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Exploring The Hydrogeologic Controls On Brackish Water And Its Suitability For Use In Hydraulic Fracturing: The Dockum Aquifer, Midland Basin, Texas

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AND ITS SUITABILITY FOR USE IN HYDRAULIC FRACTURING: THE
DOCKUM AQUIFER, MIDLAND BASIN, TEXAS

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Dedication

To all who have and continue to inspire to me to learn about our world, those who were cornered and left with no choice to listen to my enthusiastic jargon, which helped me learn how to explain concepts, and lastly my parents Cecilia and Francisco S. Reyes for pushing me to excel at all opportunities.

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AND ITS SUITABILITY FOR USE IN HYDRAULIC FRACTURING: THE
DOCKUM AQUIFER, MIDLAND BASIN, TEXAS

by

FRANCISCO R. REYES, B.S. in Environmental Sciences

THESIS

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of the Requirements
for the Degree of

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Abstract

Water scarcity in arid regions can limit or impede certain hydrocarbon production activities, such as hydraulic fracturing and well drilling. The Midland Basin, a major oil-producing area in semi-arid far west Texas and the eastern sub-basin of the Permian Basin, is already impacted by limited freshwater availability. A typical tight oil well in the Midland Basin requires $\sim 3.8\text{--}11.4 \times 10^3 \text{ m}^3$ of water per fracture treatment (Nicot et al., 2012). Despite draught conditions and limited resources, data for 2011 indicate freshwater comprises $\sim 70\%$ of the water used in hydraulic fracturing in the Midland basin. Thus, the Midland Basin represents an ideal location to consider alternative water resources for use in oil and gas operations. The purpose of this study is to characterize the hydrogeochemistry of a brackish groundwater aquifer, the Late Triassic Dockum Group, in the Midland Basin and evaluate its suitability for use in local hydraulic fracturing.

Potentiometric surface maps for the Dockum Aquifer indicate that groundwater generally flows south and east across the basin, possibly as a result of basin uplift and eastward tilting in the past 5–10 m.y. (Bein and Dutton, 1993). Transmissivity values from testing of Dockum wells follow a log-normal distribution, ranging from 2 to 990 m^2/day (geometric mean = 42 m^2/day), indicating that water yield from the unit is highly variable, but generally productive. Geochemical results suggest two dominant water types of meteoric origin within the aquifer: 1) a higher salinity (up to 70 g/L) Na-SO₄- to Na-Cl-type water found mainly in the center and western parts of the basin; and 2) a lower salinity (< 7.5 g/L) mixed ion water, with larger proportions of Ca and Mg, found on the southern and eastern basin margins. Data for $\delta^{18}\text{O}$ and $\delta^2\text{H}$ of Dockum Aquifer groundwater samples suggest that the lower salinity waters likely represent recharge from conditions cooler than the present climate. Geochemical data for these waters suggest the composition of the Ca-rich groundwaters is controlled by water-rock interaction with overlying aquifers and the lower section of the Dockum. The high salinity, Na-rich waters are thought to represent meteoric water from eastern New Mexico that experience more complex regional rock-to-water reactions with carbonates, clays, silicates, and evaporite minerals as the water travels eastward through overlying aquifers, and through the upper and lower Dockum.

Both slick water (low viscosity fluid with a friction reducer) and cross-linked gel (high viscosity fluid containing a gelling agent) fluids are used for hydraulic fracturing in the basin. The feasibility of utilizing brackish

groundwater for hydraulic fracturing, particularly with cross-linked gels, is limited by a variety of chemical conditions including high concentrations of alkaline earth metals (AEM), SO_4 , and DOC. Despite having lower salinity, the more Ca-rich water found in the down-gradient southern and eastern margins of the basin is most likely to exceed acceptable limits for AEM and/or SO_4 . Generally, the majority of the water in the basin is suitable for use with slick water hydraulic fracturing. Findings from this research provide important baseline data on potential use of brackish groundwaters in the oil and gas industry.

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Introduction

Background

Non-coastal, brackish (1,000-10,000 mg/L of Total Dissolved Solids (TDS)) groundwater systems are poorly studied and their hydrogeochemical controls are not well understood. A multitude of papers exist on the nature and origin of brines in sedimentary basins (Bethke and Marshak, 1990; Richard et al., 2012), particularly oil and gas producing basins (Bassett and Bentley, 1982; Martini et al., 1996; McIntosh et al., 2002), and overlying shallow fresh groundwater (Nativ and Smith, 1987; Dutton, 1995; Rosenberg et al., 1999). In 1965, Feth et al. published a map of brackish water for the U.S., but until the last decade little effort has gone in to the study of brackish groundwater systems. Although, fresh and brine groundwater deserve the attention needed for either municipal, agricultural, and economical means, brackish groundwater can no longer be neglected relative to other extensively studied groundwaters. To this end, entities such as the U.S. Geological Survey (USGS) and the Texas Water Development Board (TWDB) initiated investigations and assessments of brackish groundwater resources (USGS, 2013 (http://ne.water.usgs.gov/ogw/brackishgw/files/brackish_infosheet_v8.pdf); TWDB, 2014 (<https://www.twdb.state.tx.us/innovativewater/bracs/>)). Linkages and relationships of brackish groundwater systems with the overlying freshwater systems and underlying basinal brines are of critical importance, to fully comprehend complex geologic systems within a basin.

State government agencies like the TWDB initiated efforts to develop brackish waters as a valuable alternative resource, heavily relying on engineering improvements in desalination processes (LBG-Guyton Associates, 2003). Although there are several areas within the U.S., including Texas, which have alternative saline groundwater resources, these aquifers may not be economical or environmentally feasible to develop (Androwski et al., 2011). Substantial effort has been directed at these brackish groundwater resources in Texas (LBG-Guyton Associates, 2003), especially the Edwards-Trinity aquifer (Groschen and Buszka, 1997; Nance, 2004; Bumgarner et al., 2012; Wong et al., 2013) and Pecos Valley Aquifer (Meyer et al., 2012) because these are primarily potable water resources; brackish groundwater which is not a primary source for municipal and agriculture use is less well studied. Many areas of Texas have also seen a significant increase in hydrocarbon production and related activities in the last decade, partially driven by the extraction of continuous hydrocarbon resources through advances in hydraulic fracturing and directional drilling. Both well drilling and hydraulic fracturing require moderate to substantial volumes of water (Nicot et al., 2012). The area of interest in this investigation, the Permian Basin in west Texas and southern eastern New Mexico, went from a mature basin with declining production to the largest unconventional oil producer (1,179 million liters of oil produced in 2012 (Texas Railroad Commission, 2014) with current estimates for April 2014 of 2.31 million liters/day (U.S. Energy Information Administration, 2014)) in the US in a few short years. As hydrocarbon development and production within the Permian Basin continues to dramatically increase, the stress on freshwater resources will make operations challenging in the context of a significant regional drought and the needs of a growing

population. Ultimately, these factors are forcing operators to find alternative water resources like brackish groundwater.

The rapid expansion of hydraulic fracturing, a water reliant method used to increase reservoir permeability and porosity, has greatly increased in usage in the last few years leading to a boom in domestic oil and natural gas production, including the Permian Basin. Indeed, Nicot et al. (2012) reports the number of vertical hydraulically-fractured hydrocarbon wells in the basin (primarily in the Wolfberry play) has grown from <500 to >1,500 wells/yr and horizontal hydraulically-fractured wells in the Wolfcamp Shale have increased from <50 to 160 wells/yr in the Permian basin, between 2005 and 2011. This rapid expansion of hydraulic fracturing within the Permian Basin, including the Midland Basin (the eastern sub-basin of the Permian), has resulted in an increase of total water consumption (Nicot et al. (2012) reports about 1500 acre-feet). Specifically, consumptive water use for hydraulic fracturing resulted in a change from ~0.4 million gallons of water per well in 2005, to ~1 million gallons of water per well in 2012 (Nicot et al., 2012). In 2011, the Permian Basin used about 18,502,530 m³ of water for hydraulic fracturing, for which 68% is fresh water, 30% brackish water, and 2% recycled and/or reused (Nicot et al., 2012). The amount of fresh water used for hydraulic fracturing is expected to decrease through time because of supplies limitations and also because technological advances in salt-tolerant fracturing additives make it possible to use brackish and saline water resources instead of fresh water. At present, brackish groundwater sources within the basin are not well characterized. As such, the Permian Basin presents an ideal study area to examine the source and nature of brackish groundwaters and their potential for use in hydraulic fracturing.

This study specifically focuses on the Triassic Dockum Aquifer

, which spreads across portions of Texas, New Mexico, Oklahoma, Colorado and Kansas (about 154,460 km², in Texas it covers about 67,580 km²). Within the study area, the Dockum Aquifer covers most of the Midland Basin but tapers out to the west, over the Central Basin Platform (Fig. 1). The Dockum Aquifer produces groundwater ranging from fresh (<1 g/L TDS) to saline (>10 g/L TDS), with the majority being brackish. Bradley and Kalaswad (2003) estimated the Dockum Aquifer in Texas (from the panhandle to northern portion of Pecos county) contains 1.34x10¹⁰ m³ of <5,000 mg/L TDS groundwater and 3.33x10⁹ m³ of productive groundwater with 5,000-10,000 mg/L of TDS. Although not assessed, substantial volumes of water >10,000 mg/L TDS are also contained in the Dockum Aquifer. Municipal and agricultural uses for the Dockum water are fairly limited due to salinity hazards (Dutton and Simpkins, 1986) and naturally occurring radionuclides in excess of drinking water limits (Bradley and Kalaswad, 2001). No previous workers have examined the potential use of this water for oilfield applications such as drilling or hydraulic fracturing fluid.

The water source, solute source, and solute distribution in the Texas portion of the Dockum Aquifer were studied by Dutton and Simpkins (1986), Dutton and Simpkins (1989), Dutton (1995), Bradley and Kalaswad (2001), and Bradley and Kalaswad (2003). These previous studies

interpreted Dockum groundwater to originate as meteoric recharge from eastern New Mexico during wetter periods of the Holocene and Pleistocene, flowing east across the Permian Basin (Dutton and Simpkins, 1986; Dutton and Simpkins, 1989; Dutton, 1995). Geochemical evolution and solute source in the Dockum aquifer is primarily controlled by rock-to-water interactions with calcite, chalcedony, dolomite, feldspars, kaolinite, opal, pyrite and smectite. In addition, the sources for Cl and SO₄ in Dockum Aquifer groundwater were hypothesized as either 1) dissolution of underlying Permian-age halite and/or anhydrite or 2) mixing with connate Cretaceous seawater (Dutton and Simpkins, 1986). However, the Dockum $\delta^2\text{H}$ and $\delta^{18}\text{O}$ isotope data for Dockum groundwater samples from Dutton and Simpkins (1986) is strongly depleted in heavy isotopes relative to evaporated paleoseawater and does not agree with their connate Cretaceous seawater hypothesis. Dutton and Simpkins (1986) observed Dockum groundwater samples have similar $\delta^{34}\text{S-SO}_4$ values as Permian Anhydrite, which agrees with the hypothesis of groundwater dissolving underlying Permian salts. Lastly, all previous authors (Dutton and Simpkins, 1986; Dutton and Simpkins, 1989; Bradley and Kalaswad, 2001; and Bradley and Kalaswad, 2003) agree recharge today, especially in the center of the Midland basin, does not occur. Bradley and Kalaswad (2001, 2003) spent much effort characterizing the Dockum Aquifer in west Texas but little focus was directed at understanding geochemical processes which impact the distribution of major ions. Although, their scientific contribution was imperative, many geochemical processes went unanswered: Why are there so many geochemical facies in the Dockum? What conceptual model(s) can explain these geochemical facies? How can we increase our confidence of upwelling brine or water-to-rock interaction with Permian bedrock with conservative constituents?

Additionally, previous studies focus towards understanding the geochemical reactions controlling water chemistry in Dockum Aquifer groundwater were directed in the northern portion of the Permian Basin and up into the Palo Duro Basin rather than further south, where the hydrocarbon development is currently focused. This investigation focuses on the Dockum Aquifer system overlying the Midland Basin, which is the eastern sub-basin of the Permian Basin and a center of current tight oil production in the basin. The Dockum Aquifer extends to the west over the Central Basin Platform into portions of the Delaware (the western sub-basin) Basin (see Fig. 1) but has been eroded by the Pecos River to the west. Thus, the Midland Basin represents a good match between the extent of the Dockum Aquifer and the underlying unconventional hydrocarbon plays in the Permian Basin.

The Dockum is considered a continuous minor aquifer within Texas, with variable hydrological properties. In the Midland Basin, the Dockum Aquifer it is considerably thicker and contains more water than other basins where the Dockum Aquifer is found. Locally, the Dockum is divided into an upper and low hydrogeologic unit. The upper tends to be more shale rich but contains pockets and lenses of sand (McGowen et al., 1977). The lower Dockum is described as being more sand rich and the lower most section, locally known as the Santa Rosa (McGowen et al., 1977; McGowen et al., 1979; George et al., 2011), is notably for being highly

productive in areas (Bradley and Kalaswad, 2003). In the case of this current research, information as to the unit or portion of the Dockum Aquifer sampled wells were screened was generally unavailable. The aquifer is thickest (about 366 m (McGowen et al., 1977; Ewing et al., 2008)) in the lower Dockum in the west and thins eastward (30-91 m while thickness is greatest in the center of the Midland Basin and thinner towards the south but relatively thicker in the north (Bradley and Kalaswad, 2003). Reported well yields range from 2.7 to 13,628 m³/day, and transmissivity ranges from 4.5 to 428 m² per day (very unproductive to productive). Regional groundwater flows from west to east (Bradley and Kalaswad, 2003). Recharge to the aquifer occurs at the eastern and southern edges of the aquifer and at eastern outcrops of the Dockum group via flow from the Ogallala, Edwards-Trinity, and the Pecos Valley in the southwest Midland basin (Bradley and Kalaswad, 2003). Also, Bradley and Kalaswad (2003) state the Dockum Aquifer is a good resource for local usage where water quality and quantity are reasonable.

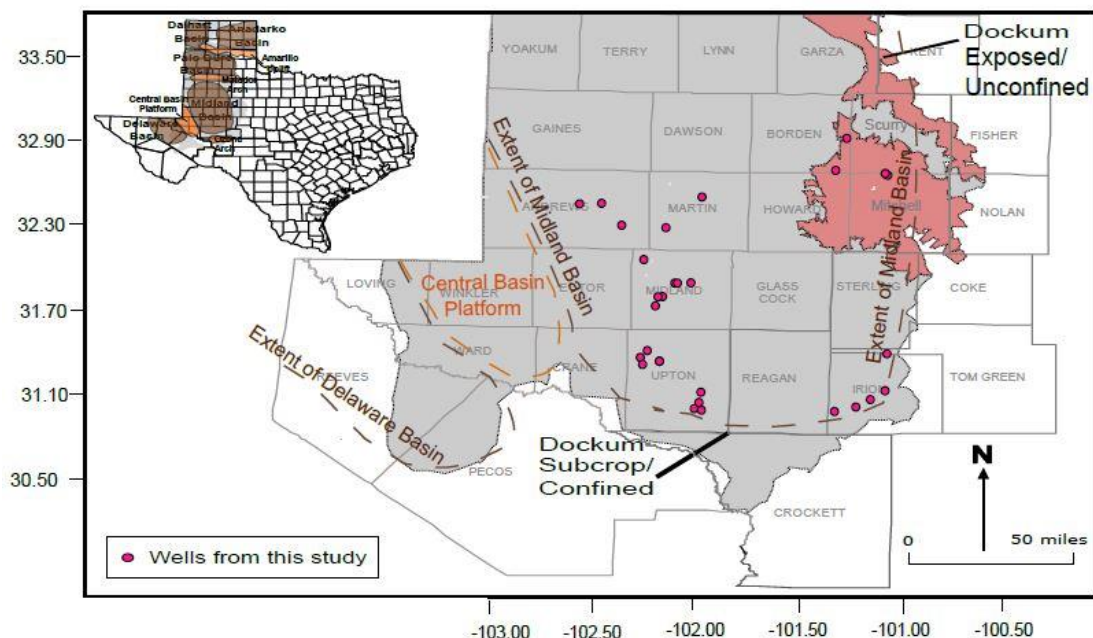


Figure 1: Map of the areal extent of the Dockum Aquifer in west Texas and the locations of groundwater wells sampled in this study. Dark grey areas represent the extent of the Dockum Aquifer which is not exposed and/or confined. The pink areas on the eastern edge of the study area represent the extent of the Dockum Aquifer which is exposed and considered unconfined. Inset image shows basins (brown) and geological uplifted areas (orange) in the Permian Basin. Background image modified from Bradley and Kalaswad, 2003.

In an attempt to constrain and identify processes controlling a brackish groundwater system and to identify potential uses of this water in oilfield operations, this study focused on: 1) Characterizing the elemental and isotopic geochemistry and hydrogeology of the Dockum Aquifer in the Midland Basin; and 2) Determine the feasibility of using these waters in hydraulic fracturing. The approach used here relies on the interpretation of data for water chemistry, isotopic analysis, hydrological parameters such as transmissivity and hydraulic head, and comparing water quality of the Dockum Aquifer with requirements for hydraulic fracturing water.

Geology Background of the Permian Basin

The Permian Basin, which extends through most of west Texas, Texas Panhandle and eastern New Mexico, totaling an area of 300,000 km² (Mazzulo, 1995), is a significant hydrocarbon-producing province. The formation of the Permian Basin, which began during the Mississippian and continued through the Permian, occurred during sea withdrawal, and subsidence from the Ouachita Foldbelt (located south of the Permian Basin). Differential subsidence resulted in sub-basins, and structurally high or uplifted regions known as the Midland Basin, Delaware Basin, Central Basin Platform, the Northwest Shelf, and Eastern Shelf.

Specifically, these basins were shallow during the early Permian when the region was covered by an interior seaway. Initially, clay and mud were deposited on the sea floor, while limestones formed on the higher parts of the basin (Hills, 1972). During the late Permian, sedimentation was constricted to smaller basins where carbonates formed on the basin margins and clastic material deposited in deeper parts of the basins. Finally, withdrawal of the sea resulted in redbed sand and evaporite deposition producing 150-215 m thick layered sequences of marine salts including anhydrite and halite (Hills, 1972). Many of the Paleozoic rocks in the Midland Basin are limestones, sandstones, shales, and in the upper Permian (Ochoan) there are thick halite (approximately 150-215 m thick) and anhydrite layers (multiple 30.5 m thick sequences in a large package of evaporates interlayered with other lithology) which serve as a major vertical flow barrier for fluids across the basin (Basset and Bentley, 1982).

A gradual shift from arid to humid conditions during the early Triassic led to erosion and the development of the unconformity between the Permian and Triassic strata (Adams, 1929; Ewing et al., 2008). The Triassic Dockum group sediments were of non-marine origin deposited in a closed continental fluvial, deltaic, and lacustrine environment (McGowen et al., 1979) and consist primarily of mudstones, sandstones, and gravel. Sediments in the Dockum group rocks were sourced from the east, south, and west, and lowlands were cut through by streams with the source of sediments being Paleozoic sedimentary rocks (McGowen et al., 1979). Regional topographic groundwater flow was post depositional after tilting towards the south and east occurred due to the Laramide Orogeny, and Basin and Range extension (Bein and Dutton, 1993).

Regional Hydrogeology

Several previous studies focused on the hydrogeology of portions of the Permian Basin; however majority of the studies are located in smaller geologic structures or geographic regions outside of the Midland Basin including: the Palo Duro Basin (Bassett and Bentley, 1982; Fisher and Kreitler, 1987; Means and Hubbard, 1987; Knauth, 1988; Eastoe et al., 1989; Bein and Dutton, 1993), High Plains/Panhandle (Dutton and Simpkins, 1986; Dutton, 1989) and Central Basin Platform (Stueber et al., 1998). While portions of the Permian Basin are well studied, the details regarding groundwater flow and dynamics within the Midland Basin have not been investigated in detail. Bassett and Bentley (1982) organized the major and minor aquifers of the Permian Basin into four hydrogeological units (Figure 3) based on stratigraphic characteristics and water types: the Upper Aquifer System (UAS), the Evaporite Confining System (ECS), Deep-Basin Brine Aquifer System (DBBAS), and the Basement Aquitard (BA).

The BA corresponds with the deep Precambrian crystalline and metamorphic bedrock at the bottom of the Permian Basin below the Ordovician Ellenburger, and is poorly studied in comparison to the other hydrological units. The UAS, ECS, and DBBAS are geochemically distinct and typically compared to one another in hydrogeochemical studies. The DBBAS is comprised of aquifers in rocks of Ordovician (Ellenburger, Simpson, and Montoya Fm.), Silurian, Devonian, Mississippian, Pennsylvanian (Strawn, Canyon, and Cisco Fm.) and early Permian (Wolfcamp, Wichita, and Clear Fork Fm.) age, underlying and kept at depth by the overlying evaporite sequences, and is approximated 915 m thick in the Midland Basin. Groundwater from the DBBAS is Na-Cl- and Ca-Cl-type with TDS concentrations ranging 45–385 g/L (Bein and Dutton, 1993), and the groundwater originates as evaporated Permian-age seawater which has undergone mixing with meteoric water (Stueber et al., 1998). The ECS corresponds with Permian (Leonardian to Ochoan) age rocks, including a thick sequence of evaporite minerals (including halite, anhydrite, sylvite, and polyhalite), as well as limestones, shales and sandstones; the approximate thickness of the ECS in the Midland Basin is 2400-2700 m. The ECS contains Na-Cl- and Ca-Cl-type groundwater that has TDS concentrations > 300g/L (Bein and Dutton, 1993) and is derived from meteoric origin, suggesting its salinity is primarily derived from dissolution of the evaporite minerals which comprise the system (Stueber et al., 1998).

The final and most well studied aquifers system, the UAS, corresponds to all water-bearing units overlying the ECS in the Midland Basin, and is generally less than 460 m thick. These fresh and brackish aquifers include the Quaternary age Pecos Valley, Tertiary age Ogallala, Cretaceous age Edwards-Trinity, and Triassic age Dockum; the Dockum underlays all other UAS aquifers in the study area. Lithological descriptions of these units are the following: 1) the Pecos Valley is alluvium consisting of caliche, clay, silt, sand, and gravel (Meyer et al., 2011), 2) the Ogallala is similar to the Pecos Valley and consists of sand, clay, and small amounts of gravel, and calcium carbonate cementation (Potratz, 1980), and 3) the Edwards-Trinity consists of limestone, dolomite, sandstone, clays, and gypsum (Nance, 2004). The Ogallala and Trinity-

Edwards aquifers are the primary resources for fresh water consumption in the region. The Dockum group will be further explained in the following paragraphs.

Stratigraphically, the Dockum Aquifer is defined by the Triassic Dockum group including (in order from oldest to youngest): the Santa Rosa Fm. (predominately sandstones and few mudstones), the Tecovas Fm. (mudstones and sandstones), the Trujillo sandstone (sandstones and mudstones), and the Cooper Canyon Fm. (mudstones with sandstone lenses) (McGowen et al., 1977 and 1979; Lehman and Chatterjee, 2005; George et al., 2011). Dutton and Simpkins (1986) defined their hydrogeochemical study of the Dockum with a lower group consisting of fine to course grained quartzose sandstone, granule to pebble conglomerate and a mud-rich upper group with discontinuous sandstones with accordance to McGowen et al. (1977 and 1979). An XRD analysis of Santa Rosa cuttings identified the following minerals with their weight percent: quartz (60.2%), illite (14.1%), albite (10.1%), muscovite (8.6%), calcite (6.4%), and kaolinite (0.5%). Analysis of a sample of the Trujillo sandstone contained similar mineralogy however, calcite and kaolinite were four- and five-fold more abundant, respectively, and illite was substantially depleted (2%). These analyses are similar to the findings of Johns (1985) and Kanhalangsy (1997), except that gypsum was not identified, unlike the gypsum cementing reported by Adams (1929).

Methods

Compiling Existing Water Chemistry and Hydrologic Data

The majority of both chemical and hydrologic data used in this investigation were taken from other sources. Midland Basin Dockum water elemental chemistry and hydrology data were taken from the Texas Water Development Board (TWDB; n=277) groundwater data website (<https://www.twdb.texas.gov/groundwater/data/gwdbbrpt.asp>). Data for the composition of waters from oil and gas wells (n=1344) were taken from the USGS Produced Waters Database (<http://energy.usgs.gov/EnvironmentalAspects/EnvironmentalAspectsofEnergyProductionandUse/ProducedWaters.aspx#3822349-data>). In instances where multiple data were available for an individual well, only the most recent data were used. Many of individual entries in these databases contain missing values for elements of interest (e.g., Ba, B, Br, and Sr). Data were explored through univariate, bivariate and multivariate statistical analyses to find and remove erroneous data. Additionally constituents for which > 50% of the entries were reported below an instruments detection limit were not used. Similarly, entries where charge balance is > 15% were also excluded. Isotope data for water samples in the study area were taken from Stueber et al. (1998), Dutton and Simpkins (1986), Bumgarner et al. (2012), and Coplen and Kendall (2000). Additionally, the modern seawater $^{87}\text{Sr}/^{86}\text{Sr}$ composition was taken from Burke et al. (1982) and $^{87}\text{Sr}/^{86}\text{Sr}$ ratio data for the Permian-age anhydrite in the Permian Basin were taken from Hovorka et al. (1993).

Sample Collection

Wells producing Dockum Aquifer groundwater (n=29) were purged until chemical parameters for pH, conductivity, oxidation reduction potential (ORP), and temperature measured in a flow-through cell were stable for at least 5 minutes (after removing a minimum of three well volumes). After that, water samples were collected from the well head and filtered to <0.45 μm using a disposable capsule filter utilizing an acrylic copolymer membrane (Geotech). Produced waters from oil and gas wells were either collected from the pump jack, or from the water-oil separator (all closed to the atmosphere) and collected into a 1-gallon collapsible polyethylene carboy (Cubitainer). Following a few minutes for density separation between oil and water, a portion of the water fraction was pulled from the bottom of the carboy, using a peristaltic pump applied to silicon tubing connected to a spigot at the bottom of the carboy. The end of the tubing was attached to a <0.45 μm capsule filter to allow the samples to be filtered on site. The soft nature of the carboys allowed the walls to collapse as the water was removed during sampling negating the need for a hole in the head space, keep the sample out of contact with the atmosphere. As such, exposure of the produced water samples to air was minimal (less than a few seconds per sample) in an attempt to prevent reactions which would vastly change the composition of the fluids relative to their composition in the reservoir. Three separate sample bottles were collected from each well: 1) Filtered and acidified (Optima grade HNO_3) water for cation concentrations and Sr isotope analysis in acid washed low-density polyethylene (LDPE)

bottles, 2) filtered water for $\delta^2\text{H}$, $\delta^{18}\text{O}$, anion concentrations, and alkalinity measurements in acid-washed high-density polyethylene (HDPE), and 3) filtered water for dissolved organic carbon (DOC) determination in combusted volatile organic analysis (VOA) amber glass bottles. Given the high salinity and low potential for significant contamination, produced water samples for the first two types of samples were collected into non-acid-washed bottles. About 25% of samples analyzed in this study were collected in the field by a third party using pre-labeled, acid-washed bottles. These samples were collected similarly to the above methods, but were not acidified until arrival at the University of Texas at El Paso (UTEP).

Analysis of Elemental Chemistry in Water Samples

Concentrations of major and minor cations (Ca, Na, Mg, K, B, Ba, Fe, Li, Sr) with a 5% HNO_3 matrix, were determined in a Perkin Elmer Optima 5300 Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES) in the Department of Geological Sciences at UTEP. Anions (Cl , SO_4 , NO_3 , and Br) were determined on a Dionex ICS-2100 Ion Chromatograph in the Department of Geological Sciences at UTEP. Dissolved organic carbon content was analyzed at the USGS Energy Resources Program Organic Geochemistry Lab in Reston, Virginia on a Shimadzu TOC-VCPH. Lastly, alkalinity was titrated using standardized concentrations of HCl on a Mettler Toledo DL15 Auto-titrator in the Department of Geological Sciences at UTEP.

Quality assurance and quality control samples such as matrix spikes, standard reference materials (USGS M-178, USGS M-182, USGS T-143), field and laboratory replicates, and field and laboratory blanks were used in all analyses for each batch of samples. All samples exhibited a charge balance error of less than 10%, except with 2 brine samples between 12-13% and 2 brine samples between 15-18 %, and the percent recovery for matrix spikes and reference materials was within $\pm 15\%$ for all constituents reported.

Analysis of Isotopes

Stable isotope compositions of hydrogen and oxygen in water were analyzed at the USGS Reston Stable Isotope Laboratory in Virginia. Hydrogen isotope ratio analyses were performed using a hydrogen equilibration technique and oxygen isotope ratio analyses were measured by using the CO_2 equilibration technique; both techniques provide results on an activity basis. To minimize the potential for apparent isotopic shifts as a result of changes in salinity alone, the data were converted to a concentration basis using the methods of Sofer and Gat (1972, 1975). Results were reported on a per mil basis relative to Vienna Standard Mean Ocean Water standard (VSMOW).

Prior to analysis of Sr isotopes ($^{87}\text{Sr}/^{86}\text{Sr}$), column chemistry using Sr-Spec resin was performed to separate and purify at least 3-5 μg of Sr from water samples in clean PTFE beakers, with minimal competition from other large cations (such as Rb, Na, Ca, Mg). Resin and PTFE columns were primed and samples flushed with the following solutions: 18.2 M Ω de-ionized water and 3N Optima grade HNO_3 . Each column chemistry run was performed with a blank,

standard reference material (USGS EN-1 standard; all measurements (mean of $0.70917 \pm 1\text{E-}05$) were within reported range of 0.70920 ± 0.00005), and either a laboratory or field duplicate. After separation, captured Sr was evaporated down, and then dissolved back into a 2% Optima grade HNO_3 solution for analysis on a Nu Plasma Multi-Collector Inductively Coupled Plasma Mass Spectrometer (MC-ICP-MS) at the Department of Geological Sciences at UTEP. The resulting $^{87}\text{Sr}/^{86}\text{Sr}$ values were corrected for interferences with ^{87}Rb and ^{86}Kr and mass based fractionation. Data were corrected using a standard-sample bracketing method, wherein the values for SRM 987, were adjusted to match the accepted $^{87}\text{Sr}/^{86}\text{Sr}$ value of 0.71025. Two standard deviation for the samples over the course of runs is approximately 0.00002.

Hydrological Data

Data for well elevation, depth to the water table, hydraulic head, and transmissivity values for Dockum Aquifer wells were measured at a few sites, but the bulk of data came from the TWDB Brackish Resources Aquifer Characterization System (BRACS) database (<https://www.twdb.texas.gov/groundwater/data/gwdbbrpt.asp>). In most cases, transmissivity was calculated from specific-capacity data using the Theis non-equilibrium equation following Mace (2001). However, if transmissivity data were reported in TWDB well log reports, then the reported values were used instead of the estimated values; in comparison, reported versus estimated transmissivity values for the same wells showed a strong power relationship to one another ($R^2 = 0.84$). However transmissivity values estimated from the Theis non-equilibrium equation were generally lower than those reported in the well logs by an average of 9%.

Geochemical Modelling

Using the USGS geochemical modeling software PHREEQC (version 3), brines from unconventional oil wells tapping the Wolfcamp, Strawn, and Spraberry reservoirs were geochemically mixed with four Dockum groundwater endmembers (Low TDS, Ca-rich groundwater; High TDS, Ca-rich groundwater; Low TDS, Na-rich groundwater; and High TDS, Na-rich groundwater) to examine for scale potential during hydraulic fracturing. Mixtures of 25% Dockum water and 75% oilfield brine, 50% of both, and 75% Dockum water and 25% oilfield brine were modeled. Using a Pitzer-type activity model, mineral saturation indices of anhydrite, aragonite, barite, calcite, celestite, dolomite, halite, and sylvite, were calculated for the Dockum groundwaters and mixtures.

Results

Dockum groundwater geochemistry

Compositionally, the majority of Dockum samples ($n = 296$) in the Midland Basin include Na-Cl, Na-Cl-SO₄, Ca-SO₄-Cl, Ca-Na-SO₄-Cl, and Ca-SO₄ type waters. A Durov diagram (Fig. 2) plotting data for all Dockum samples in excess of 1000 mg TDS/L indicates that these various water types can be lumped into two basic geochemical groups: a Na-rich group with little Ca and Mg (green circles) and a Ca-rich group (orange circles), containing relatively more Mg and Ca on an equivalence basis. Data representing the Dockum group samples indicate high variability in anion composition, especially for Ca-rich waters, although, the spread of the data are generally between Cl- and SO₄-end members. The cations in Na-rich Dockum group are dominated by Na (generally above 70% by equivalence), with some Ca and Mg (Fig. 2). Samples from the Ca-rich Dockum group exhibit greater variation in the relative contribution of cations from Na, Ca and Mg (Fig. 2); samples from this group still contains substantial amounts of Na, but are relatively Ca and Mg rich. The pH of the Dockum Aquifer samples typically range from 7 and 8, however there are significant differences (Wilcoxon Rank Sum test, $p < 0.01$) between the two groups: the Na-rich Dockum values are 0.3-0.4 pH units higher than the Ca-rich group samples. The bivariate graphs within the Durov plot provide a versatile examination of compositional differences between the two groups. Specifically, the center square represents function of the relative abundance of the individual cations versus individual anions (Fig. 2): the Dockum Na-rich group samples are primarily Na-Cl and Na-Cl-SO₄ type, while data for the Ca-rich group show substantial ionic variation (Ca-SO₄-Cl, Ca-Na-SO₄-Cl, and Ca-SO₄). The far right rectangle in Fig. 2, is a bivariate plot of cation composition versus TDS concentration. Again, a distinction between the two groups of Dockum waters is observed: 1) a brackish Ca-rich group with lower TDS concentration and 2) a brackish Na-rich group with a higher TDS concentration. Robust principal component analysis (Suppl. Fig. 1) of the same data provides similar chemical distinctions, with relatively higher alkalinity observed with the Na-rich group, potentially explaining why samples from the Na-rich group have a significantly higher pH relative to those of Ca-rich group. These two groups of Dockum Aquifer water likely represent two distinct geochemical pathways, potentially suggesting different origins and evolution.

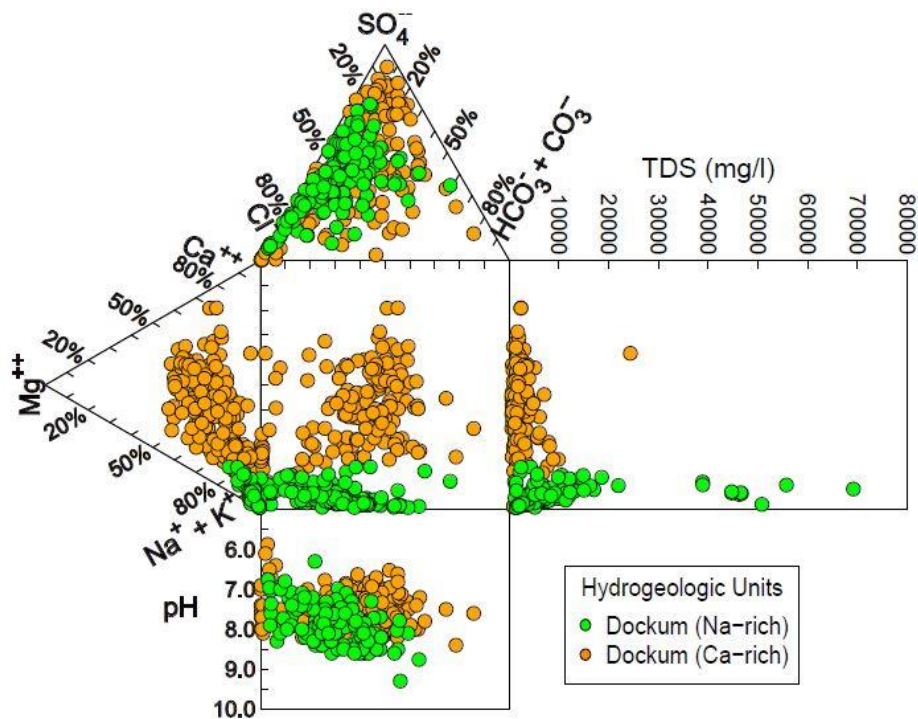


Figure 2: Durov diagram showing major ions, pH and, TDS concentration data for Dockum groundwater samples from within the Midland Basin.

Stable isotopic data for oxygen and hydrogen indicate that both the Ca- and Na- groups are of meteoric origin as both data sets plot slightly below (Fig. 3) on the Global Meteoric

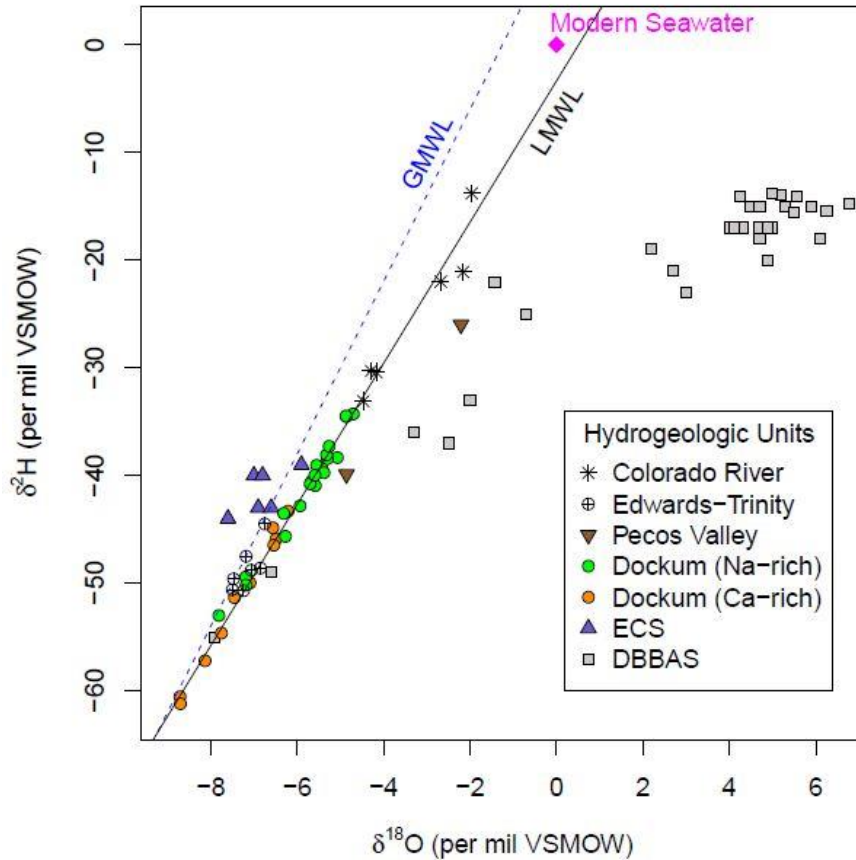


Figure 3: Bivariate plot of $\delta^2\text{H}$ versus $\delta^{18}\text{O}$ for groundwater samples from the Midland Basin. Colorado River data are from Coplen and Kendall (2000), and Edwards-Trinity, and Pecos Valley data from Bumgarner et al. (2012).

Water Line (GMWL) (Craig, 1961). Using data for the Colorado River, Edwards-Trinity aquifer, the Pecos Valley Alluvial aquifer, and the Dockum Aquifer the Local Meteoric Water Line (LMWL) can be defined as $\delta^2\text{H} = 6.55 \times \delta^{18}\text{O} - 3.37$ by similar methods from Kendall and Coplen (2001). Dockum groundwater samples are depleted in ^2H and ^{18}O relative to Colorado River and Pecos Valley water samples, but overlap with data from Edwards-Trinity groundwater. The ECS groundwaters plot near the GMWL suggesting they are of meteoric origin while the DBBAS groundwaters (Fig. 3) deviate from both the GMWL and LMWL, suggesting they are not of meteoric origin. The data for DBBAS groundwater samples plot on a linear trend starting near the LMWL and trending towards increasingly heavy values of roughly $+6\text{‰}$ $\delta^{18}\text{O}$ and -15‰ $\delta^2\text{H}$. The heaviest values are consistent with highly evaporated paleoseawater, suggesting this trend represent varying degrees of mixture between evaporated paleoseawater mixing and meteoric water of unknown age (Steuber et al., 1998). Within Dockum groundwaters, Na-rich group samples are on average more enriched in ^2H and ^{18}O than samples from the Ca-rich group (Fig. 3), likely suggesting different recharge conditions. As estimated from $\delta^{18}\text{O}$ data (Dansgaard, 1964), samples from the Ca-rich group recharged under significantly cooler

(Wilcoxon Rank Sum test, $p < 0.01$) conditions, roughly 2 °C cooler, than those from the Na-rich group. Assuming that all the Dockum groundwater was recharged under the same climate, one can conclude the Ca-rich group was recharged at a higher altitude (an estimated 400 m) than the Na-group. Overall, the stable isotope data indicate Dockum groundwater is meteoric and likely enters the Dockum Aquifer outside of the Midland Basin, since estimated temperatures and altitudes are more similar east of the Midland Basin, however further investigations are needed.

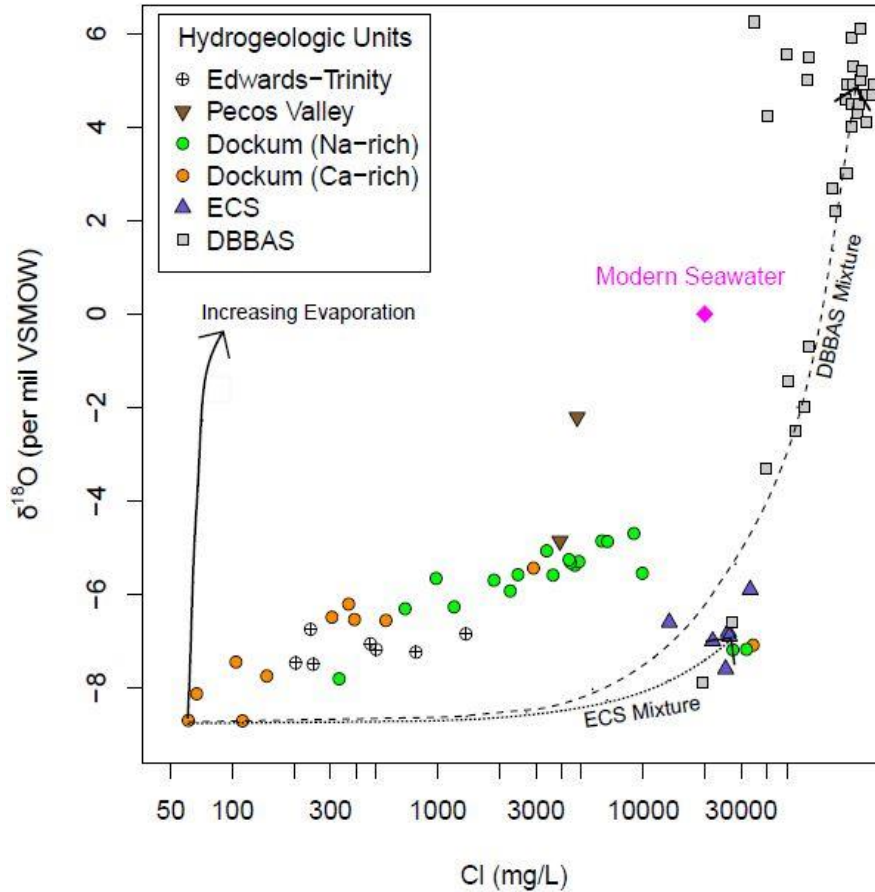


Figure 4: Bivariate plot of $\delta^{18}\text{O}$ versus Cl concentration data for groundwater samples collected within the Midland Basin. Increasing evaporation trajectory was calculated using a Rayleigh distillation model at 25 °C (model stops at 30% evaporated fraction). DBBAS-Dockum and ECS-Dockum mixture trajectories are calculated with a two component mixing model between a dilute Dockum end-member and a median value for the brine end-member.

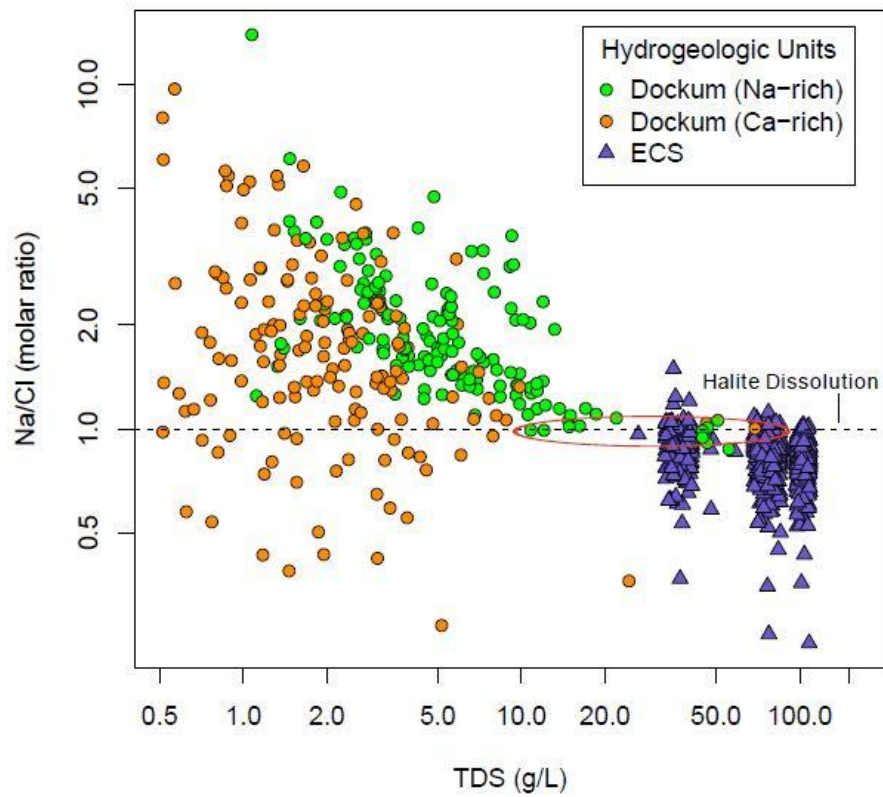


Figure 5: Bivariate plot of the Na/Cl molar ratio versus TDS data for groundwater samples collected within the Midland Basin. Red oval indicates data which are highly influenced by a large solute contribution from halite dissolution.

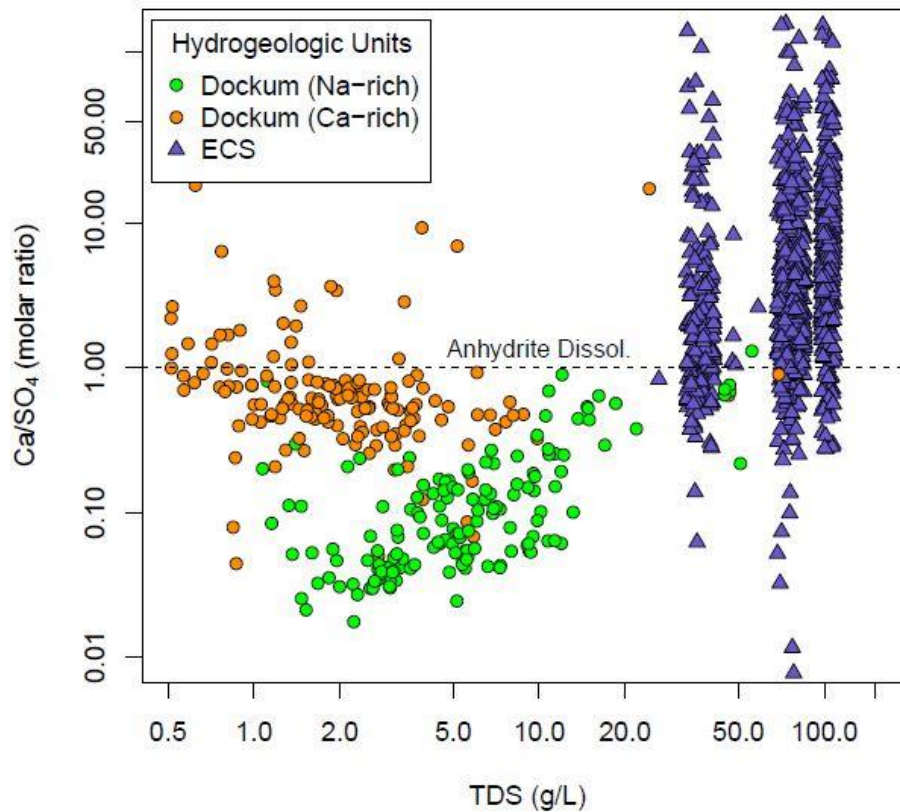


Figure 6: Bivariate plot of the Ca/SO₄ molar ratio versus TDS data for groundwater samples collected within the Midland Basin.

A reasonable approach to examine the role of mixing is to follow the behavior of conservative tracers, such as $\delta^{18}\text{O}$ and Cl (Fig. 4). Calcium-rich Dockum samples generally exhibit lower $\delta^{18}\text{O}$ values and Cl concentrations compared to the Na-rich samples (cf. Figs. 2–4). Dockum groundwater data have a positive logarithmic-linear relationship between $\delta^{18}\text{O}$ and Cl, and do not plot on an evaporation pathway (calculated with a mass-balance Rayleigh distillation model (Clark and Fritz, 1997) using fractionation factor of 9.3 at 25 °C (Majoube (1971))). Data for Edwards-Trinity groundwater generally fall on the trend defined by Dockum water types, suggesting a similar source. Mixing between Dockum and DBBAS data is not evident. However, a large contribution of ECS water appears present with at least three Dockum groundwaters, which plot in proximity to data for ECS samples along the Dockum-ECS mixing line near 30,000 mg/L of Cl. However, these three samples were collected from hydrocarbon wells producing from within the ECS which had been converted to water supply wells screened in the Dockum. Results from Fig. 4 suggest that these wells may still be allowing fluids from the ECS to migrate up into the well bore, and may not represent the formation water from within the Dockum Aquifer in bulk. From this point forward, data representing DBBAS samples will not be shown on

subsequent plots as a mixture between Dockum and DBBAS waters in the Dockum Aquifer is unsupported (Figs. 2,3).

The use of Na/Cl molar ratios can provide insight for the geochemical source for these constituents. Groundwater dissolving halite (NaCl) should approach a ratio of 1 as increasing input from the mineral occurs. The bivariate plot between Na/Cl (molar ratio) versus TDS concentration (Fig. 5) provides further evidence of geochemical differences and origin of the two distinct groups in Dockum groundwaters. The Na-rich Dockum groundwater samples have Na/Cl ratios practically above 1 and approach unity as TDS concentrations increase indicating halite is a dominant source for Na and Cl for these samples, particularly at TDS >10 g/L (Fig. 5). The Ca-rich Dockum groundwater samples exhibit greater variability in their Na/Cl ratio and do not display a similar trend between TDS and Na/Cl ratios, nor do these waters plot converge to any particular Na/Cl ratio. Although, the Na/Cl molar ratio of a few samples approaches unity, geochemical modeling results indicate that all Dockum Aquifer samples are still undersaturated with respect to halite (highest saturation index for halite is -0.86; Supp. Fig. 2). Mass balance calculations indicate that samples exhibiting Na/Cl ratios approaching unity, have dissolved up to 47.4g (0.81 mol) of halite per liter of groundwater which roughly matches the upper end of salinity for these samples (Fig. 5).

Additionally, Dockum groundwater data show as salinity increased, halite and anhydrite approach equilibrium. However, the data indicate the waters approach but stay undersaturated with respect to anhydrite possibly as a result of carbonate minerals being in equilibrium or oversaturated (Supp. Fig. 2.). Solute contribution from carbonate minerals may ultimately control the availability of Ca and preventing anhydrite to reach equilibrium. Similar to the Na/Cl molar ratio, a Ca/SO₄ molar ratio can help estimate the solute source for the Dockum Aquifer. From Figure 6, the Ca- and Na-rich Dockum data are geochemically different when related between the Ca/SO₄ molar ratio and TDS. The Ca-rich Dockum data plot close but slightly below a molar ratio of 1, which suggests these samples are experiencing anhydrite dissolution in the Dockum Aquifer, and show no obvious trends as a function of TDS concentration. Data for Na-rich Dockum Aquifer samples approach anhydrite dissolution (ratio of 1) as TDS increases, ultimately providing evidence of anhydrite dissolution adds to the salinity of this Dockum groundwater type, in addition to halite dissolution. However, the upper bounds of anhydrite solubility of roughly 3.9 g (0.028 mol) per liter of water indicates that halite is much larger contributor to salinity relative to anhydrite as is major reason while the Na-rich groundwater

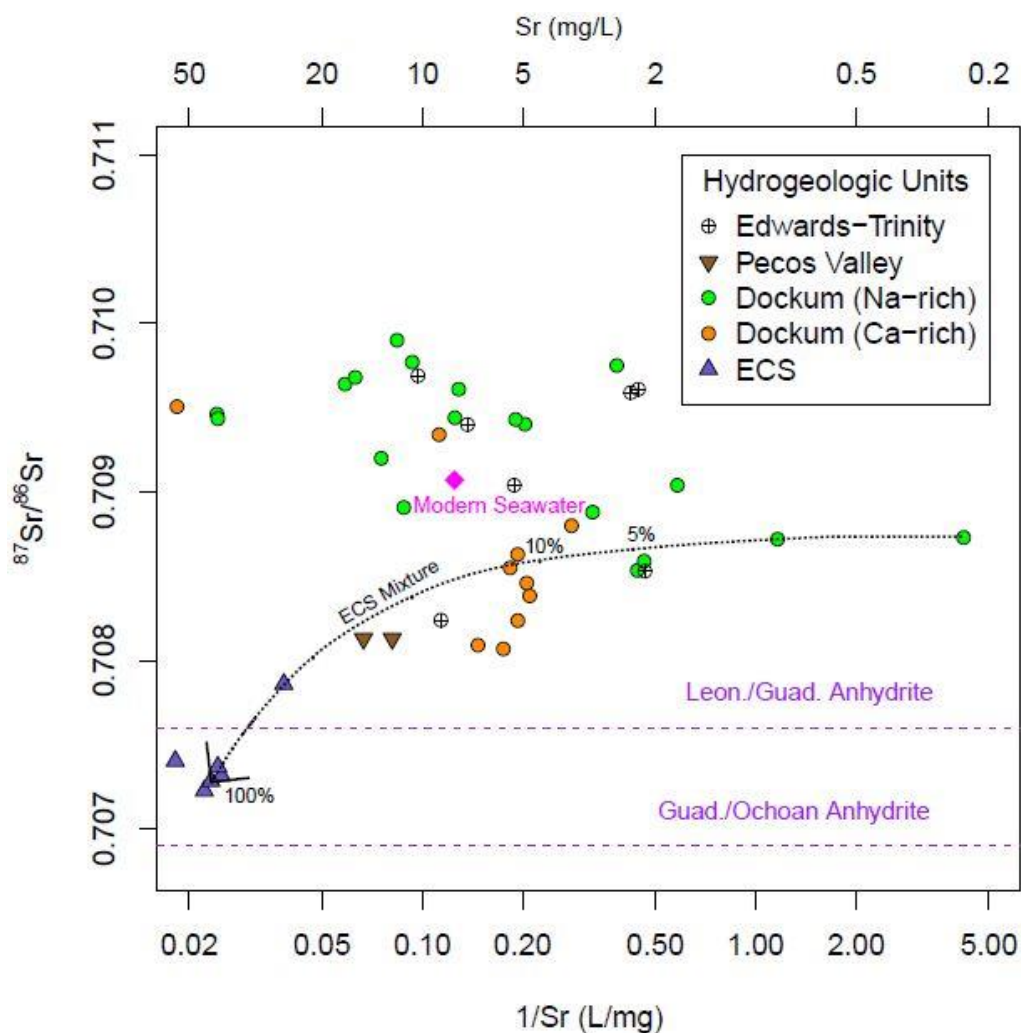


Figure 7: Bivariate plot of $^{87}\text{Sr}/^{86}\text{Sr}$ versus the inverse of the Sr concentration data for groundwater samples within Midland Basin. Two component mixing model was created using the Dockum sample with least Sr as one endmember and the median value for the ECS as the other endmember. Actual Sr concentrations shown across the upper x-axis.

contains a higher proportion of Na relative to Ca and Mg. Both Dockum groups approach equilibrium with respect to anhydrite as TDS increases (Supp. Fig. 2), however the Ca-rich group has a mineral saturation index (SI) generally an order of magnitude (-2-0 SI) higher than the Na-rich group (-3-0 SI). The relationship between Ca/SO_4 molar ratios and TDS is different for the two geochemical groups, and supports the idea that these groundwaters experience different flow paths (Fig. 6). Anhydrite is likely consistently present along the flow path with Ca-rich groundwater since data are typically observed near the Ca/SO_4 ratio of 1. As the Na-rich groundwater continues flowing, the introduction of anhydrite becomes more prominent and thereby influencing TDS. With solute sources deriving from halite (Fig. 5) and anhydrite (Fig. 6) as TDS increases, this ultimately supports the hypothesis that Dockum groundwater is reacting

with Permian evaporite layers, more so for the Na-rich Dockum groundwater than the Ca-rich group.

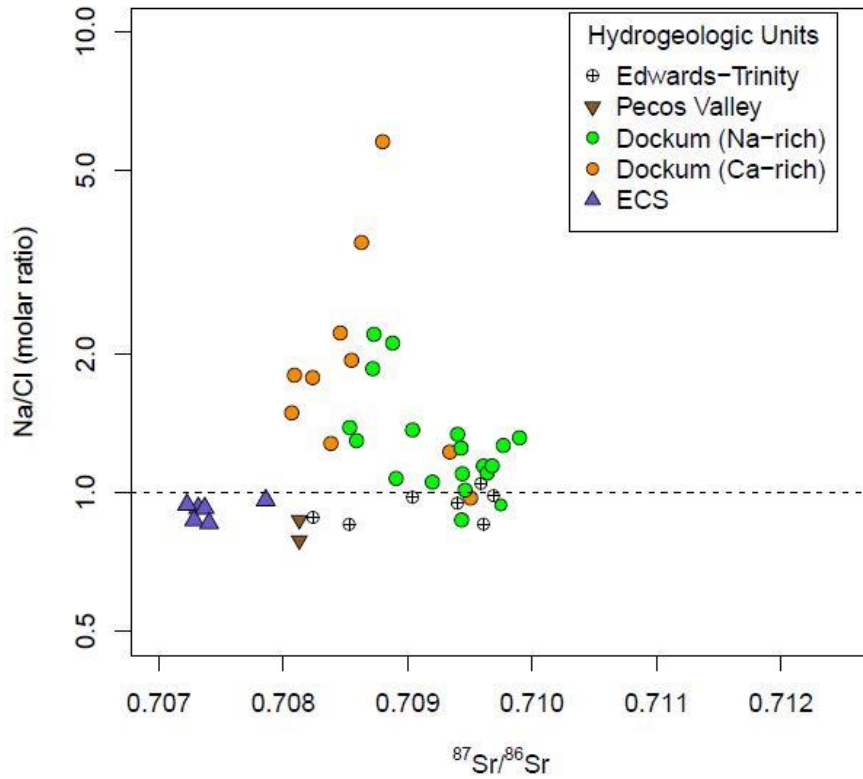


Figure 8: Bivariate plot of Na/Cl molar ratio vs $^{87}\text{Sr}/^{86}\text{Sr}$ of groundwater within Midland Basin.

Solute sources, including fluids mixing and/or rock-to-water interaction, can be tracked by examining $^{87}\text{Sr}/^{86}\text{Sr}$ compositions of samples. The median $^{87}\text{Sr}/^{86}\text{Sr}$ ratio for Dockum samples is 0.70900, while the first and third quartiles are 0.70860 and 0.70940, respectively. These values generally overlap the value for modern seawater (0.70907; Burke et al., 1982), an analog for modern precipitation, but caution should be taken since seasonal variation of can change this value (Capo et al., 1998). Also shown is the range in $^{87}\text{Sr}/^{86}\text{Sr}$ values for Leonardian to Ochoan age anhydrite deposits in the Permian Basin from Hovorka et al. (1993). A plot of $^{87}\text{Sr}/^{86}\text{Sr}$ vs $1/\text{Sr}$ (Fig. 7) indicates that Sr in Dockum groundwater samples is potentially derived from at least two different sources because samples from the Na-rich group are more radiogenic (higher $^{87}\text{Sr}/^{86}\text{Sr}$ ratio) than those of the Ca-rich group. In this figure, the Ca-rich group data do not exhibit a clear trend, while Na-rich group samples become more radiogenic with increasing Sr concentrations. Data for few Dockum samples with those of the Edwards-Trinity samples, however they do not overlap with data from Pecos Valley or ECS samples. Data for Dockum samples plot above the $^{87}\text{Sr}/^{86}\text{Sr}$ range for Permian anhydrite but two of the Ca-rich samples plot along a two end-member mixing line between a dilute Dockum end-member and the ECS end-

member. Mixing between Dockum and ECS groundwater is not evident for the majority of data plotted, however our calculated mixture model (see ECS Mixture arrow from Fig. 7) suggests at least two samples are potentially mixing, with a 10% contribution of Sr from ECS groundwater. Additional information on the role of evaporites contributing to solute chemistry is the comparison of Na/Cl molar ratio to $^{87}\text{Sr}/^{86}\text{Sr}$ data (Fig. 8). Data for the Ca-rich Dockum group samples do not exhibit much change in the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio as the Na/Cl molar ratio approaches 1 suggesting evaporites are not the dominant Sr source for these samples. Conversely, the Na-rich Dockum group samples exhibit decreasing Na/Cl molar ratios with increasing $^{87}\text{Sr}/^{86}\text{Sr}$ values; the increasing $^{87}\text{Sr}/^{86}\text{Sr}$ ratio suggests these waters are coming into contact with a source enriched in ^{87}Sr . Strontium-87 comes from radiogenic decay of ^{87}Rb ; Rb can easily substitute for K. Dissolution of K-rich Permian salts (polyhalite and sylvite), which are enriched in certain zones of the halite rich Salado Formation (Register, 1986) could reproduce the observation pattern of TDS and $^{87}\text{Sr}/^{86}\text{Sr}$ ratios increasing together (Barnaby et al., 2004). A simple mass balance calculation using the estimated dissolved halite (47.4 g) and anhydrite (3.9 g) in a Dockum brine endmember, and reported Sr concentrations and $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of Permian halite (Register, 1981) and anhydrite (Dean et al., 2000) resulted in a $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of 0.70695 and 9.47 mg/L of Sr. Interestingly, this endmember ratio is substantially lower than all reported Dockum groundwater samples. Potentially, Dockum groundwaters could have higher ratios due to non-evaporite minerals (e.g. carbonate cements, detrital clay) in the Dockum Aquifer, and/or modification from ion exchange (exchange between Rb and Sr with clays).

Spatial variability of Dockum Geochemistry and Hydrology

In order to further understand the geochemical controls of the Dockum Aquifer in the Midland Basin, the need to know how water chemistry varies spatially is imperative. From Figure 9, we observe a general increase in TDS concentration with greater well depths ($p < 0.0001$, $R^2 = 0.263$). However, depth alone does not fully explain the large variance in TDS concentration data; Dockum groundwater can be brackish at shallow depths (e.g. 6-30 m). Additionally, the Na-rich Dockum group consists of samples collected from generally deeper depths (> 152 m) relative to those from the Ca-rich Dockum group.

Hydraulic head data for Dockum groundwater wells (Fig. 10) was mapped and contoured across the Midland Basin. The contours of hydraulic head indicate a regional groundwater flow system, where Dockum groundwater generally flows from west to east (blue arrows in Fig. 10). Comparison of hydraulic head data between the Dockum and the immediately overlying unit (which changes based on location) indicates the potential for downward vertical flow from Edwards-Trinity, and Ogallala aquifers into the Dockum across the majority of the Midland Basin. Generally, wells producing Ca-rich Dockum groundwater samples are densely populated near the down gradient margins of the Midland Basin and extent of the Dockum group. A few wells for the Ca-rich Dockum groundwater are found throughout the south-central extent of the Midland basin. The majority of the wells producing Na-group Dockum groundwater are located throughout the central and northern part of the Midland Basin, and a few found with the Ca-rich

group in the southern part of the Midland Basin. There is a strong mixture of the two Dockum Aquifer groundwater groups near the exposed and unconfined portion of the Dockum Aquifer in the northeast part of the Midland Basin. This likely represents a locally driven flow and separation as a function of depth, which helps to explain the patterns from Figure 10. The most eastern cluster of groundwater wells are practically all Ca-rich group waters, which are very shallow and relatively fresh and may be zones of infiltration by local meteoric water.

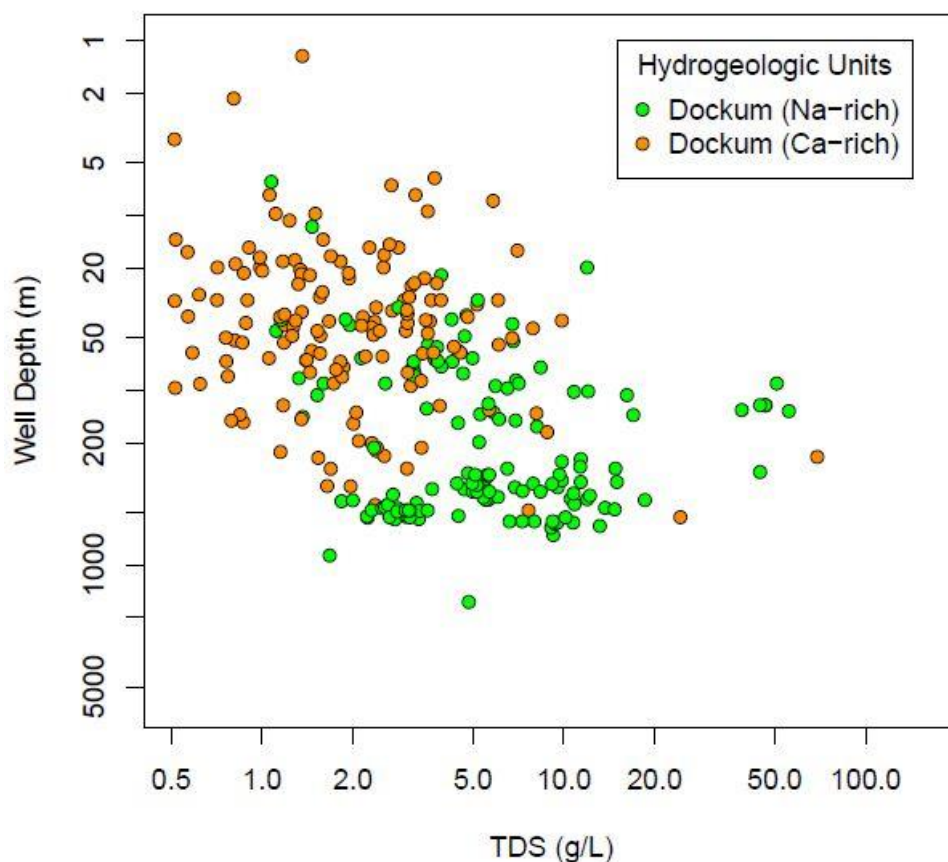


Figure 9: Bivariate plot of well depth (m) vs TDS of Dockum groundwater in the Midland Basin.

Generally, dissolved constituents in the Dockum Aquifer tend to be more concentrated towards the eastern portion of the Midland Basin (down gradient). In samples from the northern half of the Midland Basin, TDS is about 1,700 mg/L in the western most portion of the study area. Along the eastward flowpath, waters become more concentrated reaching a maximum (TDS > 100,000 mg/L) near discharge points on the eastern edge of the Dockum Aquifer (Fig. 11). This pattern of increasing salinity along the flowpath indicates that continuous mineral dissolution is an important source of solutes in Dockum groundwaters across the Midland Basin. High variability is observed in salinity data for samples from the northeast section of basin, where we find Dockum groundwater TDS concentration data range 500-150,000 mg/L, as a

function of depth (see Fig. 11). Univariate data analyses indicate two populations of Dockum well data: shallow wells (mean of 54 m) and deep wells (mean of 548 m), with an overall mean of 216 m. Ultimately, these wells which produced these samples may be drilled into different units of the Dockum Aquifer and represent poor hydrologic connection between the upper and lower units. Samples from the southern portion of the Dockum Aquifer in the Midland Basin are generally less concentrated than those from the northern half of the basin; TDS concentrations for Dockum Aquifer samples from the southern portion of the Basin are below 1,000 mg/L in the west but become more brackish towards the southeastern edge of the basin with TDS concentrations > 6,500 mg/L. Generally, this geographic pattern with TDS concentration is similar to those of Na (Suppl. Fig. 2) and Cl (Suppl. Fig. 3). However, alkaline earth metals (Suppl. Fig. 4) show a pattern opposite of this general spatial arrangement, specifically, higher AEM concentrations are found southwest of the basin, where Na and Cl concentrations are the lowest. The distribution of SO₄ concentration (Fig. 12) is dictated by large inputs in small localities not driven by the direction of groundwater flow, unlike the TDS spatial trend (Fig. 11), potentially suggesting areas of prevalent anhydrite dissolution.

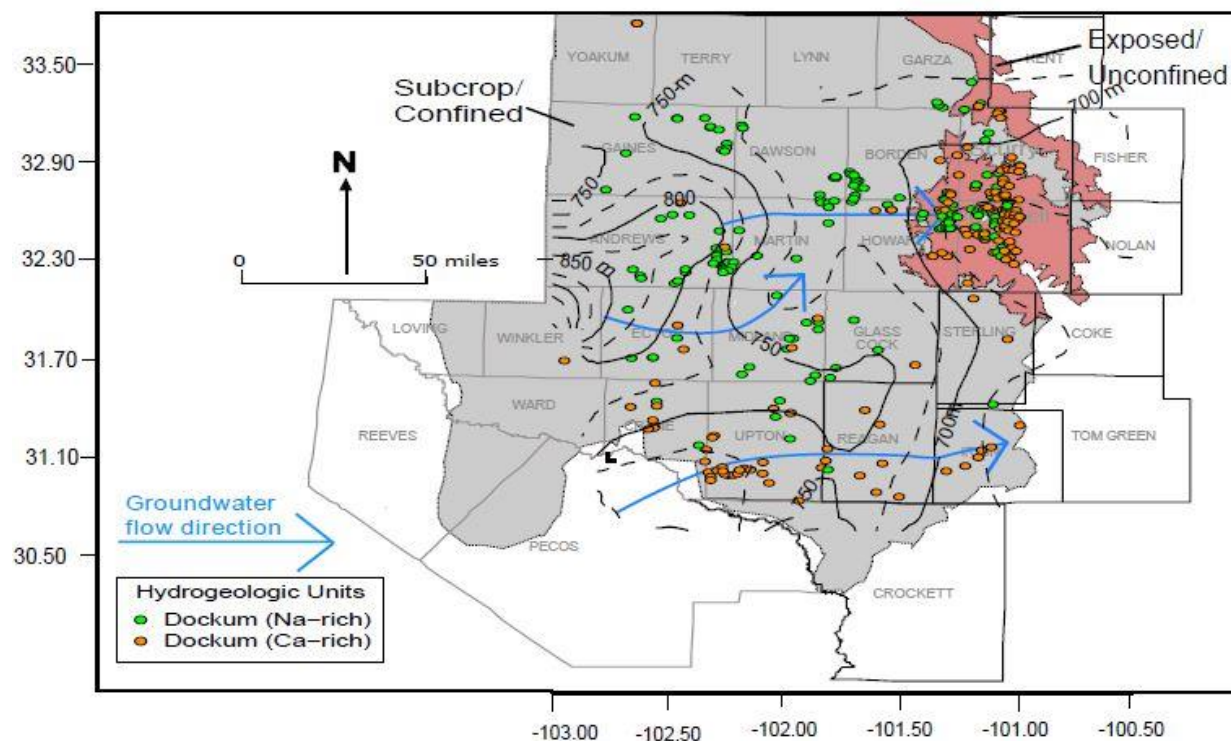


Figure 10: Map of hydraulic head (meters) gradient with the flow direction of Dockum aquifer is shown in blue arrows (roughly west to east) and location of type of water. Grey area is the extent of the subsurface Dockum formation, and the pink area is the extent of the exposed Dockum formation.

Geographically, SO₄ concentrations in Dockum Aquifer groundwater samples are greatest (> 3166 mg/L) in wells from the northwest Midland Basin (Gaines, Terry, and Dawson counties), while generally high SO₄ concentrations (>1764-3166 mg/L) are found in wells from the south central and north central part of the basin; along the basin edges SO₄ concentrations are generally lower. Nitrate concentrations are well below 0.2 mg/L throughout the majority of the basin, however, concentrations are considerably higher near the northeastern and south central portions of the Midland Basin (Suppl. Fig. 6). Elevated NO₃ in rural groundwater is often associated with shallow sources including from agricultural and septic sources supporting the idea that this area is one of input from for local, shallow recharge.

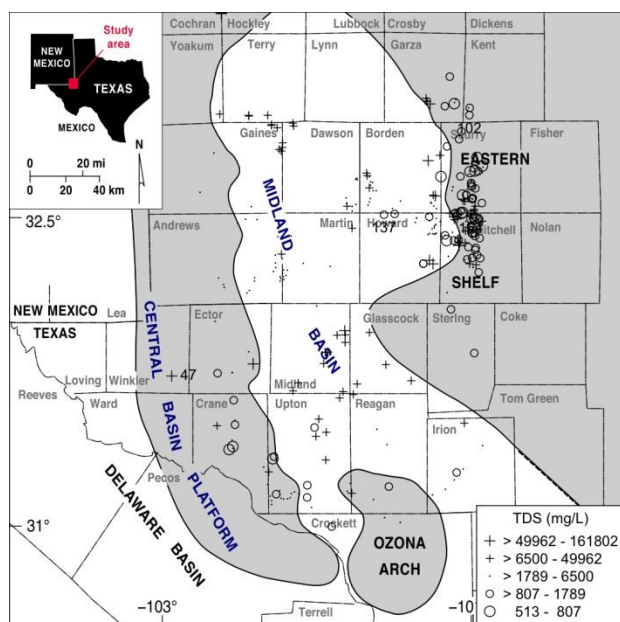


Figure 11: Spatial distribution of the concentration of Total Dissolved Solids (TDS) in the Dockum Aquifer within the Midland Basin. Symbol type and size based on the lowest 5th percentile (large circles), the 5th to 25th percentile (small circles), the 25th to 75th percentile (dots), and 75th to 95th percentile (small crosses), and finally, data above the 95th percentile (large crosses).

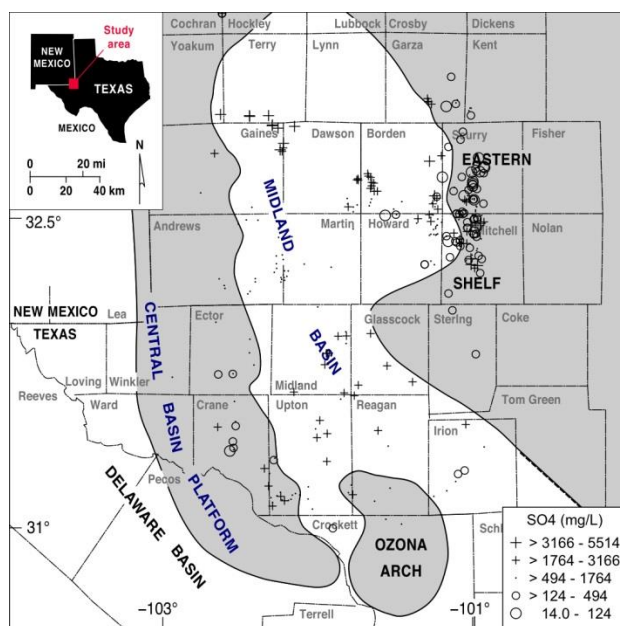


Figure 12: Spatial distribution of the SO_4 concentration in Dockum Aquifer groundwater samples within the Midland Basin. Symbol type and size based on the lowest 5th percentile (large circles), the 5th to 25th percentile (small circles), the 25th to 75th percentile (dots), and 75th to 95th percentile (small crosses), and finally, data above the 95th percentile (large crosses).

Discussion

Solute Sources and Geochemical Reactions

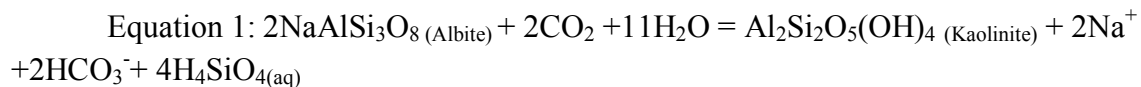
The recharge origin of the Dockum Aquifer most likely dictates the geochemical reactions occurring within the Midland basin, especially if these groundwaters originate from different regions. Recharge temperatures estimated from $\delta^{18}\text{O}$ results indicate the Ca-rich group waters recharged under conditions roughly 2 °C cooler than the Na-rich group water; these differences in recharge temperature can be a function of differences in climate during recharge, variation in elevation of recharge sites, or both. The Ca-rich water near the southwest corner of the basin may represent recharge from regional groundwater flow from far west Texas and/or southeast New Mexico, and runoff from Barilla, Davis, and Glass Mountains into overlying aquifers (Bumgarner et al., 2012). Elevation estimates from the $\delta^{18}\text{O}$ results (1700-2400 m above mean sea level) for these samples correspond with higher elevations in these regions. The Na-rich waters are thought to recharge from slightly lower elevations in eastern and northeastern New Mexico and in agreement with the $\delta^{18}\text{O}$ estimated elevations of 1200-1700 m above mean sea level (similar to findings from Dutton and Simpkins, 1989). If Na-rich waters follow the same flow path as Dockum waters from the Southern High Plains, which flow towards the southeastern margin of the Permian Basin (samples from Dutton and Simpkins, 1989), then these waters may reflect recharge from the late-middle to late Pleistocene. However, Dockum

groundwater data from this study are isotopically heavier than those of Dutton and Simpkins (1989) suggesting the Dockum groundwater in the Midland Basin is younger or/and from lower elevation recharge sites than for waters samples further north. Dockum groundwaters from this study are isotopically more similar to the Ogallala samples than the Dockum samples from Dutton and Simpkins (1989). If Dockum groundwaters in the Midland Basin are more enriched in heavier isotopes (^2H and ^{18}O) than the Dockum groundwaters in the Southern High Plains (see Dutton and Simpkins, 1989), then the Dockum groundwater in the Midland Basin may represent younger recharge.

The groundwater evolution of the brackish Dockum Aquifer is a series of geochemical reactions. The earlier stages of reactions involve rock-to-water interactions with Na-rich feldspars, ion exchange with clays, and minimal anhydrite and halite dissolution during regional groundwater flow. The upper Dockum is considerably thicker near the north-central portion of the Midland Basin, while its presence dissipates towards the south (McGowen et al., 1977); earlier stages of groundwater flow are likely occurring in this portion of the Dockum. The Na-rich groundwater is found at deeper depths and is not recent meteoric recharge (Dutton and Simpkins, 1986; Ewing et al., 2008), but likely experienced greater modification during past lateral and vertical groundwater flow through permeable portions of the upper Dockum. Potentially, the Na-rich group may represent groundwater which flowed through a more reactive silicate or clay Dockum unit modifying the solutes to a more Na-rich composition before entrance into the deeper, sandstone-rich portion of the aquifer, where dissolution of large quantities of evaporite minerals begins. The Na/Cl ratio of the majority (both Ca- and Na-rich groups) of Dockum groundwater is above 1, which is evidence for the addition of Na from weathering of clays and feldspars (Dutton and Simpkins, 1986). Although, Na is introduced into both groups, the Na-rich groundwater is likely experiencing ion exchange (Dutton and Simpkins, 1986) between Ca (derived from carbonate dissolution) and Na (from Na-rich clays). Ion exchange in the Dockum would modify the groundwater in two steps: 1) loss of Ca and gain of Na with no change in TDS, and 2) finally, lowering the mineral saturation of calcite by allowing for further dissolution of carbonates which increases alkalinity (see Fig. 2; similar to the Na- HCO_3 groundwater from Dutton and Simpkins (1986), and brines from Bein and Dutton (1993)). This ion exchange reaction is clearly evident for the Na-rich group but not for the Ca-rich group.

Although, both water types are in equilibrium or saturated with respect to carbonate minerals, elevated alkalinity in the Na-rich group can also be from silicate weathering because a decrease in the molar ratio of Ca/HCO_3 results in an increase in the molar ratio of Na/Cl (a trend not seen with data from the Ca-rich group samples; Supp. Fig. 8). The majority of Ca/HCO_3 and $\text{Ca}+\text{Mg}/\text{HCO}_3$ molar ratio data for Na-rich group samples are approximately 100-1,000 times greater than the stoichiometric value for carbonate dissolution, and as TDS concentrations increase the ratios become larger. This relationship ultimately suggests that carbonate mineral dissolution is not the dominant source for Ca in the Na-rich group; anhydrite dissolution and feldspar weathering appear more important sources of Ca. Feldspar weathering is likely most

common in the west-central, northwest, and northern most section of the Midland Basin were HCO_3^- concentrations are highest and waters are in equilibrium or saturated with respect to calcite. As regional groundwater flow continue east, further silicate mineral dissolution occurs adding more Na and HCO_3^- (see equation 1), and the introduction of evaporite minerals.



The prominent and later stage geochemical reaction modifying the Na-rich groundwater composition and salinity is the introduction of halite and anhydrite minerals. Results from oxygen and hydrogen isotopes indicate Dockum groundwaters are meteoric, have not experienced substantial evaporation, and are not likely in hydraulic connection with DBBAS groundwater. However, data for a handful of samples suggest there is contact with Permian bedrock or mixing with brine upwelling out of the ECS in the northeast Midland Basin, near Borden and Howard county. Specifically, the Na-rich Dockum groundwater samples contain environmental clues which suggest an interaction between evaporite sequences, brines held in the ECS or detrital Permian salt with the Dockum Aquifer. The Na-rich group approach molar ratios suggestive of halite and anhydrite dissolution as TDS increases (Fig. 5,6), approach equilibrium with respect to halite and anhydrite (Supp. Fig. 2), and exhibit $^{87}\text{Sr}/^{86}\text{Sr}$ ratios that increase as Na/Cl molar ratio approaches the value for halite dissolution (Fig. 8). This supports the hypothesis of water-to-rock interactions with K or Na rich minerals as the source of the radiogenic signal in the Sr-isotope data. Barnaby et al (2004), observed a similar trend in data for produced water brine samples from the Indian Basin and Dragster Draw fields (west of the Guadalupe mountains in southeastern New Mexico), and inferred this relationship to be due to the dissolution of K-bearing evaporite minerals releasing Rb into the brines from the Salado potash zone. Register (1981) found Salado halite to have radiogenic $^{87}\text{Sr}/^{86}\text{Sr}$ ratios (median value 0.7112) but also found detrital clays within the halite to be very radiogenic (ranging from 0.7185-0.7632). Detrital halite and clay deposited within the Dockum group or original halite in the underlying evaporite sequences may be a source of the radiogenic signature in the Na-rich group; halite is sometimes identified in Dockum well logs and occurs in thick sequences of the underlying Salado Formation. The solutes, suggestive of Permian salt, increase along the down gradient groundwater flow path throughout the Midland Basin for the Dockum Aquifer. Overall, the introduction of anhydrite from overlying aquifers with ion exchange and weathering of feldspars and clays, likely dominates the Na and SO_4 source but as the groundwater flows further east into sandstone rich Dockum, ion exchange decreases (lowering the Na/Cl ratio), but weathering of feldspars slowly continues, and pockets of salt dissolution sites likely modify the Na-rich group heavily.

A few Dockum groundwater samples (~5 %) are very likely interacting with halite because their Na/Cl ratio is near 1 and have TDS greater than 10 g/L (Fig. 5). The localities of these wells are near areas (Borden, Howard and Mitchell county in the northeastern portion of the basin, and

near Upton and Crane county in the southwestern region of basin) of prominent Permian salt dissolution (Hovorka and Nava, 2000) or are down-gradient from these known salt dissolution sites (see Fig. 8). Sodium-rich groundwaters in these regions are meteoric waters that have experienced rock-to-water interactions with detrital Permian salt in the Dockum, Dockum groundwater flowing through dissolution zones and then upwelling from ECS layer, upwelling of ECS brine or some fraction of both.

The composition of Ca-rich Dockum group groundwater in the Midland Basin is primarily influenced by the inflow from overlying aquifers experiencing water-to-rock interactions with carbonates, sandstones and potentially anhydrite (Groschen and Buszka, 1997; Nance, 2002; Bumgarner et al., 2012) and particularly in the northeast is influenced by recent recharge. Generally, the hydraulic head data of wells screened in the Dockum Aquifer relative to overlying fresh and brackish aquifers suggest downward flow into the Dockum is possible (data not shown) and therefore is a potential source for the relatively dilute brackish Ca-rich Dockum groundwater in the southwest Midland Basin. In addition, the Ca-rich solutions are in equilibrium with respect to dolomite, quartz, and calcite, and slightly under-saturated in respect to gypsum (Supp. Fig. 2); these findings are similar to those of Nance's (2004) data for the overlying Edwards-Trinity aquifer. Nance (2004) stated the Edwards-Trinity contains an economical source of gypsum, but the hydrological connection within Edwards-Trinity units is questionable, since the flow of SO_4 rich water may be geographically and hydrologically isolated or is not evenly distributed. The Dockum groundwater samples analyzed for $\delta^2\text{H}$ and $\delta^{18}\text{O}$ (Fig. 3), share isotopic and Cl concentration (Fig. 4) similarities with overlying Edwards-Trinity groundwater in the Pecos region (data from Bumgarner et al., 2012); this relationship suggests mixing between aquifers or similar recharge sites. However a few Ca-rich Dockum groundwaters contain less Cl, are moderately depleted in ^{18}O (Fig. 4) relative to Edwards-Trinity data, and located near the edge of the Midland basin and on the Ozona Arch (Fig. 10) this geochemical signature may represents a different recharge site for these Ca-rich groundwater samples, relative to data from Bumgarner et al. (2012).

The $^{87}\text{Sr}/^{86}\text{Sr}$ data for Ca-rich Dockum groundwater samples do not plot within the range of Permian-age anhydrite, a likely source of Sr in waters that have reacted with evaporite minerals, likely suggesting these waters gain their Sr from other sources (e.g. Edwards-Trinity aquifer) than upwelling ECS groundwater in the Midland Basin. Register (1981) and Hovorka et al. (1993) described anhydrite minerals with lower $^{87}\text{Sr}/^{86}\text{Sr}$ ratios (0.7069-0.7076) since anhydrite has low concentrations of Rb relative to Sr, and reflect the Sr isotopic composition of Permian seawater. The Ca-rich Dockum Aquifer groundwater samples likely have lower $^{87}\text{Sr}/^{86}\text{Sr}$ ratios than the Na-rich samples due to water-to-rock interaction with anhydrite. Conversely, data for Edwards-Trinity samples do not overlap with Ca-rich samples on the $^{87}\text{Sr}/^{86}\text{Sr}$ versus $1/\text{Sr}$ plot (Fig. 7), suggesting different sources of Sr or at least a unit within the Edwards-Trinity that is not in contact with anhydrite. The source for SO_4 and lower $^{87}\text{Sr}/^{86}\text{Sr}$ ratios in the Dockum Aquifer could potentially be from discrete pockets of detrital anhydrite, which was introduced to the

Dockum during deposition; anhydrite is typically found in Dockum well logs in the Midland Basin but is not pervasive. Other potential source for SO_4 is the oxidation of pyrite and Nance (2004) noted pyrite can be found in trace amounts in the Edwards-Trinity and in Dockum well logs. One hypothesis (Dutton and Simpkins, 1986; Nance, 2004) with little concrete evidence, is that the solutes may have originated during paleohydrologic conditions which favored upwelling of underlying aquifers (e.g. Permian groundwater) into overlaying aquifers. Lastly, the Ca-rich Dockum group is found at shallower depths and focused along the southwestern and northeastern Midland Basin likely representing local recharge and meteoric water mixing only with the lower Dockum group since the upper mud-rich Dockum group thins out and is not present in these localities (McGowen et al., 1977).

With any study, limitations exist, and their existence ultimately influences the interpretations. Isotope geochemistry for the Dockum Aquifer was primarily sampled from wells on the western and southern portions of the Midland Basin; samples need to be collected from the northwest to northeast to fully understand the influence of salt dissolution sites along groundwater flow paths. The densely populated wells in the northeast portion of the basin may influence the interpretation of groundwater flow. The two end-member mixing models do not promote the hypothesis of mixing between ECS brines in the Midland Basin/Central Basin Platform with the majority of Dockum groundwater, but other tracers promote the hypothesis. However, the ECS data in this study are from the San Andres Formation in the Central Basin Platform from Stueber et al. (1998), other formations within the ECS in the Midland Basin could have isotopically different signatures for $^{87}\text{Sr}/^{86}\text{Sr}$, $\delta^2\text{H}$, and $\delta^{18}\text{O}$. Different isotope signatures could drastically change the interpretation of the mixing models used in this study, and provide stronger confidence. A few Edwards-Trinity groundwater samples exhibit similar $^{87}\text{Sr}/^{86}\text{Sr}$ ratios (See Fig. 7) to some of the Na-rich samples closer to the southern basin; potentially a source for the considerably high (median is 1,631 mg/L) SO_4 concentrations. The Trinity-Edwards groundwater samples with isotope data are from Bumgarner et al. (2012), these samples were collected near the edge of the southern Midland Basin and closer to the Pecos region. Trinity-Edwards and Ogallala isotope data could vary in the Midland Basin, and the data would help to better differentiate the origin of the Na- and Ca-rich Dockum groundwaters. Lastly, Dockum groundwater samples need to be collected for isotope geochemistry from New Mexico to identify if upwelling brines are impacting the chemistry before flowing into the Midland Basin.

The suitability of the Dockum Aquifer as a hydraulic fracturing fluid.

Ultimately, the chemistry of the water from Dockum Aquifer fits the water quality requirements for hydraulic fracturing in the Midland Basin. Two basic types of hydraulic fracturing are employed in the basin. Cross-link gel fracturing fluids employ boron or zirconate based cross-linker, which increases viscosity once the fluid enters the reservoir to help force proppant into the newly opened fractures. Within the Permian Basin, these cross-link gels are primarily applied in vertical wells (e.g., Wolfberry and Strawberry plays) where multiple low permeability, organic rich horizons are fracture stimulated and hydrocarbons and produced waters are pulled from

multiple depths. Slickwater fracturing fluids employ a water solution containing a friction reducer (often polyacrylamide) which requires less pressure from the pumps to force the fracturing fluid down the borehole. Slickwater fracture treatments are primarily used in horizontal wells drilled into organic rich shales, including the Wolfcamp, “Cline”, Woodford, and Barnett. From Table 1, the general requirements for Cross-Link Gel Systems are practically all within the required limits. However, one potential issue with the use of Dockum Aquifer groundwaters with Cross-Link Gel Systems is relatively elevated SO_4 concentration in some areas; the general required limits range from 200-1000 ppm (or mg/L). The lower limits of SO_4 are mainly problematic for the higher salinity; Na-rich waters have higher concentrations of SO_4 than the Ca-rich waters, especially in the northwest portion of the basin and deeper zones in the northeastern section of the basin (see Fig. 13). Potentially, dilution or mixing with SO_4 -poor produced waters may solve this issue for area producing SO_4 -elevated groundwater, depending on the Cross Link Gel System requirements for a specific company. Other SO_4 reduction or removal techniques include the use of nanofiltration or sulfate selective ion exchange resins. The general requirements for slickwater systems are considerably simpler, with no issues for pH and few data exceeding TDS concentration thresholds (less than 7% of data exceed 40,000 mg/L) for Dockum groundwater, but the multivalent ion (alkaline earth metals and SO_4) required limit may be problematic for the Na-rich group and the Ca-rich group in areas of elevated TDS.

In an attempt to understand the potential for scale formation during hydraulic fracturing or to mimic instances of mixing recycled produced water with brackish groundwater, geochemical modeling was performed to examine relative mixtures of Dockum end-members and formation brine (data from the unconventional Wolfcamp, Strawn, and Spraberry reservoirs). Modeling results indicate that mixtures of Dockum groundwater end-members (high and low TDS for Na-rich, and high and low TDS for Ca-rich) and 25-75% contributions from produced waters are typically saturated with respect to carbonate minerals (calcite, magnesite, celestite, and aragonite). The highest saturation index for calcite was found between brine from the Wolfcamp reservoir and Dockum brackish water; modeling results suggest that calcite might precipitate in Wolfcamp, Strawn, and Spraberry reservoirs during or after hydraulic fracturing. With respect to gypsum, all mixtures are slightly under-saturated (SI is between -0.9 and -0.1), while mixtures between high TDS Ca-rich and Na-rich Dockum and brines from the Wolfcamp are in equilibrium or near saturation suggesting that gypsum formation is unlikely. All mixtures are under-saturated with respect to halite by at least a magnitude or two. Additionally, all mixtures are under-saturated in respect to barite (BaSO_4), which is important given its extremely low saturation index, difficulty in removing it from pipes and the reservoir, and its potential to accumulate radium in high concentrations. Overall, mineral precipitation during the injection of the Dockum should be manageable, especially if scale-inhibitors are used.

Geographically, the northwest and north central portions of the Midland Basin are areas where the multivalent ion requirement may be problematic or require dilution for slickwater systems. Areas not colored in the Midland Basin from Fig. 13, are areas with best potential for the use as a

hydraulic fracturing fluid. Another consideration on the development on the use of Dockum Aquifer groundwater in hydraulic fracturing fluid, is whether or not an operator wants to invest on a water supply which is found at considerable deep depths. Shallower wells are likely to be fresh water and a potential drinking water resource; ultimately a water resource one may want to avoid to minimize impacts to stressed freshwater resources.

Table 1: General chemical requirements for cross link gel and slickwater hydraulic fracturing fluid systems (personal communication with operators in the Permian Basin). Red colored text refers to requirements that are not met by most Dockum groundwater.

| Hydraulic Fracturing System | Cross Link Gel Systems | Slickwater Systems |
|-----------------------------|------------------------|--------------------|
| pH | 6.0-8.0 | >5 |
| Ca + Mg | <2,000 ppm | -- |
| Fe | <20 ppm | -- |
| SO ₄ | 200-1,000 ppm | -- |
| Cl | <40,000 ppm | -- |
| HCO ₃ | <1,000 ppm | -- |
| B | <10 ppm | -- |
| Multivalent Ions | -- | <5,000 ppm |
| TDS | -- | <40,000 ppm |
| Reducing agent | <25 ppm | -- |

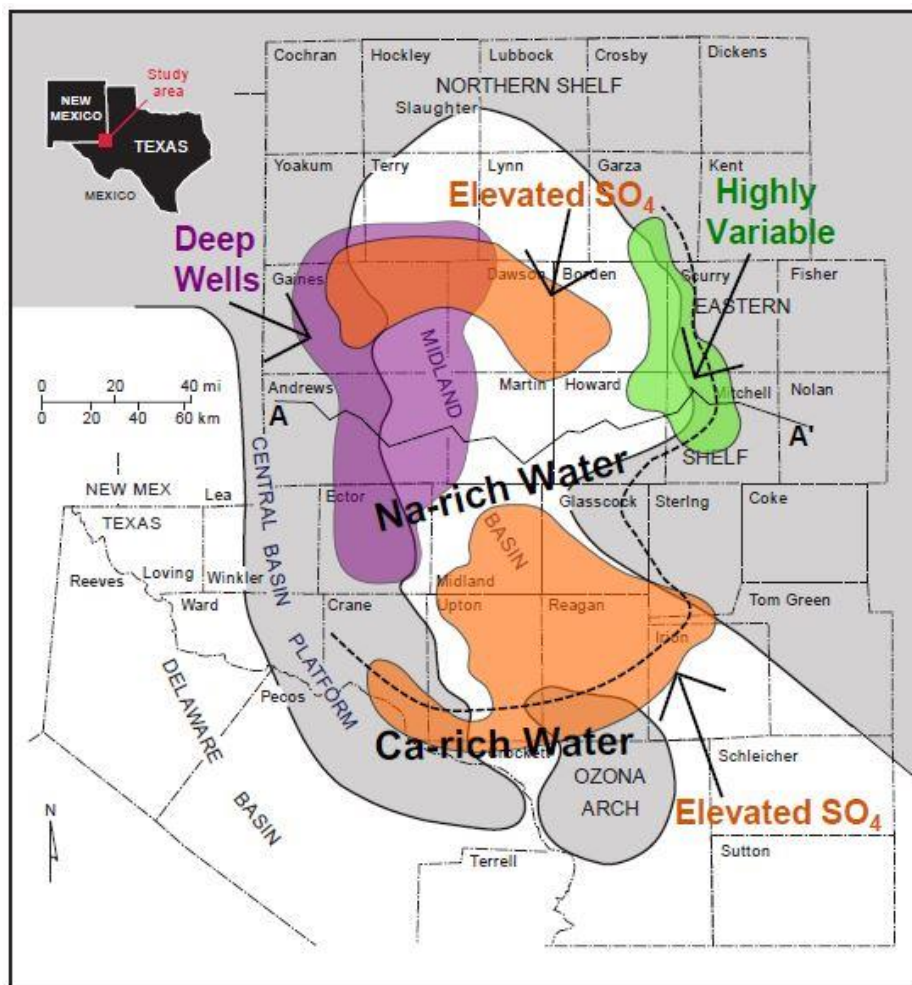


Figure 13: Spatial map of the suitability of Dockum Aquifer groundwater for use in hydraulic fracturing fluid. The green area is highly variable in chemistry due to depth-related groundwater flow. A to A' prime correspond to a transect used in Fig. 14.

Summary

Previously published data for Dockum groundwater were combined with results from recently sampled Dockum groundwater in the Midland Basin were re-studied with a focus on elemental and isotope geochemistry. Although the Dockum groundwaters can be separated into several hydrochemical facies (e.g. Na-Cl, Na-Cl-SO₄, Ca-SO₄-Cl), distinct differences in the dominant cations (Na and Ca) with total dissolved solids (TDS) were identified, which provide a more

practical method to distinguish geochemical controls over the Dockum Aquifer groundwaters. The primary solute sources for the Dockum include: 1) dissolution of anhydrite from overlying aquifers, and dissolution of anhydrite and halite either within the Dockum and/or from the top of the Salado Formation; 2) Na-rich feldspar weathering; and 3) ion exchange between of Na for Ca on clays present within the Dockum group. The northern part of the Midland Basin is dominated by higher TDS, Na-rich groundwater; while the southern and northeastern edges of the basin are primarily produce lower TDS, Ca-rich groundwater. Calcium-rich Dockum Aquifer groundwater is generally present at shallower depths, even at the northeast margin of Midland Basin. Likely this type of water is relatively young, recently water with significant contributions of groundwater from overlying aquifers (e.g., Ogallalla and Edwards-Trinity). The Na-rich groundwater corresponds with older (relative to Ca-rich groundwater), deeper groundwater which is likely modified from past vertical and lateral flow within the permeable upper Dockum units and either dissolution of detrital halite and anhydrite within the Dockum Aquifer or from dissolution of the top of the Salado evaporites along the flow path from west to east; this Na-rich water appears to have infiltrated west of the Midland Basin, and potentially during a warmer climate and/or lower recharge elevation near east to east-central New Mexico relative to Ca-rich samples.

A more exhaustive study is needed to have a better understanding about the geochemical differences of the two types of Dockum groundwater. Whether Ca-rich group is younger or older than the Na-rich group, is unknown; groundwater age dating is necessary to determine recharge ages and residence time of these water types along a west to east transect in the Midland Basin. Additionally, it is necessary to collect Dockum groundwater and overlying aquifers in New Mexico where groundwater flow is in the direction of the Midland Basin, these data may help add to the story of the Dockum groundwater's beginnings. Research should also be directed at the potential sources for SO_4 by using ^{34}S - SO_4 isotopes of aquifer material in the Dockum and overlying units, and the groundwater within these units. Preliminary ^{34}S - SO_4 isotope data of Dockum groundwater (unpublished data) indicate a few Na-rich samples fall within the ^{34}S - SO_4 isotope range of Permian anhydrite, while Ca-rich samples have considerably lower values, but these data are few and densely populated in the western Midland Basin.

Combining results from the various aspects of this work, the following conceptual model for the nature and controls of Dockum group groundwater in the vicinity of the Midland Basin is proposed (Fig. 14). The Na-rich Dockum groundwater recharged in eastern New Mexico then followed a regional flow to the east. This meteoric source flows downward through aquifers overlying the Dockum during which solutes are added by rock-to-water interaction between carbonates, sandstones, and anhydrite. As this water continues its flow, eventually reaching the permeable section of the upper Dockum, its composition modified by ion exchange with the abundant clay minerals, weathering of Na and K feldspars and silicates, calcite saturation, and dissolution of detrital Permian anhydrite and a small proportion of halite (the source of chloride). As the salinity increases in the lower Dockum, the groundwater reaches equilibrium with

silicates, weathering of feldspars and silicates decreases, and the relative contribution of halite to groundwater salinity increases. As the groundwater continues flowing further east, upwelling of Na-Cl brines near salt dissolution sites (see Hovorka and Nava (2000)) likely influence and ultimately bring the Na/Cl molar ratio near 1 and cause TDS to increase dramatically (>10,000 mg/L).

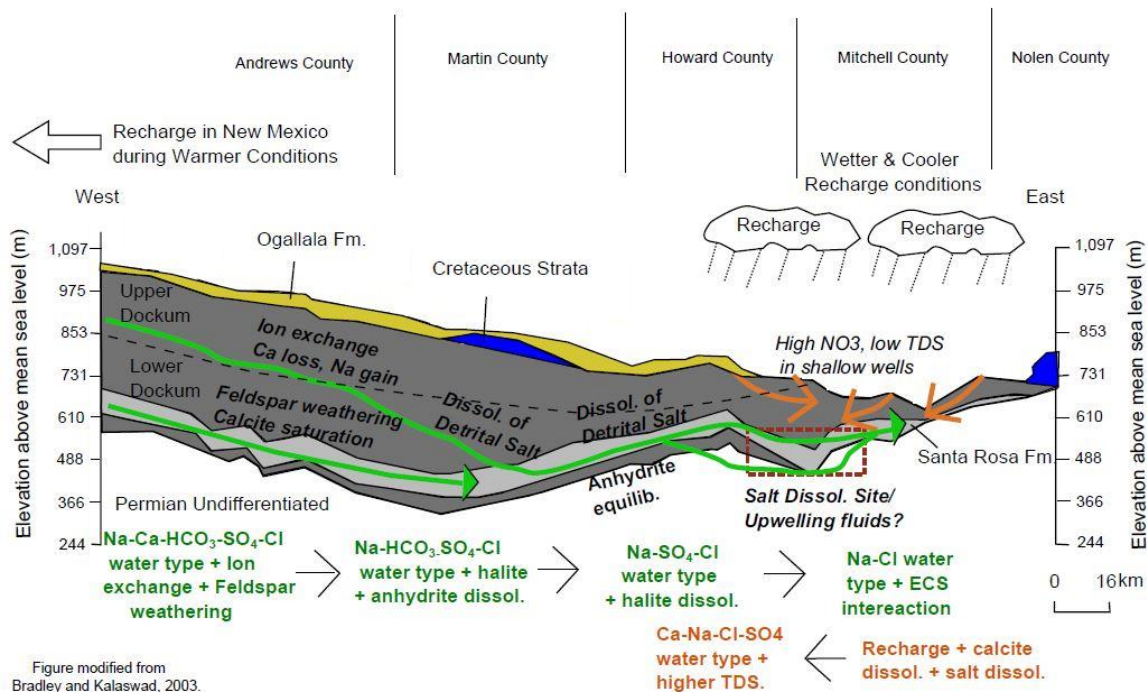


Figure 14: Conceptual model (from transect A-A' from Fig. 13) for the Na-rich groundwater of the northern Midland Basin; image is modified from Bradley and Kalaswad, 2003.

The second part to the conceptual model explains the Ca-rich Dockum groundwater. Meteoric water was recharged from the Barilla, Davis, and Glass Mountains (Bumgarner et al., 2012), as groundwater flowed in the direction towards the Midland Basin, this meteoric water interacted with overlying aquifer groundwater and their aquifer matrix (carbonates and silicates), such as the Edwards-Trinity (Bumgarner et al., 2012). Anhydrite within the Edwards-Trinity or detrital Permian anhydrite within the Dockum then results in the addition of SO_4 and Ca. This model explains the presence of brackish groundwater found in the southwest edge of the Dockum Aquifer. A simplified model can explain the very shallow Ca-rich Dockum groundwater in the northeast of the Midland Basin. This water is dominated by recent recharge found at shallow depths, near the most eastern edge of the basin and contains TDS general less than 1,000 mg/L. The solutes for this Ca-rich Dockum groundwater are likely rock-to-water interaction only within the Dockum.

Overall, the Dockum Aquifer presents an alternative for a hydraulic fracturing fluid to the use of surface or fresh groundwater. Transmissivity data for wells screened in the Dockum Aquifer are very limited and contain great variability. Some wells have reasonably high transmissivity data to indicate they can support water oil and gas activities in the Midland Basin, but there are some locations where water yields may be significantly lower (wells likely not drilled in the sand-rich portions of the Dockum unit, see McGowen et al., 1979). Chemically, the Na-rich waters in the north to northwest portion of the basin may require dilution (depending on specific company fracturing requirements), and are also the deepest wells found in the Midland Basin. The majority of the Dockum is not suitable for drinking or agricultural use (Dutton and Simpkins, 1986), but is suitable for hydraulic fracturing. An informal poll of operators who have or begun to use Dockum Aquifer waters as an alternative hydraulic fracturing fluid are satisfied with its use in their operations but more work is necessary to better understand the full impacts.

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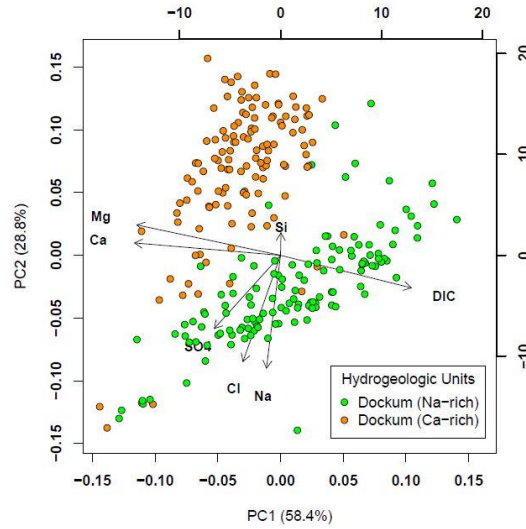
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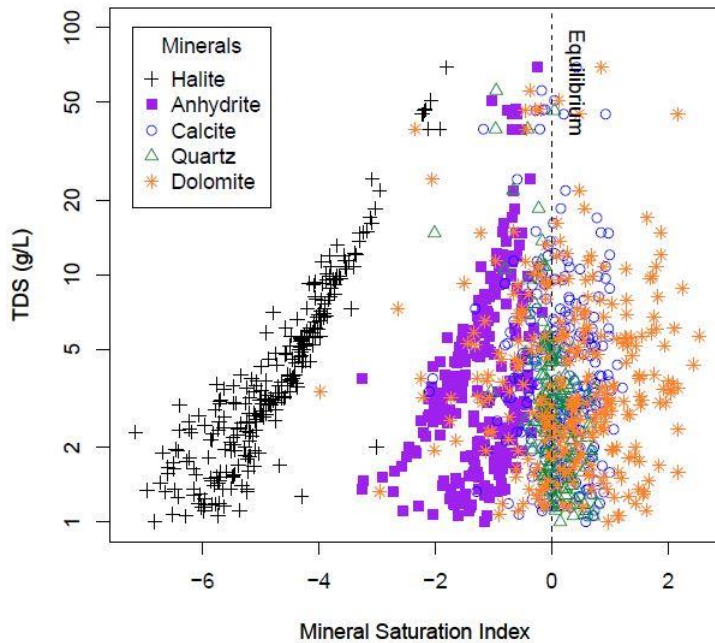
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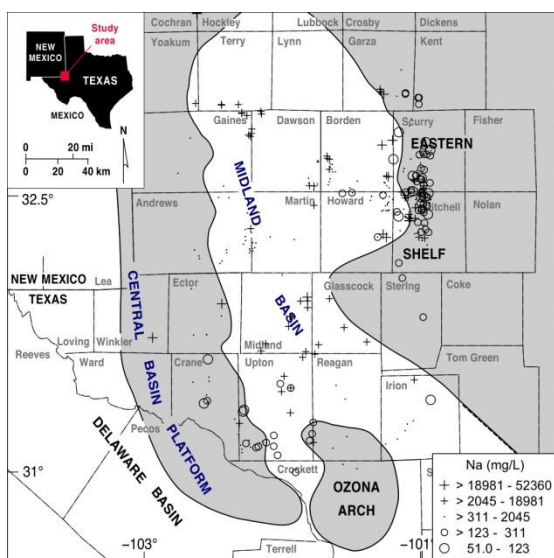
Appendix



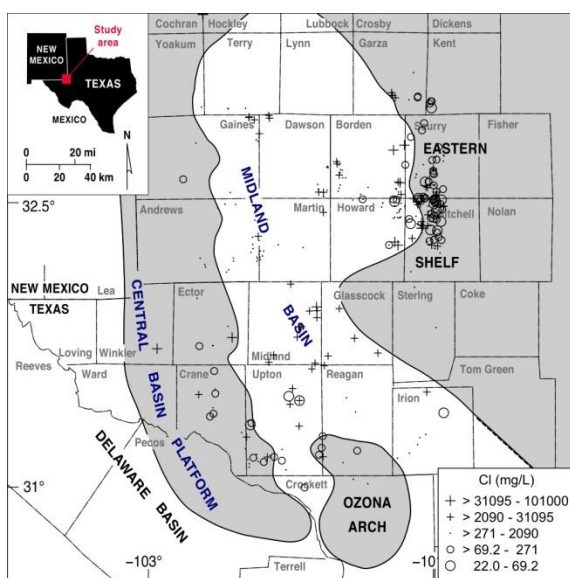
Suppl. Fig. 1: Biplot of robust principal component analysis showing constituent loadings and samples scores for the first two components (variance = 87.2%). Data plotted are for Dockum groundwater samples in the Midland Basin.



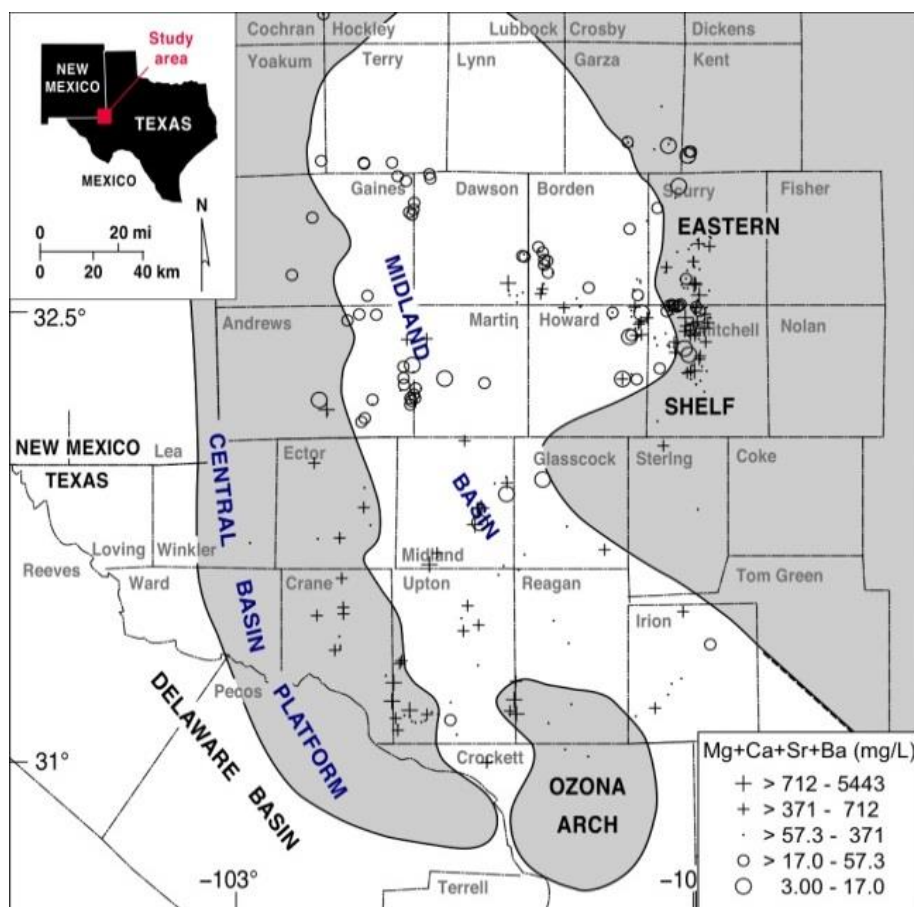
Suppl. Fig. 2: TDS concentration data versus mineral saturation indices for Dockum groundwater samples within the Midland Basin. Saturation Indices were calculated using a Pitzer activity model in PHREEQC geochemical modeling software, except for the quartz saturation indices which were calculated using a Dubye Hückle activity model.



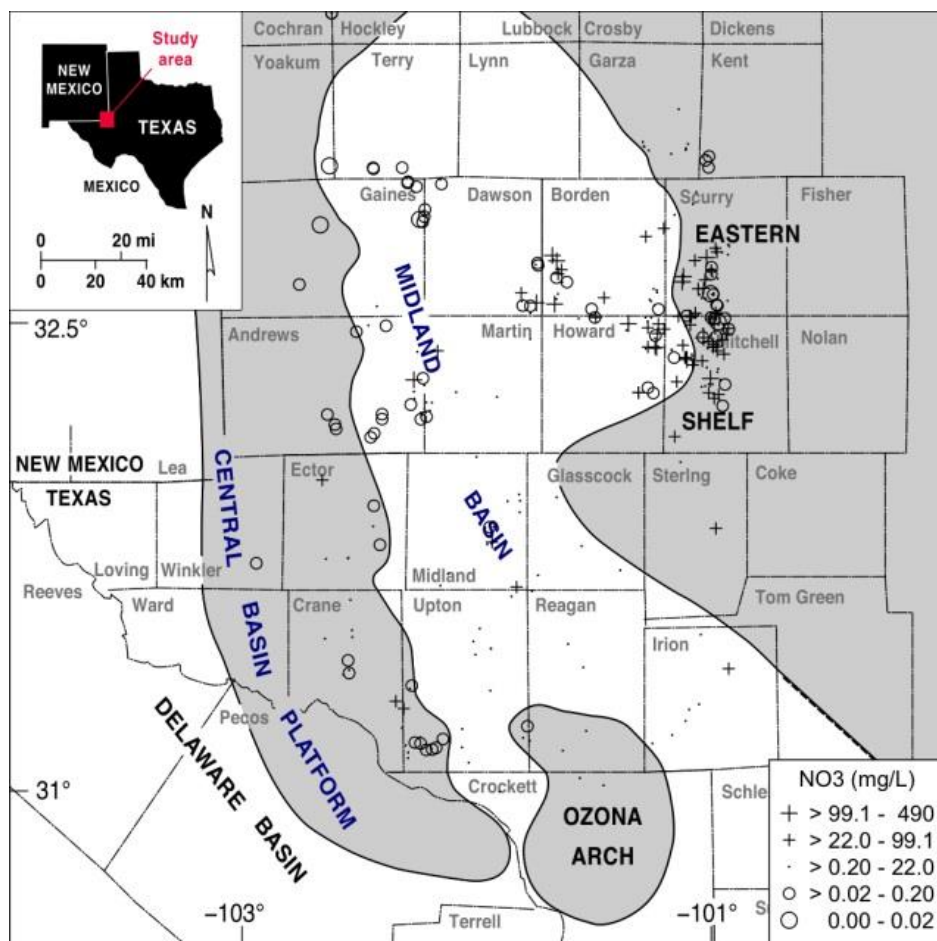
Suppl. Fig. 3: Spatial map of Na concentrations in Dockum Aquifer groundwater samples. Symbol type and size based on the lowest 5th percentile (large circles), the 5th to 25th percentile (small circles), the 25th to 75th percentile (dots), and 75th to 95th percentile (small crosses), and finally, data above the 95th percentile (large crosses).



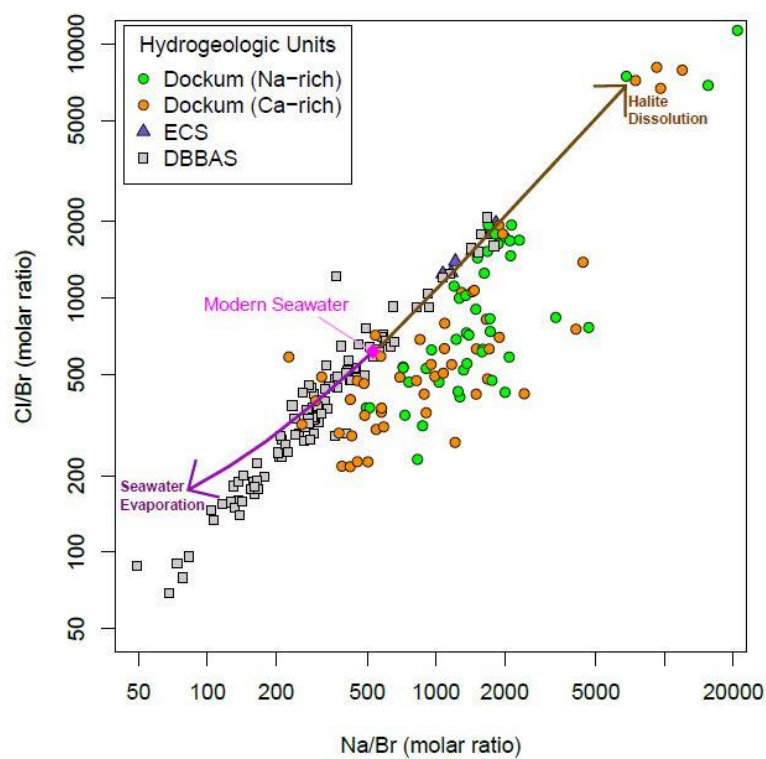
Suppl. Fig. 4: Spatial map of Cl concentrations in Dockum Aquifer groundwater samples. Symbol type and size based on the lowest 5th percentile (large circles), the 5th to 25th percentile (small circles), the 25th to 75th percentile (dots), and 75th to 95th percentile (small crosses), and finally, data above the 95th percentile (large crosses).



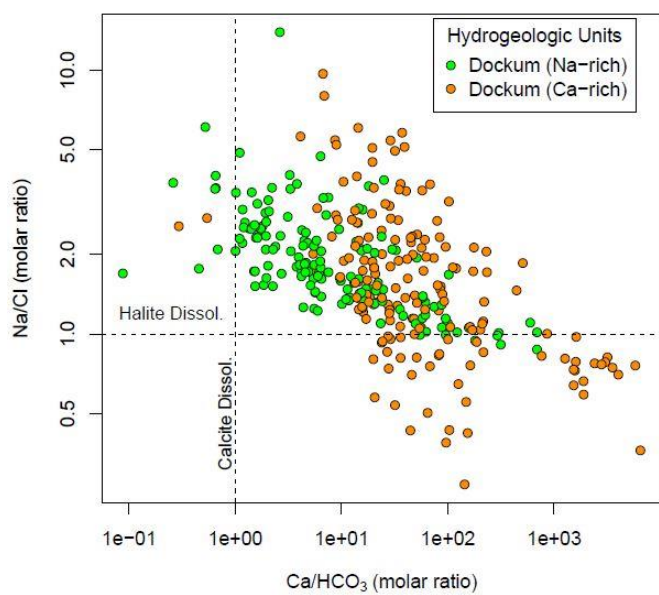
Suppl. Fig. 5: Spatial map of alkaline earth metal concentrations in Dockum Aquifer groundwater samples. Symbol type and size based on the lowest 5th percentile (large circles), the 5th to 25th percentile (small circles), the 25th to 75th percentile (dots), and 75th to 95th percentile (small crosses), and finally, data above the 95th percentile (large crosses).



Suppl. Fig. 6: Spatial map of NO₃ concentrations in Dockum Aquifer groundwater samples. Symbol type and size based on the lowest 5th percentile (large circles), the 5th to 25th percentile (small circles), the 25th to 75th percentile (dots), and 75th to 95th percentile (small crosses), and finally, data above the 95th percentile (large crosses).



Suppl. Fig. 7: Bivariate plot showing Cl/Br versus Na/Br molar ratio data for Midland Basin groundwater samples.



Suppl. Fig. 8: Bivariate plot showing Na/Cl vs Ca/HCO₃ molar ratio data for Midland Basin Dockum groundwater samples.

Table 2: Groundwater well information and parameters.

| ID | Formation | Year | Latitude | Longitude | Depth (ft) | Temp C | SEC (mS/cm ³) | Density (g/cm ³) |
|---------------|--------------------|------|----------|-----------|------------|--------|---------------------------|------------------------------|
| TEX-96-12-1 | Dockum | 2012 | 31.207 | -101.784 | 1489.0 | NA | 21.3 | 0.9999 |
| TEX-96-12-2 | Dockum | 2012 | 31.791 | -101.956 | 1281.0 | 20.56 | 2.305 | 1.0046 |
| TEX-96-12-3 | Dockum | 2012 | 31.846 | -101.946 | 1474.0 | 21 | 2.13 | 1.0059 |
| TEX-911-12-1 | Dockum | 2012 | 31.161 | -101.775 | 1579.0 | 30.45 | 8.366 | 1.0068 |
| TEX-730-13-1 | Dockum | 2013 | 32.411 | -102.168 | 1680.0 | 26.39 | 4.882 | 1.0056 |
| TEX-730-13-2 | Dockum | 2013 | 32.407 | -102.255 | 1720.0 | 22.17 | 8.28 | 1.0060 |
| TEX-730-13-3 | Dockum | 2013 | 31.930 | -101.816 | 1180.0 | 25.21 | 14.57 | 1.0123 |
| TEX-730-13-4 | Dockum | 2013 | 31.847 | -101.928 | 1100.0 | 25.17 | 17.5 | 1.0138 |
| TEX-731-13-1 | Dockum | 2013 | 31.479 | -102.016 | 1160.0 | 20.84 | 2.173 | 1.0073 |
| TEX-731-13-2 | Dockum | 2013 | 31.269 | -101.777 | NA | 20.39 | 2.651 | 1.0037 |
| TEX-731-13-3 | Dockum | 2013 | 32.071 | -102.002 | NA | 26.39 | 10.03 | 1.0089 |
| TEX-917-13-1 | Dockum | 2013 | 31.152 | -101.250 | NA | 20.92 | 2.695 | 1.0059 |
| TEX-917-13-2 | Dockum | 2013 | 31.278 | -101.051 | 640.0 | 22.1 | 2.945 | 1.0064 |
| TEX-917-13-3 | Dockum | 2013 | 31.179 | -101.166 | 730.0 | 20.77 | 3.6 | 1.0079 |
| TEX-917-13-4 | Dockum | 2013 | 31.224 | -101.109 | 780.0 | 20.91 | 3.669 | 1.0069 |
| TEX-918-13-1 | Dockum | 2013 | 31.929 | -101.869 | NA | 25.58 | 14.18 | 1.0116 |
| TEX-918-13-2 | Dockum | 2013 | 32.609 | -101.245 | NA | 21.84 | 32.86 | 1.0223 |
| TEX-918-13-3 | Dockum | 2013 | 32.580 | -101.040 | 426.0 | 21.25 | 83.4 | 1.0471 |
| TEX-918-13-4 | Dockum | 2013 | 32.590 | -101.050 | 432.0 | 21.23 | 83.52 | 1.0490 |
| TEX-918-13-5 | Dockum | 2013 | 32.803 | -101.202 | NA | 22.29 | 93.04 | 1.0524 |
| TEX-713-P1 | Dockum | 2012 | 31.170 | -101.803 | 1165.0 | 21.2 | 1.87 | 1.0003 |
| TEX-713-P2 | Dockum | 2013 | 32.263 | -101.915 | 980.0 | NA | 6.2 | 1.0077 |
| TEX-912-P1 | Dockum | 2012 | 32.278 | -102.089 | NA | 22.28 | 2.148 | 0.9998 |
| TEX-912-P2 | Dockum | 2013 | 32.449 | -101.773 | 1180.0 | NA | 8.7 | 1.0101 |
| TEX-912-P3 | Dockum | 2012 | 31.456 | -101.940 | 1600.0 | 24.95 | 21.19 | 1.0039 |
| TEX-912-P4 | Dockum | 2012 | 31.437 | -102.007 | 1375.0 | 25.44 | 15.33 | 1.0049 |
| TEX-912-P5 | Dockum | 2012 | 31.521 | -101.988 | 1546.0 | 23.07 | 2.669 | 1.0068 |
| TEX-912-P6 | Dockum | 2012 | 31.501 | -101.043 | 1396.0 | 25.82 | 15.46 | 1.0116 |
| TEX-918-13-B2 | Wolfberry | 2013 | 31.928 | -101.880 | NA | 22.1 | 123.9 | 1.0629 |
| TEX-731-13-4 | Wolfcamp | 2013 | NA | NA | NA | 28.28 | 138 | 1.0766 |
| TEX-919-13-B1 | Wolfcamp | 2013 | NA | NA | 9920.0 | 41.63 | 134.4 | 1.0724 |
| TEX-919-13-B2 | Wolfcamp | 2013 | NA | NA | 9562.1 | 23.53 | 137.8 | 1.0749 |
| TEX-919-13-B3 | Wolfcamp | 2013 | NA | NA | 9920.0 | 31.1 | 122 | 1.0671 |
| TEX-919-13-B4 | Wolfcamp | 2013 | NA | NA | 9920.0 | 23.42 | 152.5 | 1.0848 |
| TEX-918-13-B1 | Clearfork/Glorieta | 2013 | 32.590 | -101.050 | NA | 25.92 | 142.5 | 1.0807 |

Table 3: Major elemental chemistry for groundwater samples, units in mg/L.

| ID | Formation | Ca (mg/L) | Mg (mg/L) | Na (mg/L) | K (mg/L) | Sr (mg/L) | Cl (mg/L) | SO4 (mg/L) | Alk (mg/L) | TDS (mg/L) |
|---------------|--------------------|-----------|-----------|-----------|----------|-----------|-----------|------------|------------|------------|
| TEX-96-12-1 | Dockum | 326 | 164.5 | 185.2 | 11.35 | 5.45 | 146.8 | 1257 | 224.8 | 2371 |
| TEX-96-12-2 | Dockum | 277 | 136.6 | 3719 | 55.06 | 11.9 | 4355 | 2425 | 226.2 | 10770 |
| TEX-96-12-3 | Dockum | 258 | 140.5 | 3642 | 56.25 | 10.71 | 4432 | 2462 | 173.5 | 10840 |
| TEX-911-12-1 | Dockum | 573 | 0.100 | 4587 | 0.460 | 13.27 | 6704 | 2555 | 184.8 | 14750 |
| TEX-730-13-1 | Dockum | 13 | 4.146 | 992.6 | 12.46 | 0.238 | 693.4 | 918.7 | 577.8 | 3155 |
| TEX-730-13-2 | Dockum | 57 | 25.46 | 1582 | 21.63 | 2.160 | 1879 | 1234 | 288.9 | 4478 |
| TEX-730-13-3 | Dockum | 187 | 66.33 | 2951 | 46.45 | 5.246 | 3638 | 2409 | 332.3 | 9547 |
| TEX-730-13-4 | Dockum | 272 | 98.90 | 3448 | 62.20 | 7.773 | 4650 | 2558 | 294.0 | 11390 |
| TEX-731-13-1 | Dockum | 171 | 84.36 | 229 | 25.37 | 3.568 | 61.43 | 925.6 | 234.3 | 1645 |
| TEX-731-13-2 | Dockum | 247 | 120.1 | 254 | 25.26 | 5.173 | 112.5 | 1190 | 216.9 | 2310 |
| TEX-731-13-3 | Dockum | 88.0 | 28.28 | 2000 | 33.35 | 1.718 | 2252 | 1708 | 369.5 | 6468 |
| TEX-917-13-1 | Dockum | 118.8 | 111.7 | 352.4 | 15.00 | 5.168 | 305.3 | 716.8 | 298.9 | 1962 |
| TEX-917-13-2 | Dockum | 164.8 | 101.0 | 355.9 | 14.50 | 5.711 | 367.6 | 483.6 | 259.7 | 2094 |
| TEX-917-13-3 | Dockum | 175.5 | 127.1 | 459.2 | 20.30 | 6.805 | 393.1 | 628.2 | 309.6 | 2398 |
| TEX-917-13-4 | Dockum | 192.8 | 132.9 | 463.5 | 16.50 | 4.761 | 559.4 | 863.0 | 291.5 | 2543 |
| TEX-918-13-1 | Dockum | 140.3 | 62.67 | 2945 | 27.10 | 4.920 | 3389 | 2377 | 307.3 | 9609 |
| TEX-918-13-2 | Dockum | 520.5 | 167.1 | 6900 | 51.30 | 11.36 | 9903 | 3303 | 277.1 | 21940 |
| TEX-918-13-3 | Dockum | 1413 | 435.7 | 17960 | 136.0 | 41.27 | 27330 | 2199 | 105.9 | 38890 |
| TEX-918-13-4 | Dockum | 1405 | 433.4 | 18040 | 66.30 | 40.99 | 31870 | 2589 | 105.6 | 55700 |
| TEX-918-13-5 | Dockum | 1921 | 607.6 | 21680 | 187.0 | 54.35 | 34310 | 2625 | 62.90 | 38860 |
| TEX-713-P1 | Dockum | 245.9 | 163.7 | 150.4 | 8.83 | 4.86 | 103.8 | 973.1 | 280.3 | 1967 |
| TEX-713-P2 | Dockum | 83.11 | 30.37 | 1345 | 12.50 | 3.085 | 980.7 | 1192 | 286.1 | 4816 |
| TEX-912-P1 | Dockum | 50.00 | 24.7 | 1448 | 21.0 | 0.86 | 1200 | 1356 | 555.3 | 4561 |
| TEX-912-P2 | Dockum | 59.02 | 27.03 | 2208 | 8.970 | 2.264 | 2457 | 1436 | 466.5 | 6888 |
| TEX-912-P3 | Dockum | 326.8 | 163.5 | 2325 | 65.2 | 8.9 | 2923 | 1856 | 214.9 | 7640 |
| TEX-912-P4 | Dockum | 345.8 | 210.8 | 3471 | 82.1 | 7.98 | 4867 | 1784 | 175.7 | 10550 |
| TEX-912-P5 | Dockum | 421.8 | 205.7 | 4666 | 112 | 15.88 | 6286 | 2275 | 221.3 | 13700 |
| TEX-912-P6 | Dockum | 615.8 | 333.2 | 6445 | 146 | 17.04 | 9010 | 2609 | 52.1 | 18570 |
| TEX-918-13-B2 | Wolfberry | 3429 | 469.7 | 26080 | 450.1 | 612.7 | 40170 | 125 | 315.2 | 87810 |
| TEX-731-13-4 | Wolfcamp | 4431 | 522.6 | 30860 | 1113 | 755.7 | 62580 | 274.4 | 169.3 | 102200 |
| TEX-919-13-B1 | Wolfcamp | 1447 | 175.6 | 31100 | 982.2 | 402.2 | 34710 | 318.7 | 677.5 | 96600 |
| TEX-919-13-B2 | Wolfcamp | 1510 | 178.1 | 32380 | 863.5 | 485.8 | 39740 | 116.5 | 759.0 | 99050 |
| TEX-919-13-B3 | Wolfcamp | 2842 | 334.9 | 27610 | 729.4 | 896.3 | 49590 | 293.2 | 358.8 | 87520 |
| TEX-919-13-B4 | Wolfcamp | 2520 | 305.8 | 36010 | 1096 | 421.7 | 63920 | 497.3 | 444.5 | 113000 |
| TEX-918-13-B1 | Clearfork/Glorieta | 3982 | 1471 | 32080 | 66.30 | 77.349 | 50400 | 2384 | 694.5 | 110400 |

Table 4: Minor elemental chemistry for groundwater samples, units in mg/L.

| ID | Formation | B (mg/L) | Ba (mg/L) | Li (mg/L) | Fe (mg/L) | Si (mg/L) | Br (mg/L) | NO3 (mg/L) | DOC (mg/L) |
|---------------|--------------------|----------|-----------|-----------|-----------|-----------|-----------|------------|------------|
| TEX-96-12-1 | Dockum | 1.11 | 0.007 | 0.217 | NA | 4.8 | 1.527 | 1.82 | 0.693 |
| TEX-96-12-2 | Dockum | 0.712 | 0.047 | 1.671 | NA | 3.64 | 9.586 | 3.23 | 0.169 |
| TEX-96-12-3 | Dockum | 0.608 | 0.04 | 1.512 | NA | 4.00 | 10.00 | 3.53 | 0.231 |
| TEX-911-12-1 | Dockum | 0.523 | 0.035 | 1.903 | NA | 0.07 | 10.49 | 2.55 | 0.214 |
| TEX-730-13-1 | Dockum | NA | 0.078 | 1.325 | 0.180 | 4.464 | 3.347 | 0.51 | 0.819 |
| TEX-730-13-2 | Dockum | NA | 0.104 | 2.165 | 1.878 | 2.734 | 3.378 | 0.875 | 0.819 |
| TEX-730-13-3 | Dockum | NA | 0.224 | 3.667 | 0.099 | 3.890 | 4.870 | 1.62 | 0.819 |
| TEX-730-13-4 | Dockum | NA | 0.253 | 4.434 | 4.140 | 3.941 | 6.007 | 1.98 | 0.819 |
| TEX-731-13-1 | Dockum | NA | 0.039 | 0.708 | 0.100 | 3.584 | 0.327 | 7.905 | 0.819 |
| TEX-731-13-2 | Dockum | NA | 0.041 | 0.724 | 0.015 | 4.260 | 0.525 | 15.891 | 0.819 |
| TEX-731-13-3 | Dockum | NA | 0.099 | 2.802 | 0.689 | 4.372 | 3.000 | 1.12 | 0.819 |
| TEX-917-13-1 | Dockum | 0.989 | 0.011 | 0.936 | 2.056 | 3.754 | 3.155 | 1.57 | 0.305 |
| TEX-917-13-2 | Dockum | 0.416 | 0.013 | 1.024 | 2.923 | 3.738 | 2.890 | 4.23 | 0.305 |
| TEX-917-13-3 | Dockum | 0.634 | 0.012 | 1.166 | 6.278 | 3.758 | 2.913 | 22.1 | 0.305 |
| TEX-917-13-4 | Dockum | 0.552 | 0.010 | 1.290 | 1.598 | 4.122 | 4.284 | 1.96 | 0.305 |
| TEX-918-13-1 | Dockum | 0.260 | 0.005 | 5.479 | 0.440 | 3.660 | 20.65 | 7.85 | 0.305 |
| TEX-918-13-2 | Dockum | 0.600 | 0.012 | 14.19 | 2.137 | 1.623 | 20.00 | 19.6 | 0.305 |
| TEX-918-13-3 | Dockum | 1.500 | 0.031 | 39.93 | 3.297 | 0.645 | 34.42 | 43.05 | 0.305 |
| TEX-918-13-4 | Dockum | 1.518 | 0.031 | 32.99 | 2.989 | 0.652 | 37.05 | 46.3 | 0.305 |
| TEX-918-13-5 | Dockum | 1.600 | 0.032 | 50.41 | 29.13 | 2.226 | 40.00 | 44.9 | 1.42 |
| TEX-713-P1 | Dockum | 0.654 | 0.007 | 0.168 | NA | 5.94 | 1.034 | 1.13 | 0.603 |
| TEX-713-P2 | Dockum | 0.210 | 0.009 | 3.797 | 0.061 | 3.258 | 6.390 | 2.3 | NA |
| TEX-912-P1 | Dockum | 0.685 | 0.018 | 0.408 | NA | 5.78 | 3.707 | 1.51 | 0.149 |
| TEX-912-P2 | Dockum | 0.450 | 0.011 | 4.492 | 0.036 | 3.521 | 14.96 | 6.31 | NA |
| TEX-912-P3 | Dockum | 0.362 | 0.024 | 1.309 | NA | 3.08 | 6.252 | 2.81 | 0.048 |
| TEX-912-P4 | Dockum | 0.651 | 0.044 | 1.712 | NA | 0.96 | 7.178 | 3.37 | 0.655 |
| TEX-912-P5 | Dockum | 0.673 | 0.045 | 2.181 | NA | 3.78 | 8.654 | 8.58 | 0.143 |
| TEX-912-P6 | Dockum | 0.707 | 0.047 | 2.8 | NA | 3.52 | 10.47 | 9.7 | 0.325 |
| TEX-918-13-B2 | Wolfberry | 40.69 | 2.587 | 92.79 | 26.93 | 4.443 | 309.2 | 68.45 | 98.41 |
| TEX-731-13-4 | Wolfcamp | NA | 1.531 | 76.95 | 7.605 | 9.110 | 509.2 | 18.8 | 82.21 |
| TEX-919-13-B1 | Wolfcamp | 33.45 | 1.965 | 108.7 | 12.02 | 7.166 | 266.5 | 65.4 | 252.0 |
| TEX-919-13-B2 | Wolfcamp | 33.66 | 2.546 | 119.6 | 72.68 | 3.999 | 310.8 | 63.6 | 198.8 |
| TEX-919-13-B3 | Wolfcamp | 48.23 | 3.715 | 110.8 | 30.85 | 11.846 | 379.8 | 62.2 | 285.9 |
| TEX-919-13-B4 | Wolfcamp | 27.25 | 1.528 | 131.4 | 57.22 | 4.281 | 610.1 | 73.6 | 155.0 |
| TEX-918-13-B1 | Clearfork/Glorieta | 8.66 | 0.049 | 73.96 | 0.71 | 10.5 | 229.8 | 66.7 | 14.36 |

Table 5: Isotope chemistry for groundwater samples.

| ID | Formation | Sr ratio | Sr ratio error | $\delta^{18}\text{O}$ (permil) | $\delta^2\text{H}$ (permil) |
|---------------|--------------------|----------|----------------|--------------------------------|-----------------------------|
| TEX-96-12-1 | Dockum | 0.70855 | 1.00E-05 | -7.74 | -54.7 |
| TEX-96-12-2 | Dockum | 0.70990 | 8.00E-06 | -5.25 | -37.4 |
| TEX-96-12-3 | Dockum | 0.70977 | 8.00E-06 | -5.31 | -38.2 |
| TEX-911-12-1 | Dockum | 0.70920 | 8.00E-06 | -4.86 | -34.7 |
| TEX-730-13-1 | Dockum | 0.70873 | 8.30E-06 | -6.31 | -43.5 |
| TEX-730-13-2 | Dockum | 0.70859 | 6.30E-06 | -5.70 | -40.8 |
| TEX-730-13-3 | Dockum | 0.70943 | 7.40E-06 | -5.58 | -40.1 |
| TEX-730-13-4 | Dockum | 0.70961 | 1.00E-05 | -5.37 | -39.9 |
| TEX-731-13-1 | Dockum | 0.70880 | 8.20E-06 | -8.69 | -61.2 |
| TEX-731-13-2 | Dockum | 0.70863 | 8.80E-06 | -8.70 | -60.6 |
| TEX-731-13-3 | Dockum | 0.70904 | 9.00E-06 | -5.93 | -42.9 |
| TEX-917-13-1 | Dockum | 0.70824 | 6.34E-06 | -6.48 | -46.0 |
| TEX-917-13-2 | Dockum | 0.70807 | 7.70E-05 | -6.20 | -43.4 |
| TEX-917-13-3 | Dockum | 0.70809 | 5.88E-06 | -6.53 | -46.5 |
| TEX-917-13-4 | Dockum | 0.70838 | 8.22E-06 | -6.55 | -44.9 |
| TEX-918-13-1 | Dockum | 0.70940 | 7.04E-06 | -5.07 | -38.4 |
| TEX-918-13-2 | Dockum | 0.70891 | 8.42E-06 | -5.54 | -39.3 |
| TEX-918-13-3 | Dockum | 0.70946 | 7.46E-06 | -7.15 | -50.1 |
| TEX-918-13-4 | Dockum | 0.70944 | 7.44E-06 | -7.14 | -50.8 |
| TEX-918-13-5 | Dockum | 0.70951 | 5.70E-06 | -7.04 | -50.8 |
| TEX-713-P1 | Dockum | 0.70846 | 1.80E-05 | -7.44 | -51.4 |
| TEX-713-P2 | Dockum | 0.70888 | 7.20E-06 | -5.66 | -40.6 |
| TEX-912-P1 | Dockum | 0.70872 | 1.00E-05 | -6.27 | -45.7 |
| TEX-912-P2 | Dockum | 0.70854 | 8.16E-06 | -5.58 | -41.0 |
| TEX-912-P3 | Dockum | 0.70934 | 1.00E-05 | -5.43 | -39.3 |
| TEX-912-P4 | Dockum | 0.70944 | 6.00E-06 | -5.29 | -38.6 |
| TEX-912-P5 | Dockum | 0.70968 | 1.00E-05 | -4.85 | -34.7 |
| TEX-912-P6 | Dockum | 0.70964 | 6.00E-06 | -4.68 | -34.6 |
| TEX-918-13-B2 | Wolfberry | 0.70909 | 7.28E-06 | 4.31 | -15.2 |
| TEX-731-13-4 | Wolfcamp | 0.70907 | 1.00E-05 | 5.08 | -15.4 |
| TEX-919-13-B1 | Wolfcamp | 0.70899 | 9.12E-06 | 6.27 | -16.4 |
| TEX-919-13-B2 | Wolfcamp | 0.70893 | 9.48E-06 | 6.80 | -15.7 |
| TEX-919-13-B3 | Wolfcamp | 0.70947 | 7.48E-06 | 5.62 | -15.2 |
| TEX-919-13-B4 | Wolfcamp | 0.70893 | 4.66E-06 | 5.54 | -16.8 |
| TEX-918-13-B1 | Clearfork/Glorieta | 0.70802 | 6.46E-06 | -1.31 | -23.8 |

Vita

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