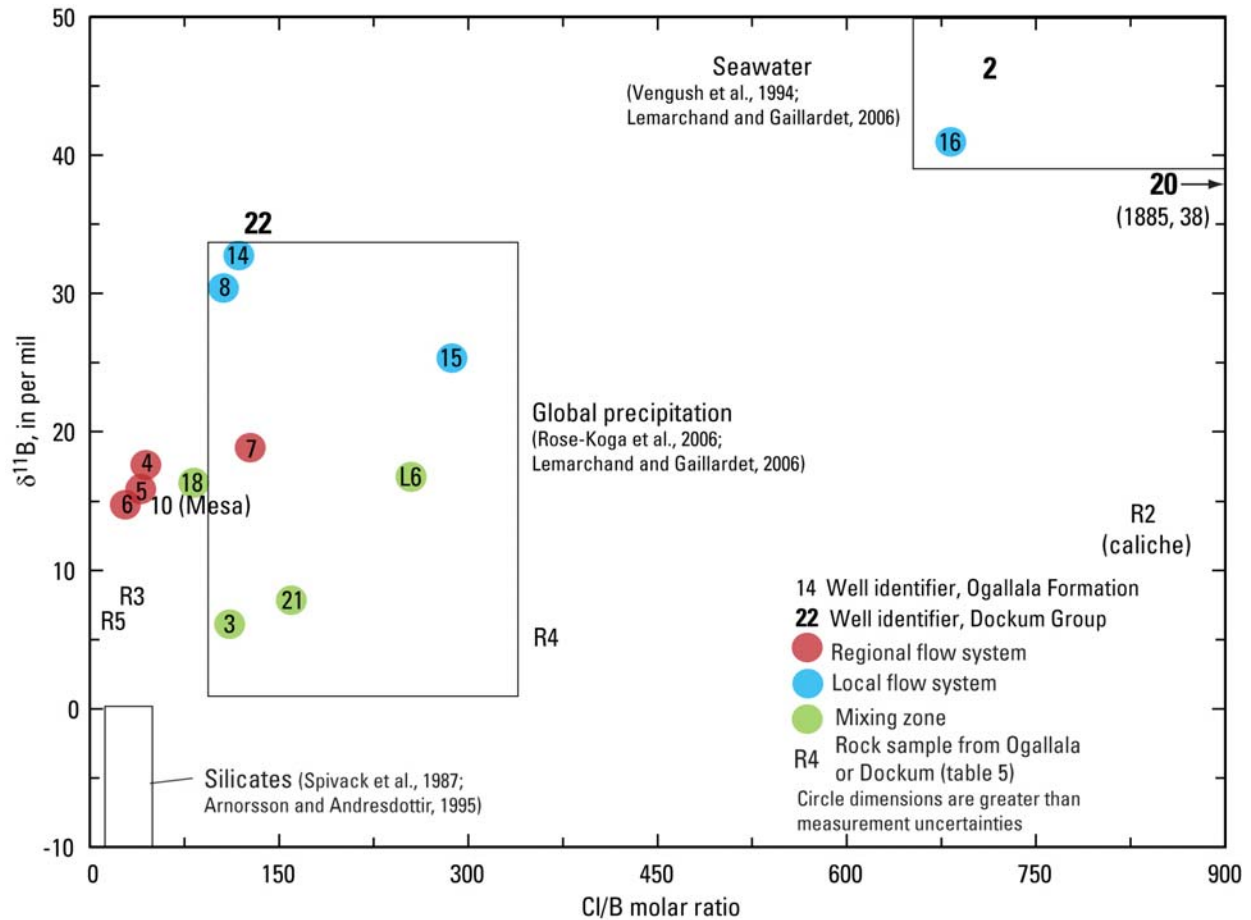


Figure 21. Chloride/boron molar ratios and $\delta^{11}\text{B}$ values in groundwater and rock samples at the study site in relation to possible boron sources.

Closer examination of B concentrations and $\delta^{11}\text{B}$ values at the study site indicates an adsorption effect in the local flow system with distance from the Mesa and dilution of the Permian-bed/Dockum saltwater signal upon mixing with the regional flow system (fig. 22). Additionally, the likely land use influence in the mixing zone is strongly apparent. The $\delta^{11}\text{B}$ values in the mixing zone decrease to the lowest groundwater $\delta^{11}\text{B}$ values and are similar to the sediment $\delta^{11}\text{B}$ values for the Ogallala and Dockum exposures in Sheep Canyon (fig. 22). The decrease in $\delta^{11}\text{B}$ values suggests increased contribution from weathering of silicate rocks, but the larger than expected decrease in concentrations suggest a loss of B in the mixing zone. If $\delta^{11}\text{B}$ values did not substantially change from the $\delta^{11}\text{B}$ values indicated by groundwater in well 16 (a

local flow system signal with a B concentration of 1,740 $\mu\text{g/L}$ and $\delta^{11}\text{B}$ of +41‰) and this water mixed according to the mixing component fractions from the Sr analysis with regional water averaging 120 $\mu\text{g/L}$ and a $\delta^{11}\text{B}$ value of +17‰, an expected B concentration and $\delta^{11}\text{B}$ value can be estimated for groundwater in the mixing zone (table 9). Results of these inverse calculations indicate that the mixing zone influence is substantially reducing B concentrations and $\delta^{11}\text{B}$ values more than what is expected from simple mixing of source waters.

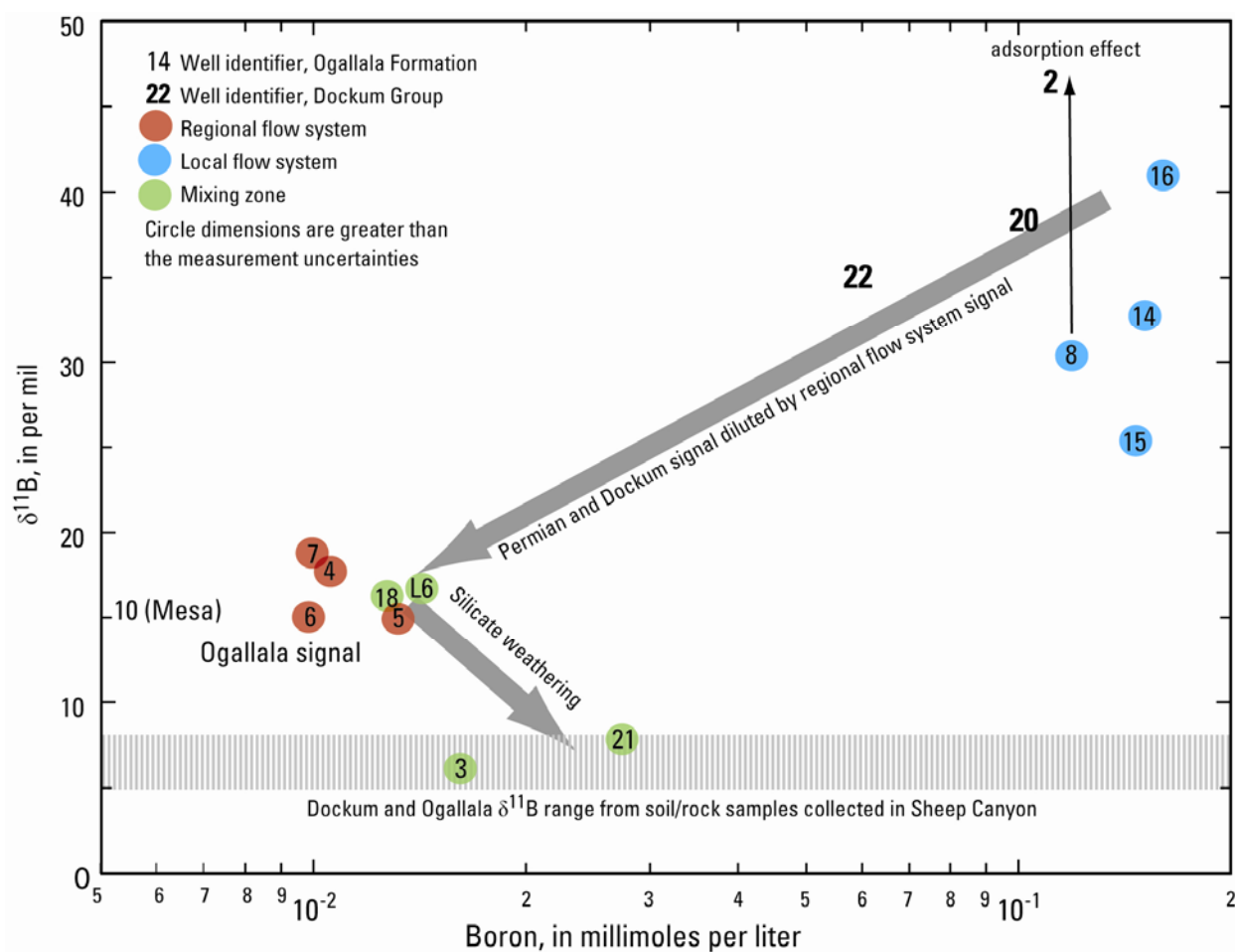


Figure 22. Boron concentrations and $\delta^{11}\text{B}$ values for groundwater at the study site, June 2006.

Table 9. Comparison of actual boron concentrations and isotope ratios in the mixing zone with calculated values estimated from the likely source-water mixing fractions determined by Sr concentration and $^{87}\text{Sr}/^{86}\text{Sr}$ inverse calculations.

Mixing components	$\delta^{11}\text{B}$ (‰)	Expected $\delta^{11}\text{B}$ value	% difference	Boron ($\mu\text{g/L}$)	Expected concentration	% difference	Permian-bed saltwater	Local flow system water	Regional flow system water
<i>Mixing zone:</i>				<i>Mixing fractions (table 8)*:</i>					
Well 3	+6	+18	-200%	180	217	-21%	0.10	0.10	0.80
Well 21	+8	+13	-63%	300	768	-156%	0.22	0.27	0.51
Well L6	+17	+17	0%	155	671	-333%	0.16	0.23	0.61

* Chemical-weathering fraction distributed proportionally between the three source waters.

AGRICULTURE AND GROUNDWATER GEOCHEMISTRY

Many of the previously discussed geochemical tracers indicated an additional influence in the mixing zone that could not be attributed to the possible source waters in Southern High Plains aquifer and the upper Dockum aquifer. Examining the geochemical and groundwater-age results along with the flow directions and land use, it appears that agricultural recharge is strongly affecting groundwater in the mixing zone with the strongest effect near wells 3 and 21. All mixing-zone wells are downgradient or adjacent to active or recently active agricultural areas (figs. 3 and 9). Agricultural recharge would explain the variable and unexpected sulfate, age, δD , $\delta^{18}\text{O}$, and $\delta^{11}\text{B}$ values for groundwater in the mixing zone. Sulfate values could be altered by application of fertilizers (sulfate is a common additive) and crop uptake (sulfate is a micronutrient) that may also explain the low nitrate concentrations in mixing zone groundwater (table 4). Groundwater ages could be reduced by exposure to atmospheric helium and tritium and would explain the younger water in well 21 compared to the regional flow system and why the other mixing zone wells did not reflect older ages that would be expected with mixing of the local and regional flow systems (table 4).

Groundwater δD and $\delta^{18}\text{O}$ values in the mixing zone were heavier than expected. Given the mixing of the local and regional flow systems, δD and $\delta^{18}\text{O}$ values in the mixing zone should

have plotted between values for these two systems (closer to the regional values because of its dominance in the area), but the values were incrementally heavier than δD and $\delta^{18}O$ values in the regional flow system values and indicated the presence of no local water (fig. 17). Evaporation from application of the mixed-zone water to crops in this area and subsequent recharge of this water to the aquifer would increase both δD and $\delta^{18}O$ values in mixing-zone groundwater (transpiration does not fractionate soil water; Gonfiantini et al., 1998). By using the water-source fractional components from the Sr analysis, it is possible to reinterpret the mixing zone δD and $\delta^{18}O$ values by estimating the mixing-zone groundwater isotopic signature prior to evaporation from agricultural use (table 10 and fig. 23). The calculated δD and $\delta^{18}O$ values provide a logical fit to the mixing model and substantiate the assertion that mixing zone water has undergone additional evaporation through irrigation.

Table 10. Inverse calculation of δD and $\delta^{18}O$ values using mixing fractions determined by Sr concentrations and $^{87}Sr/^{86}Sr$ ratios to examine evaporation from application of mixing-zone water to agricultural fields in the Southern High Plains aquifer at the study site.

Mixing components	δD (‰)	Expected δD value	Per mil difference	$\delta^{18}O$ (‰)	Expected $\delta^{18}O$ value	Per mil difference	Permian-bed saltwater	Local flow system water	Regional flow system water
<i>Mixing zone:</i>				<i>Mixing fractions (table 8)*:</i>					
Well 3	-44.60	-47.73	-3.13	-6.09	-6.69	-0.60	0.10	0.10	0.80
Well 21	-44.59	-50.81	-6.22	-5.85	-7.17	-1.32	0.21	0.27	0.52
Well L6	-43.90	-49.44	-5.54	-5.86	-6.97	-1.11	0.16	0.23	0.61

* Chemical weathering fraction distributed proportionally between the three source waters.

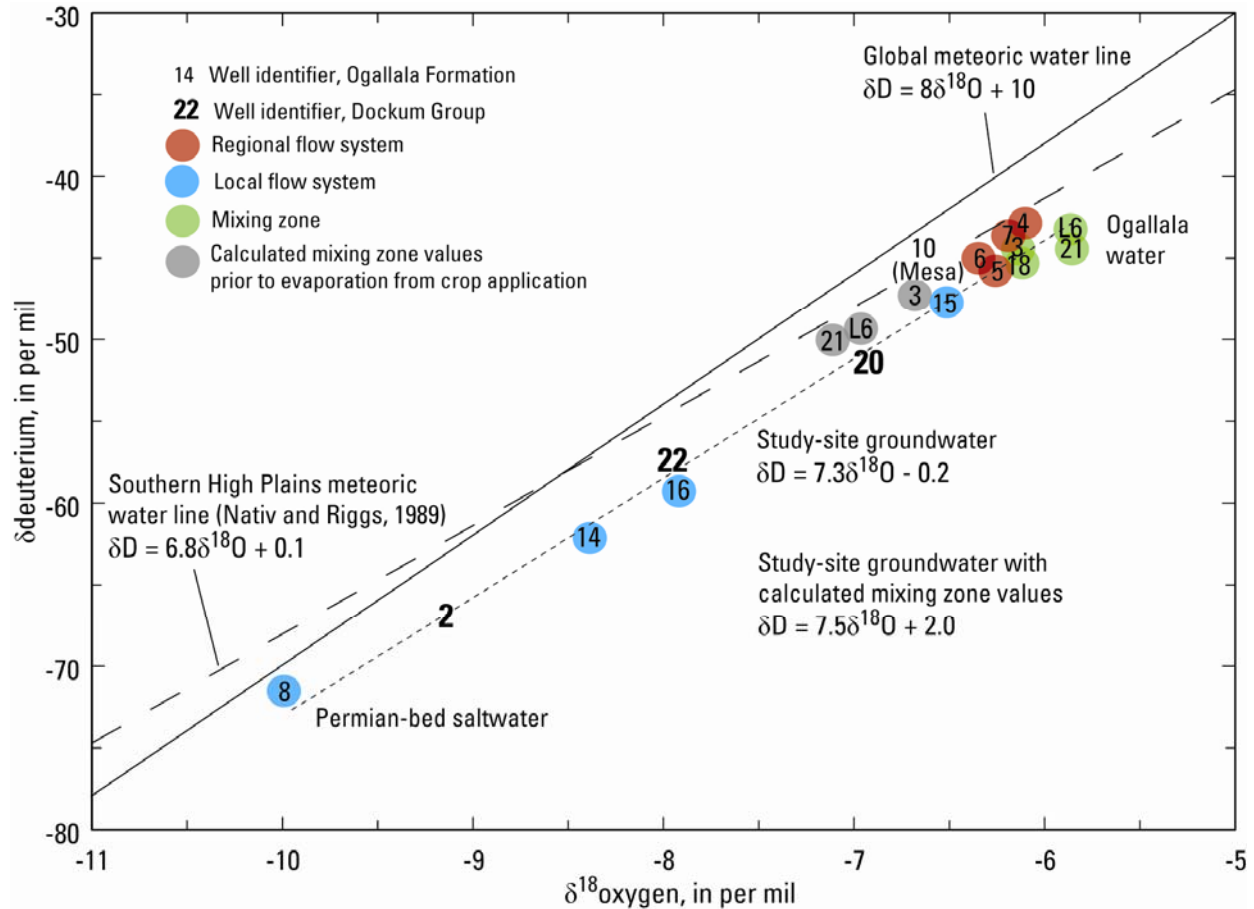


Figure 23. Groundwater δD and $\delta^{18}O$ values at the study site and calculated isotope ratios for the mixed zone wells from inverse calculations (table 10) using water source fractions as determined by strontium concentration and $^{87}Sr/^{86}Sr$ ratios (table 8).

The alteration of groundwater geochemistry in the mixing zone from agricultural recharge is also visible in the Sr inverse calculation results for chemical weathering (table 8). Strontium is not fractionated by biological processes and the vegetation $^{87}Sr/^{86}Sr$ ratio would reflect the available water source (Capo et al., 1998). Larger $^{87}Sr/^{86}Sr$ ratios were calculated for the chemical weathering contributions in the mixing zone compared to the upper Dockum aquifer and the local flow system. These larger values suggest a greater weathering of silicate Sr-bearing minerals. It is possible that some of this Sr is a result of fertilizer application but such a contribution would be difficult to quantify given the variability of Sr concentrations and $^{87}Sr/^{86}Sr$

ratios in fertilizers, although $^{87}\text{Sr}/^{86}\text{Sr}$ ratios in fertilizer tend to be more radiogenic (Böhlke and Horan, 2000; Widory et al., 2004).

Boron is considered an essential plant micro-nutrient and can be limiting to crop production through either boron toxicity or deficiency (Gupta, 1993). Boron is necessary for optimal growth and yield of cotton (Zhao and Oosterhuis, 2002) and grains (Shorrocks, 1997), both common crops in the study site region. Boron is absorbed from soil solution typically by roots as boric acid, which is common in soils and solutions with a pH less than 8 (Kakihana et al., 1977; Hershey et al., 1986; Hu and Brown, 1997; Mather and Porteous, 2001). Plants respond directly to the activity of B in soil solution and only indirectly to B adsorbed on soil constituents (Goldberg, 1997), indicating stronger uptake of B from solution than at the porewater-sorption surface interface. Boron is commonly incorporated into fertilizers or applied separately to crops to provide sufficient B to amend B-poor soils of which igneous alluvial sediments are generally deficient in B (Shorrocks, 1997). Fertilizer B (borate) isotope analysis has indicated $\delta^{11}\text{B}$ values of about -15 to +10‰ (Vengosh et al., 1994; Komor, 1997; Leenhouts et al. 1998; Zhang et al., 2006).

The current understanding of B as a plant nutrient and its uptake in soil suggests that the presence of B in mixing zone groundwater applied as irrigation would result in the preferential uptake of solution B and the later advection of soil or fertilizer B into the soil profile and possible return to the underlying aquifer. The transport of B in the mixing zone likely consists of the following pathway: 1) crop application of groundwater containing a B concentration and isotope signature representative of the mixing of local flow system and regional flow system waters, 2) B in solution is likely uptaken by the crop preferentially over any adsorbed B in fertilizer or the soil, 3) when crop growth is small or nonexistent, the remaining soil water and adsorbed B is flushed deeper into the soil profile from precipitation events or irrigation, 4) soil

water is driven downward through piston-flow where additional chemical weathering of soil/vadose zone minerals occur, 5) sufficient piston-flow provides agriculturally-modified recharge to the mixing zone. With the removal of the heavier B isotope signature in the irrigation water (mixing-zone groundwater) from plant uptake and the entrainment of lighter B isotopes from possible fertilizer sources and soil and vadose zone weathering, the $\delta^{11}\text{B}$ values of the local recharge to groundwater at and downgradient of agricultural areas is lighter than other groundwater mixtures but also contains a higher B concentration than the regional flow system because of fertilizer/soil B or additional weathering in the vadose zone (figs. 21 and 22).

Chapter 5: Flowpaths in the Southern High Plains Aquifer Along the Western Caprock Escarpment

Information derived from the formation properties, potentiometric surfaces, geochemical characteristics, and groundwater ages, was used to estimate the extent of source water influences in the study area and modify the conceptual flowpath model (figs. 24 and 25). Old water (greater than 20,000 years) with a distinct Permian-salt signal is migrating from the salt beds through fractures in the Dockum shales with the strongest flow closest to the Western Caprock Escarpment. This water likely originates in the Pecos River Basin and crosses beneath the hydrologic divide of the Western Caprock Escarpment through the Permian bedded salts. This water either continues through the fractures near the Mesa and enters the Dockum aquifer(s) or enters the local flow system of the Southern High Plains aquifer and flows eastward. Longer residence of the water in the Dockum prior to entering the Southern High Plains aquifer alters the Permian-salt signal through chemical weathering that contributes solutes and exchange/adsorption that changes solute ratios. Water in the local flow system of the Southern High Plains aquifer flows away from the Mesa and mixes with the regional flow system in the mixing zone, but local flow system contributions are variable by location because of structural highs in the Dockum/Ogallala contact that shape local flow system flowpaths.

Water from the regional flow system contributes the majority of water in the mixing zone, substantially reducing the geochemical signal of the saltwater migrating from the Permian salts through the Dockum shales and into the mixed alluvium of the Southern High Plains aquifer. The resulting mixing-zone water also is affected by agricultural recharge that was previously mixing-zone water that has undergone evaporation and chemical alteration through crop effects (plant uptake), interaction with possible crop treatments (fertilizers), and water-rock interactions in the soil and vadose zone. A mixing zone also appears to be present in the upper

Dockum aquifer where Permian-bed/Dockum saltwater underlying the local flow system in the Dockum likely mixes with regional Dockum water. The regional Dockum water is older than the regional water of the Southern High Plains regional flow system, and this longer residence time produces a geochemical signal different than the Southern High Plains aquifer, although more similar to the regional flow system of the Southern High Plains aquifer than the saltwater of the Permian salts.

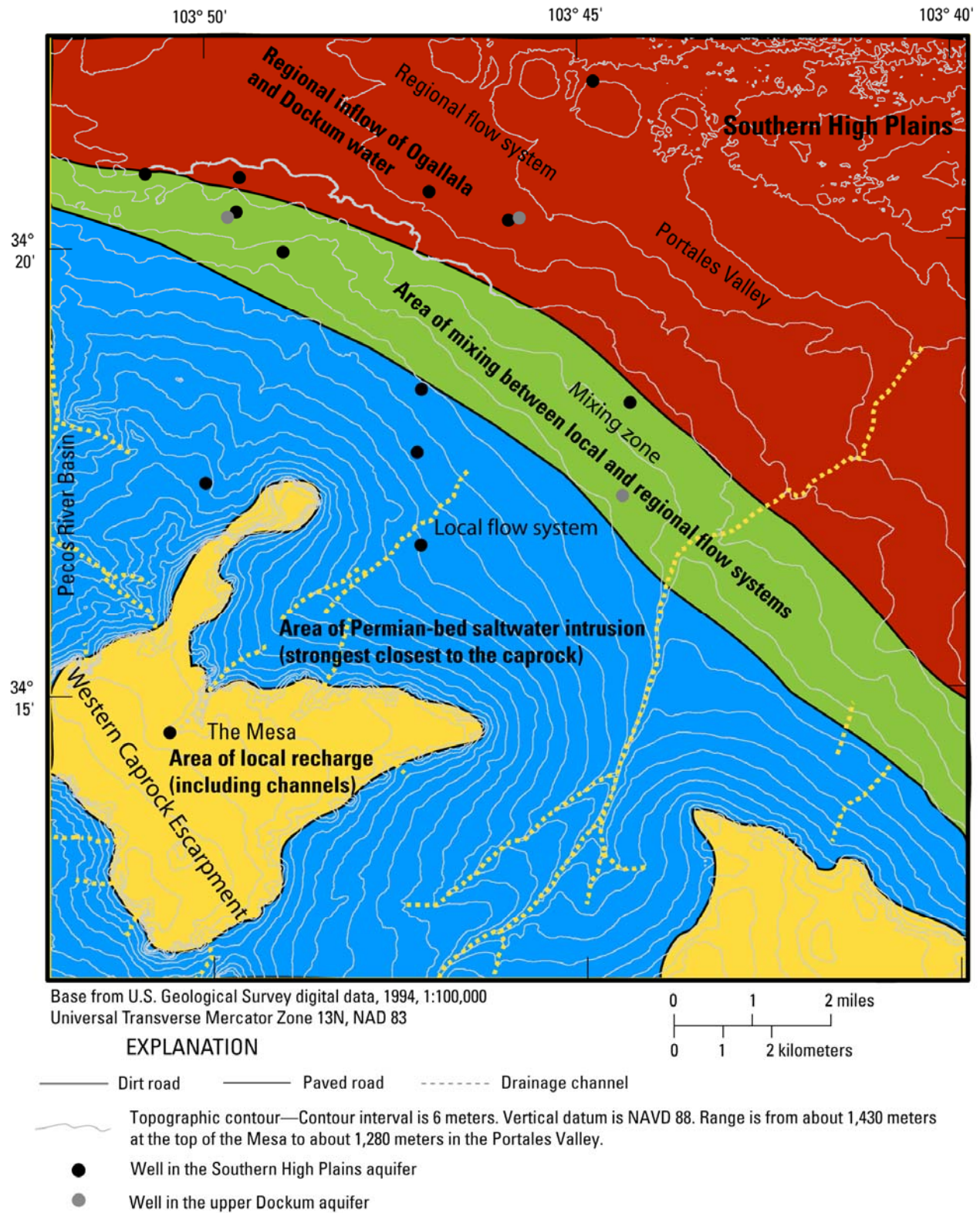


Figure 24. Likely source-water origins and cross-formational flow in the Southern High Plains aquifer.

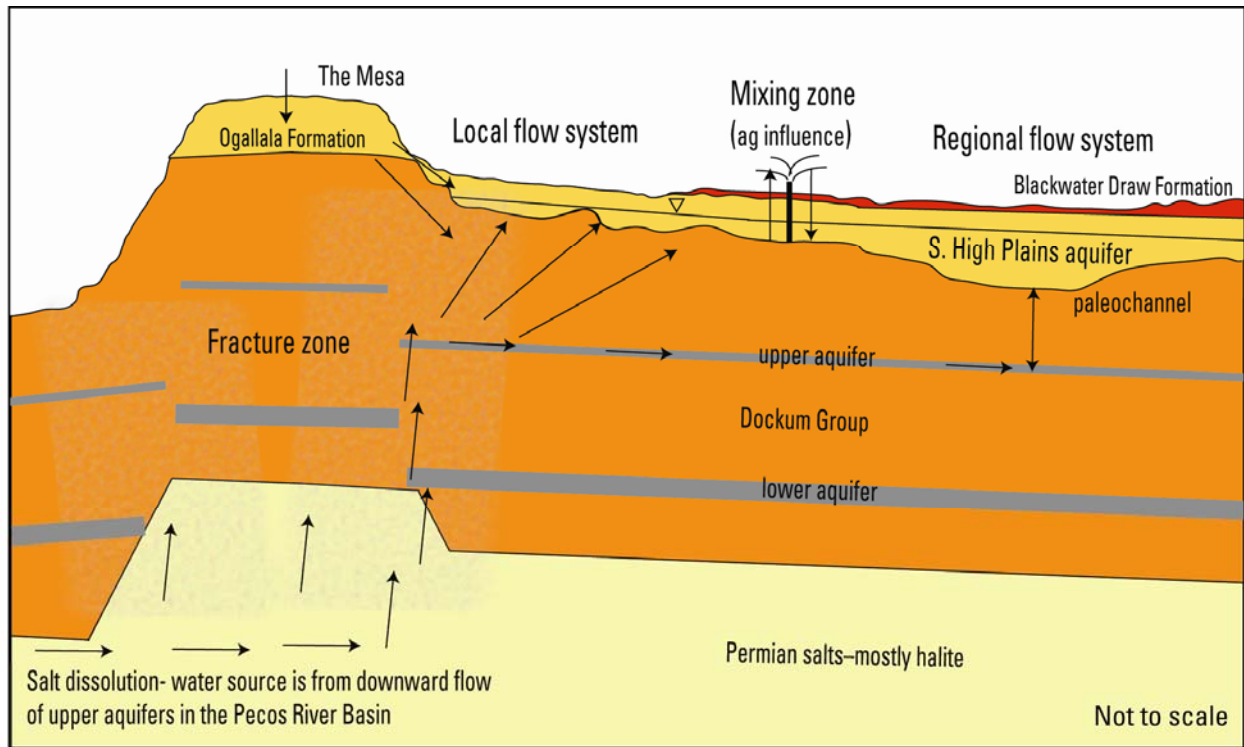


Figure 25. Study-supported conceptual model of groundwater flowpaths in the Southern High Plains along the Western Caprock Escarpment.

Chapter 6: Conclusions and Summary

The High Plains aquifer system is the most heavily used aquifer in the world, and the Southern High Plains aquifer has substantially decreased in saturated thickness because of groundwater mining. Sustainable management of groundwater resources requires sufficient knowledge of the distribution of fresh and saline groundwater and the processes affecting saltwater intrusion that may influence the beneficial use of groundwater. Chemical and isotopic tracers including $^3\text{H}/^3\text{He}$, ^{14}C , δD , $\delta^{18}\text{O}$, $^{87}\text{Sr}/^{86}\text{Sr}$, and $\delta^{11}\text{B}$ were examined in combination to determine source waters, saltwater origin, cross-formational flow, and water-rock interactions in the Southern High Plains aquifer along the Western Caprock Escarpment. The coupling of multiple groundwater tracers—major and trace elements and δD , $\delta^{18}\text{O}$, $^{87}\text{Sr}/^{86}\text{Sr}$, and $\delta^{11}\text{B}$ —was necessary to identify all possible source waters and the effects of water-rock interactions to fully resolve the geochemical evolution of groundwater along the periphery of the Southern High Plains aquifer.

Sub-aquifers or local flow systems are present in the Southern High Plains aquifer along the Western Caprock Escarpment that was formed by the dissolution and subsidence of buried, Permian bedded salts. The study site's local flow system drains a Na-Cl, high dissolved solids (2,000 to 9,500 mg/L) groundwater from the escarpment until it mixes with a regional aquifer or regional flow system that is more oxygenated and a mixed cation- HCO_3^- water type with low dissolved solids (390 to 520 mg/L). The local flow system contains old water (5,500 to 21,000 years) that is similar in age and composition to the underlying, upper Dockum aquifer (Na-Cl water type, 970 to 13,000 mg/L dissolved solids, 12,000 to 27,000 years). The δD and $\delta^{18}\text{O}$ values for the local flow system (-71.74 to -47.96‰ and -9.95 to -6.52‰, respectively) and upper Dockum aquifer (-67.20 to -51.70‰ and -9.11 to -6.93‰) were lower and more variable

compared to the regional flow system (-45.97 to -43.29‰ and -6.30 to -6.09‰). Groundwater δD and $\delta^{18}O$ values in the mixing zone (-45.19 to -43.90‰ and -6.14 to -5.85‰) indicate further evaporation. Groundwater evolution could not be fully resolved using these traditional tracers because of large variations in element, age, δD , and $\delta^{18}O$ values within each system.

Further evidence of source waters, saltwater origin, and the geochemical evolution of groundwater was compiled by coupling $^{87}Sr/^{86}Sr$ and $\delta^{11}B$ values with major ion, trace element, age, δD , and $\delta^{18}O$ values. The $^{87}Sr/^{86}Sr$ range of 0.70845 to 0.70906 and Sr concentrations of 0.90 to 31 mg/L were sufficient to estimate source-water fractions and contributions from chemical weathering through inverse calculations. Boron concentrations (59 to 1,740 mg/L) and $\delta^{11}B$ values (+6.0 to +46.0‰) were used to resolve the influence of agricultural recharge in the mixing zone that was ambiguously identified with the other tracers. Alteration of B and $\delta^{11}B$ values in the mixing zone indicate the loss of B and decrease in $\delta^{11}B$ values likely from plant uptake, adsorption, and weathering contributions in the soil and vadose zone prior to recharge beneath or near agricultural fields. With confirmation of this additional influence in the mixing zone, results from the Sr inverse calculations were used to reinterpret δD and $\delta^{18}O$ values to account for agricultural recharge.

Analysis of the geochemical tracers produced a conceptual flow model of the groundwater along the Western Caprock Escarpment of the Southern High Plains. Results of this study supported some previous investigations but provided substantial clarity to the presence of groundwater in the upper Dockum aquifer and its effect on the Southern High Plains aquifer along the Western Caprock Escarpment. Groundwater interaction with Permian bedded salts and Dockum Group shales produces a high dissolved-solids groundwater with a strong halite signal that strongly influences groundwater composition in the Southern High Plains aquifer. Cross-formational flow from the Permian bedded salts into the Dockum Group provides a water source

where it was suggested that no source likely existed because of the hydrologic divide of the escarpment (Dutton and Simpkins, 1986), and this water likely originates in the Pecos River Basin and crosses beneath the hydrologic divide through the Permian bedded salts. The mixing of young (less than 100 years), local recharge from surface pathways at the Western Caprock Escarpment and much older (greater than 20,000 years) saltwater from the Permian salts and Dockum Group is spatially variable and dependent on available flowpaths created by fracturing of the Dockum Group shales because of Permian salt subsidence. The cross-formational flow from the upper Dockum aquifer into the Southern High Plains aquifer is a substantial water source in the local flow system along the escarpment as it mixes with local, surface recharge. The mixed groundwater in local systems of the Southern High Plains aquifer along the Western Caprock Escarpment mixes with regional flow systems of larger saturated thickness where the geochemical signal of the halite-influenced saltwater is substantially reduced but visible in a thin mixing zone.

The Dockum Group shales and agricultural recharge alter the geochemical signal of certain tracers limiting the use of these tracers for identifying source waters, mixing patterns, and water-rock interactions. Major and trace elements were influenced by natural (mineral dissolution and adsorption) and anthropogenic (irrigation) effects that alter concentrations and compositions, but are useful for general identification of hydrochemical facies changes. Groundwater ages determined by $^3\text{H}/^3\text{He}$ and ^{14}C methods were sufficient at discriminating major divisions in source waters. The utility of δD and $\delta^{18}\text{O}$ for examining groundwater in agricultural areas was limited by the effect of evaporation on agricultural recharge, but these values were used to estimate the effect of evaporation in conjunction with other tracers. The $^{87}\text{Sr}/^{86}\text{Sr}$ ratio was the least influenced by agricultural recharge, but its utility is minimized by the limited difference in $^{87}\text{Sr}/^{86}\text{Sr}$ ratios derived from silicates that compose the major formations in

the Southern High Plains. The $\delta^{11}\text{B}$ values were the most useful tracer for identifying both natural and anthropogenic effects because of the large $\delta^{11}\text{B}$ range and the adsorption of B with flow through the Dockum Group shales and uptake of B by field crops. Overall, coupling of multiple tracers, both traditional and nontraditional, was necessary to identify natural and anthropogenic processes that influence the groundwater geochemical evolution in the Southern High Plains aquifer.

References

- Arnorsson, S., Andresdottir, A., 1995. Process controlling the distribution of boron and chlorine in natural waters in Iceland. *Geochim. Cosmochim. Acta* 59, 4125–4146.
- Bair, E.S., 1987. Regional hydrodynamics of the proposed high-level nuclear-waste repository sites in the Texas Panhandle. *J. of Hydrol.* 92, pp. 149–172.
- Baker, Jr., C.H., Leonard, R.B., 1995. Hydrochemistry of aquifer systems and relation to regional flow patterns in Cretaceous and older rocks underlying Kansas, Nebraska, and parts of Arkansas, Colorado, Missouri, New Mexico, Oklahoma, South Dakota, Texas, and Wyoming. *US Geol. Surv. Water-Resources Investigations Report* 94-4144.
- Banner, J.L., Wasserburg, G.J., Dobson, P.F., Carpenter, A.B., Moore, C.H., 1989. Isotopic and trace element constraints on the origin and evolution of groundwaters from central Missouri. *Geochim. Cosmochim. Acta* 53, 383–398.
- Banner, J.L., Musgrove, M., Capo, R.C., 1994. Tracing groundwater evolution in a limestone aquifer using Sr isotopes: effects of multiple sources of dissolved ions and mineral–solution reactions. *Geology* 22, 687– 690.
- Barth, S., 2000. Utilization of boron as a critical parameter in water quality evaluation—implications for thermal and mineral water resources in SW Germany and N Switzerland. *Envi. Geol.* 40, 73–89.
- Beyerle, U., Aeschbach-Hertig, W., Hofer, M., Imboden, D.M., Baur, H., Kipfer, R., 1999. Infiltration of river water to a shallow aquifer investigated with $^3\text{H}/^3\text{He}$, noble gases, and CFCs. *J. of Hydrol.* 220, 169–185.
- Blunier, T., Brook, E.J., 2001. Timing of millennial-scale climate change in Antarctica and Greenland during the last glacial period. *Science* 291, 109–112.
- Böhlke, J.K., Horan, M., 2000. Strontium isotope geochemistry of groundwaters and streams affected by agriculture, Locust Grove, MD. *Appl. Geochem.* 15, 599–609.
- Bouwer, H., Rice, R.C., 1976. A slug test method for determining hydraulic conductivity of unconfined aquifers with completely or partially penetrating wells. *Water Resour. Res.* 12, pp. 423–428.

- Bradley, R.G., Kalaswad, S., 2003. The Groundwater Resources of the Dockum Aquifer in Texas. Texas Water Development Board Report 359.
- Brand, J.P., 1952. Cretaceous of the Llano Estacado of Texas. Bureau of Economic Geology, University of Texas at Austin, Report of Investigations 20.
- Broadhead, R.F., King, W.E., 1988. Petroleum geology of Pennsylvanian and lower Permian strata, Tucumcari Basin, east-central New Mexico. New Mexico Bureau of Mines & Mineral Resources Bulletin 119, 75 p.
- Brook, E.J., White, J.W.C., Schilla, A.S.M., Bender, M.L., Barnett, B., Severinghaus, J.P., Taylor, K.C., Alley, R.B., Steig, E.J., 2005. Timing of millennial-scale climate change at Siple Dome, West Antarctica, during the last glacial period. *Quaternary Science Reviews* 24, 1333–1343.
- Brookins, D.G., 1988. Seawater $^{87}\text{Sr}/^{86}\text{Sr}$ for the late Permian Delaware Basin evaporates, New Mexico, USA. *Chem. Geol.* 69, 209–214.
- Bullen, T.D., Kendall, C., 1998. Tracing of weathering reactions and water flowpaths, a multi-isotope approach. In: Kendall, C., McDonnell, J.J. (Eds.), *Isotope tracers in catchment hydrology*. Elsevier Science B.V., Amsterdam, pp. 611–643 (Chapter 18).
- Bullen, T.D., Krabbenhoft, D.P., Kendall, C., 1996. Kinetic and mineralogic controls on the evolution of groundwater chemistry and $^{87}\text{Sr}/^{86}\text{Sr}$ in a sandy silicate aquifer, northern Wisconsin, USA. *Geochim. Cosmochim. Acta* 60, 1807–1821.
- Bullen, T.D., White, A.F., Blum, A.E., Harden, J.W., Schulz, M.S., 1997. Chemical weathering of a soil chronosequence on granitoid alluvium, II: mineralogic and isotopic constraints on the behavior of strontium. *Geochim. Cosmochim. Acta* 61, 291–306.
- Burke, W.H., Dennison, R.E., Hetherington, E.A., Koepnick, R.B., Nelson, H.F., Otto, J.B., 1982. Variation of seawater $^{87}\text{Sr}/^{86}\text{Sr}$ throughout Phanerozoic time. *Geol.* 10, 516–519.
- Cannon Air Force Base, 2002. Management action plan, Air Combat Command, Cannon Air Force Base, New Mexico, December 2002. Air Force project ACCH20027544, 266 p.
- Capo, R.C., Stewart, B.W., Chadwick, O.A., 1998. Strontium isotopes as tracers of ecosystem processes—theory and methods. *Geoderma* 83, 515–524.

- Coplen, T.B., Wildman, J.D., Chen, J., 1991. Improvements in the gaseous hydrogen-water equilibration technique for hydrogen isotope ratio analysis. *Anal. Chem.* 63, 910–912.
- Dansgaard, W., 1964. Stable isotopes in precipitation. *Tellus* 16, 436–468.
- Dansgaard, W., Johnsen, S.J., Clausen, H.B., Dahl-Jensen, D., Gundestrup, N.S., Hammer, C.U., Hvidberg, C.S., Steffensen, J.P., Sveinbjörnsdottir, A.E., Jouzel, J., Bond, G., 1993. Evidence for general instability of past climate from a 250-kyr ice-core record. *Nature* 364, 218–220.
- Dick-Peddie, W., 1993. New Mexico vegetation—past, present, and future. Albuquerque, University of New Mexico Press, 244 p.
- Dove, P.M., Rimstidt, J.D., 1994. Silica-water interactions. In: Heaney, P.J., Prewitt, C.T., Gibbs, G.V. (Eds.), *Reviews in mineralogy, silica—physical behavior, geochemistry, and materials applications*, vol. 29. Mineralogical Society of America, Washington, D.C., pp. 259–308 (Chapter 8).
- Dutton, A.R., 1987. Hydrogeologic and hydrochemical properties of salt-dissolution zones, Palo Duro Basin, Texas Panhandle—preliminary assessment. Geological Circular 87-2, Bureau of Economic Geology, University of Texas at Austin, 32 pp.
- Dutton, A.R., 1989. Hydrogeochemical processes involved in salt-dissolution zones, Texas Panhandle, U.S.A.. *Hydrol. Proc.* 3, 75–89.
- Dutton, A.R., 1995. Groundwater isotopic evidence for paleorecharge in U.S. High Plains aquifers. *Quat. Res.* 43, 221–231.
- Dutton, A.R., Simpkins, W.W., 1986. Hydrogeochemistry and water resources of the Triassic Lower Dockum Group in the Texas Panhandle and eastern New Mexico. Report of Investigations 161, Bureau of Economic Geology, University of Texas at Austin.
- Dutton, A.R., Simpkins, W.W., 1989. Isotopic evidence for paleohydrologic evolution of ground-water flowpaths, Southern Great Plains, U.S.A. *Geology* 17, 653–656.
- Dutton, A.R., Mace, R.E., Reedy, R.C., 2001. Quantification of spatially varying hydrogeologic properties for a predictive model of groundwater flow in the Ogallala aquifer, northern Texas panhandle. In: Lucas, S.G., Ulmer-Scholle, D.S. (Eds.), *Geology of Llano Estacado*. New Mexico Geological Society, Socorro, pp. 297–307.

- Dutton, S.P., Finley, R.J., Galloway, W.E., Gustavson, T.C., Handford, C.R., Presley, M.W., 1979. Geology and geohydrology of the Palo Duro Basin, Texas Panhandle, Geological Circular 79-1, Bureau of Economic Geology, University of Texas at Austin.
- Eby, G.N., 2004. Principles of environmental geochemistry. Brooks/Cole-Thomson Learning, Pacific Grove, California.
- Eisenhut, S., Heumann, K.G., Vengosh, A., 1996. Determination of boron isotopic variations in aquatic systems with negative thermal ionization mass spectrometry as a tracer for anthropogenic influences, *Fresenius J. of Anal. Chem.* 354, 903–909.
- Epstein, S., Mayeda, T., 1953. Variation of O-18 content of water from natural sources. *Geochim. Cosmochim. Acta* 4, 213–224.
- Fahlquist, L., 2003. Groundwater quality of the Southern High Plains aquifer, Texas and New Mexico, 2001. US Geol. Surv. Open-File Report 03-345.
- Falk, S.E., 2005. Estimated groundwater age and rate of recharge in the southern High Plains Aquifer, Cannon Air Force Base, Curry County, New Mexico, 2004. University of New Mexico, Dept. of Civil Engineering, Master's thesis.
- Fenneman, N.M., Johnson, D.W., 1946. Physical Divisions of the United States. US Geol. Surv., scale 1:7,000,000.
- Genereux, D.P., Hooper, R.P., 1998. Oxygen and hydrogen isotopes in rainfall-runoff studies. In: Kendall, C., McDonnell, J.J. (Eds.), *Isotope tracers in catchment hydrology*. Elsevier Science B.V., Amsterdam, pp. 319–346 (Chapter 10).
- Goldberg, S., 1997. Reactions of boron with soils. *Plant and Soil* 193, 35–48.
- Goldstein, A.G., Collins, E.W., 1984. Deformation of Permian strata overlying a zone of salt dissolution and collapse in the Texas Panhandle. *Geol.* 12, 314–317.
- Goldstein, S.L., Jacobsen, S.B., 1988. Nd and Sr isotopic systematics of river water suspended material—implications for crustal evolution. *Earth and Planet. Sci. Lett.* 87, 249–265.
- Gonfiantini, R., Fröhlich, K., Araguás-Araguás, L., Rozanski, K., 1998. Isotopes in groundwater hydrology. In: Kendall, C., McDonnell, J.J. (Eds.), *Isotope tracers in catchment hydrology*. Elsevier Science B.V., Amsterdam. pp. 203–246 (Chapter 7).

- Granata, G.E., 1981. Regional sedimentation of the late Triassic Dockum Group, west Texas and eastern New Mexico. University of Texas at Austin, Master's thesis.
- Gupta, U., 1993. Boron and its role in crop production. CRC Press, Boca Raton, Florida.
- Gustavson, T.C., 1986. Geomorphic development of the Canadian river valley, Texas Panhandle—an example of regional salt dissolution and subsidence. *Geol. Soc. of Am. Bull.* 97, 459–472.
- Gustavson, T.C., 1996. Fluvial and eolian depositional systems, paleosols, and paleoclimate of the upper Cenozoic Ogallala and Blackwater Draw Formations, Southern High Plains, Texas and New Mexico. Bureau of Economic Geology, University of Texas at Austin, Report of Investigations 239.
- Gustavson, T.C., Finley, R.J., 1985. Late Cenozoic geomorphic evolution of the Texas Panhandle and northeastern New Mexico—case studies of structural controls on regional drainage development. Bureau of Economic Geology, University of Texas at Austin, Report of Investigations 148.
- Gustavson, T.C., Finley, R.J., McGillis, K.A., 1980. Regional dissolution of Permian salt in the Anadarko, Dalhart, and Palo Duro Basins of the Texas Panhandle. Bureau of Economic Geology, University of Texas at Austin, Report of Investigations 106.
- Gustavson, T.C., Holliday, V.T., Hovorka, S.D., 1995. Origin and development of playa basins, sources of recharge to the Ogallala Aquifer, Southern High Plains, Texas and New Mexico. Bureau of Economic Geology, University of Texas at Austin, Report of Investigations 229.
- Hart, D.L., McAda, D.P., 1985. Geohydrology of the High Plains aquifer in southeastern New Mexico. *US Geol. Surv. Hydrologic Investigations Atlas HA-679*.
- Hem, J.D., 1989. Study and interpretation of the chemical characteristics of natural water. *US Geol. Surv. Water-Supply Paper 2254*.
- Hem, J.D., Roberson, C.E., Lind, C.J., Polzer, W.L., 1973. Chemical interactions of aluminum with aqueous silica at 25°C. *US Geol. Surv. Water-Supply Paper 1827-E*.
- Hershey, J.P., Fernandez, M., Milne, P.J., Millero, F.J., 1986. The ionization of boric acid in NaCl, Na–Ca–Cl, Na–Mg–Cl solutions at 25 °C. *Geochim. Cosmochim. Acta* 50, 143–148.

- Hess, J., Bender, M.L., Schilling, J.G., 1986. Evolution of the ratio of strontium-87 to strontium-86 in seawater from Cretaceous to present. *Science* 231, 979–984.
- Holliday, V.T., 1990. Sedimentation, soil stratigraphy, and age of the Blackwater Draw Formation, in Gustavson, T.C. (ed.), *Geologic framework and regional hydrology: upper Cenozoic Blackwater Draw and Ogallala Formations, Great Plains*. University of Austin, Bureau of Economic Geology, 10–22.
- Hu, H., Brown, P.H., 1997. Absorption of boron by plant roots. *Plant and Soil* 193, 49–58.
- Ingraham, N.L., 1998. Isotopic variations in precipitation. In: Kendall, C., McDonnell, J.J., *Isotope tracers in catchment hydrology*. Elsevier Science B.V., Amsterdam, pp. 87–118 (Chapter 3).
- Insightful Corporation, 2005. *S-PLUS 7.0 guide to statistics, volume 2*. Seattle, Insightful Corporation, Seattle.
- Johns, D.A., 1989. Lithogenetic stratigraphy of the Triassic Dockum Formation, Palo Duro Basin, Texas. Bureau of Economic Geology, University of Texas at Austin, Report of Investigations 182, 71 p.
- Johnson, T.M., DePaolo, D.J., 1994. Interpretation of isotopic data in groundwater–rock systems—model development and application to Sr isotope data from Yucca Mountain. *Water Resour. Res.* 30, 1571–1587.
- Johnson, T.M., DePaolo, D.J., 1997. Rapid exchange effects on isotope ratios in groundwater systems—development of a transport–dissolution–exchange model. *Water Resour. Res.* 33, 187–195.
- Kakihana, H., Kotaka, M., Satoh, S., Nomura, M., and Makoto Okamoto, M., 1977. Fundamental Studies on the ion-exchange separation of boron isotopes. *Bulletin of the Chemical Society of Japan* 50, 158–163.
- Knowles, T., Nordstrom, P., Klemm, W.B., 1984. Evaluation of the groundwater resources of the High Plains of Texas. Texas Department of Water Resources, Austin, Report 288, vol. 1.
- Komor, S.C., 1997. Boron contents and isotopic compositions of hog manure, selected fertilizers, and water in Minnesota. *J. of Env. Qual.* 26, 1212–1222.

- Langman, J.B., Gebhardt, F.E., Falk, S.E., 2004. Groundwater hydrology and water quality of the Southern High Plains aquifer, Melrose Air Force Range, Cannon Air Force Base, Curry and Roosevelt Counties, New Mexico, 2002-03. US Geol. Surv. Scientific Investigations Report 2004-5158.
- Langman, J.B., Falk, S.E., Gebhardt, F.E., Blanchard, P.J., 2006. Groundwater hydrology and water quality of the Southern High Plains aquifer, Cannon Air Force Base, Curry County, New Mexico, 1994-2005. US Geol. Surv. Scientific Investigations Report 2006-5280.
- Langmuir, D., 1997. Aqueous environmental geochemistry. Prentice-Hall, Inc., Upper Saddle River, New Jersey.
- Leeman, W.P., Sisson, V.B., 1996. Geochemistry of boron and its implications for crustal and mantle processes. In: Crew, E.S., Anovitz, L.M. (Eds.), *Boron—Mineralogy, Petrology and Geochemistry*, vol. 33. Mineral. Soc. Am., Chantilly, Virginia, pp. 645–707.
- Leenhouts, J.M., Basset, R.L., Maddock, T., 1998. Utilization of intrinsic boron isotopes as co-migrating tracers for identifying potential nitrate contamination sources. *Groundwater* 36, 240–250.
- Lemarchand, D., Gaillardet, J., 2006. Transient features of the erosion of shales in the Mackenzie basin (Canada), evidences from boron isotopes. *Earth and Planet. Sci. Lett.* 245, 174–189.
- Lemarchand, E., Schott, J., Gaillardet, J., 2005. Boron isotopic fractionation related to boron sorption on humic acid and structure of surface complexes formed. *Geochim. Cosmochim. Acta* 69, 3519–3533.
- Mather, J.D., Porteous, N.C., 2001. The geochemistry of boron and its isotopes in groundwaters from marine and non-marine sandstone aquifers. *Appl. Geochem.* 6, 821–834.
- Maupin, M.A., Barber, N.L., 2005. Estimated withdrawals from principal aquifers in the United States, 2000. US Geol. Surv. Circular 1279.
- McGookey, D.A., Gustavson, T.C., Hoadley, A.D., 1985. Regional cross-sections of mid-Permian to Quaternary strata of the Texas Panhandle—distribution of evaporites and zones of evaporite dissolution and collapse. Bureau of Economic Geology, University of Texas at Austin, Open-File Report OF-WTWI-1985-48.

- McGowen, J.H., Granata, G.E., Seni, S.J., 1979. Depositional framework of the lower Dockum Group (Triassic), Texas Panhandle. Bureau of Economic Geology, University of Texas at Austin, Report of Investigations 97.
- McGuire, V.L., Johnson, M.R., Schieffer, R.L., Stanton, J.S., Sebree, S.K., Verstraeten, I.M., 2003. Water in storage and approaches to groundwater management, High Plains aquifer, 2000. US Geol. Surv. Circular 1243.
- McLemore, V.T., 2001. Oasis State Park. In: Lucas, S.G., Ulmer-Scholle, D.S. (Eds.), *Geology of Llano Estacado*. New Mexico Geological Society, Socorro, pp. 34–37.
- McMahon, P.B., Böhlke, J.K., Lehman, T.M., 2004. Vertical gradients in water chemistry and age in the Southern High Plains aquifer, Texas, 2002. US Geol. Surv. Scientific Investigations Report 2004-5053.
- McMahon, P.B., Böhlke, J.K., 2007. Transport—Linking the chemistry of recharge and the used resource in the High Plains aquifer. In: McMahon, P.B., Dennehy, K.F., Bruce, B.W., Gurdak, J.J., Qi, S.L. (Eds.), 2007. *Water-quality assessment of the High Plains Aquifer, 1999–2004*, US Geol. Surv. Professional Paper 1749, pp. 49–72 (Chapter 2).
- McMahon, P.B., Dennehy, K.F., Bruce, B.W., Gurdak, J.J., Qi, S.L., 2007. *Water-quality assessment of the High Plains Aquifer, 1999–2004*. US Geol. Surv. Professional Paper 1749.
- Merlivat, L., Jouzel, J., 1979. Global climatic interpretation of the deuterium-oxygen 18 relationship for precipitation. *Journal of Geophysical Research* 84, 5029–5033.
- Mook, W.G., Van der Plicht, J., 1999. Reporting ^{14}C activities and concentrations. *Radiocarbon* 41, 227–239.
- Musharrafieh, G.R., Logan, L.M., 1999. Numerical simulation of groundwater flow for water rights administration in the Curry and Portales Valley underground water basins, New Mexico. New Mexico Office of the State Engineer, Technical Division Hydrology Bureau, Santa Fe, Report 99-2.
- Nativ, R., 1992. Recharge into Southern High Plains aquifer—possible mechanisms, unresolved questions, *Env. Geol.* 19, 21–32.

- Nativ, R., 1988. Hydrogeology and hydrochemistry of the Ogallala aquifer, Southern High Plains, Texas Panhandle and eastern New Mexico. Bureau of Economic Geology, University of Texas at Austin, Report of Investigations 177.
- Nativ, R., Gutierrez, G.N., 1988. Hydrogeology and hydrochemistry of Cretaceous aquifers, Texas Panhandle and eastern New Mexico. Bureau of Economic Geology, University of Texas at Austin, Geological Circular 88-3.
- Nativ, R., Riggio, R., 1989. Meteorologic and isotopic characteristics of precipitation events with implications for groundwater recharge, Southern High Plains. *Atmos. Res.* 23, 51–82.
- Nativ, R., Smith, D.A., 1987. Hydrogeology and geochemistry of the Ogallala aquifer, Southern High Plains, *J. of Hydrol.* 91, p 217–253.
- Nicholson, J.H., 1960. Geology of the Texas Panhandle. In: *Aspects of the geology of Texas, a symposium*. Bureau of Economic Geology, University of Texas, Austin, publication 6017, pp. 51–64.
- Nimz, G.J., 1998. Lithogenic and cosmogenic tracers. In: Kendall, C., McDonnell, J.J., *Isotope tracers in catchment hydrology*. Elsevier Science B.V., Amsterdam, pp. 247–289 (Chapter 8).
- Oi, T., Nomura, M., Musashi, M., Osaka, T., Okamoto, M., Kakihana, H., 1989. Boron isotopic compositions of some boron minerals. *Geochim. Cosmochim. Acta* 53, 3189–3195.
- Paces, T., 1978. Reversible control of aqueous aluminum and silica during the irreversible evolution of natural waters. *Geochim. Cosmochim. Acta* 42, 1487–1493.
- Palmer, M.R., Swihart, G.R., 1996. Boron isotope geochemistry—an overview. In: Crew, E.S., Anovitz, L.M. (Eds.), *Boron—mineralogy, petrology and geochemistry*, vol. 33. Mineral. Soc. Am., Chantilly, Virginia, pp. 709–744 (Chapter 13).
- Palmer, M.R., Spivack, A.J., Edmond, J.M., 1987. Temperature and pH controls over isotopic fractionation during absorption of boron marine clay, *Geochim. Cosmochim. Acta* 51, 2319–2323.
- Rose-Koga, E.F., Sheppard, S.M.F., Chaussidon, M., Carignan, J., 2006. Boron isotopic composition of atmospheric precipitations and liquid-vapor fractionations. *Geochim. Cosmochim. Acta* 70, 1603–1615.

- Scanlon, B.R., Goldsmith, R.S., 1997. Field study of spatial variability in unsaturated flow beneath and adjacent to playas. *Water Resour. Res.* 33, 2239–2252.
- Scanlon, B.R., Angle, E.S., Christian, B., Pi, J., Martinez, K., Reedy, R., Boghici, R., Petrossian, R., 2003. Evaluation of enhanced recharge potential to the Ogallala aquifer in the Brazos River Basin, Hale County, Texas. Texas Water Development Board Report 355.
- Schlosser, P., Stute, M., Sonntag, C., Munnich, K.O., 1989. Tritogenic ^3He in shallow groundwater. *Earth and Planet. Sci. Lett.* 94, 245–256.
- Schwarcz, H.P., Agyei, E.K., McMullen, C.C., 1969. Boron isotopic fractionation during adsorption from seawater. *Earth and Planet. Sci. Lett.* 6, 1–5.
- Senger, R.K., Fogg, G.E., Kreitler, C.W., 1987. Regional underpressuring in deep-brine aquifers, Palo Duro Basin, Texas 2—the effects of Cenozoic basin development. *Water Resour. Res.* 23, 1494–1504.
- Seni, S.J., 1980. Sand-body geometry and depositional systems, Ogallala Formation, Texas. Bureau of Economic Geology, University of Texas at Austin, Investigation 105.
- Shorrocks, V.M., 1997. The occurrence and correction of boron deficiency. *Plant and Soil* 193, 121–148.
- Simpkins, W.W., Gustavson, T.C., Alhades, A.B., Hoadley, A.D., 1981. Impact of evaporite dissolution and collapse on highways and other cultural features in the Texas Panhandle and eastern New Mexico. Bureau of Economic Geology, University of Texas at Austin, Geological Circular 81-4.
- Solomon, D.K., Cook, P.G., Sanford, W.E., 1998. Dissolved gases in subsurface hydrology. In: Kendall, C., McDonnell, J.J. (Eds.), *Isotope tracers in catchment hydrology*. Elsevier Science B.V., Amsterdam, pp. 291–318 (Chapter 9).
- Spivack, A.J., Palmer, M.R., Edmond, J.M., 1987. The sedimentary cycle of the boron isotopes. *Geochim. Cosmochim. Acta* 51, 1939–1949.
- Stewart, B.W., Capo, R.C., Chadwick, O.A., 1998. Quantitative strontium isotope models for weathering, pedogenesis, and biogeochemical cycling. *Geoderma* 82, 173–195.

- Stumm, W., Morgan, J.J., 1996. Aquatic chemistry—chemical equilibria and rates in natural waters: New York, John Wiley & Sons, Inc.
- Stute, M., Schlosser, P., Clark, J.F., and Broecker, W.S., 1992. Paleotemperatures in southwestern United States derived from noble gases in ground water. *Science* 256, 1000–1003.
- Trauger, F.D., 1972. Groundwater in east-central New Mexico. In: Kelly, V.C., Trauger, F.D. (Eds.), *Guidebook of east-central New Mexico, 23rd Field Conference*. New Mexico Geological Society, Socorro, pp. 201–207 (Economic Geology Chapter).
- Tuan, Y.F., Everard, C.E., Widdison, J.G., 1969. *The climate of New Mexico*. New Mexico State Planning Office, Santa Fe.
- U.S. Environmental Protection Agency, 1983. Method for chemical analysis of water and wastes. EPA-600/4-79-020, March 1983 and subsequent revisions. U.S. Environmental Protection Agency, Washington, D.C.
- U.S. Environmental Protection Agency, 1986. Test methods for evaluating solid waste, physical/chemical methods. 3d edition, November 1986 and subsequent updates. U.S. Environmental Protection Agency, Washington, D.C.
- U.S. Geological Survey, 2006. $^3\text{H}/^3\text{He}$ dating background. US Geol. Surv., Reston Chlorofluorocarbon Laboratory analysis background information.
- Vengosh, A., Heumann, K.G., Juraske, S., Kasher, R., 1994. Boron isotope application for tracing sources of contamination in groundwater. *Env. Sci. and Tech.* 28, 1968–1974.
- Walker, J.R., 1978. Geomorphic evolution of the Southern High Plains. *Baylor Geological Studies*, Baylor University, Bulletin No. 35.
- Western Regional Climate Center, 2007a. New Mexico climate summaries for cooperator stations, Clovis, New Mexico, station 291939, period of record monthly climate summary, period of record: 11/24/1910 to 12/ 31/2005. accessed January 29, 2007, <http://www.wrcc.dri.edu/cgi-bin/cliMAIN.pl?nmclov>.
- Western Regional Climate Center, 2007b. Monthly average pan evaporation. accessed January 29, 2007, <http://www.wrcc.dri.edu/htmlfiles/westevap.final.html>.

- Widory, D., Kloppmann, W., Chery, L., Bonnin, J., Rochdi, H., Guinamant, J., 2004. Nitrate in groundwater—an isotopic multi-tracer approach. *J. of Cont. Hydrol.* 72, 165–188.
- Wilde, F.D., Radtke, D.B., 2005. Field measurements, section 6.0. In Wilde, F.D. (Ed.), *US Geol. Surv. Techniques of Water-Resources Investigations*, book 9, variously paged (Chapter A6).
- Zhang, W., Liu, C., Zhao, Z., 2006. Boron isotopic geochemistry of karst groundwater in Guiyang City, China. *Chinese J. of Geochem.* 25, 172.
- Zhao, D., Oosterhuis, D.M., 2002. Cotton carbon exchange, nonstructural carbohydrates, and boron distribution in tissues during development of boron deficiency. *Field Crops Res.* 78, 75–87.

Curriculum Vita

Jeff Langman was born in San Juan Capistrano, California. The son of Wendell and Deanne Langman, he graduated from Granada Hills High School, Granada Hills, California, in the spring of 1987 and entered California Polytechnic State University, San Luis Obispo in the fall. Following graduation in 1992, he worked for the Department of the Treasury prior to returning to California Polytechnic State University, San Luis Obispo to seek his Master's in Agriculture—Natural Resources. During this time, he worked for the California Regional Water Quality Board where he participated in the National Monitoring Program for the Morro Bay Estuary. Following graduation in 1997, he worked for Environmental Science Associates in San Francisco as an Associate Hydrologist. In 2000, he began his career with the U.S. Geological Survey in New Mexico where he remains today. He has authored a range of U.S. Geological Survey documents related to the water resources of the Rio Grande, Southern High Plains, and Tularosa Basin. In the fall of 2005, he entered the Graduate School at the University of Texas at El Paso to seek his doctoral degree while continuing to work for the U.S. Geological Survey.

Permanent Address:

800 Mississippi Ave

El Paso, Texas 79902