

Geochemical Assessment of the Hueco Bolson, New Mexico and Texas, 2016–17



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Front cover.

Background. Franklin Mountains near the Hueco Bolson study area near El Paso, Texas, September 2016. Photograph by Monica Langhorst, U.S. Geological Survey.

Lower left. U.S. Geological Survey scientist collecting water-quality samples in the Hueco Bolson study area near El Paso, Texas, September 2016. Photograph by Chris Braun, U.S. Geological Survey.

Lower middle. U.S. Geological Survey scientist assessing the physical properties of water before sample collection from a groundwater well in the Hueco Bolson study area near El Paso, Texas, September 2016. Photograph by Monica Langhorst, U.S. Geological Survey.

Lower right. Groundwater well sampled in the Hueco Bolson study area near El Paso, Texas, September 2016. Photograph by Chris Braun, U.S. Geological Survey.

Back cover. U.S. Geological Survey field sampling crew arriving at a groundwater well that was sampled in the Hueco Bolson study area near El Paso, Texas, September 2016. Photograph by Chris Braun, U.S. Geological Survey.

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By Patricia B. Ging, Delbert G. Humberson, and Scott J. Ikard

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Conversion Factors

U.S. customary units to International System of Units

Multiply	By	To obtain
Length		
foot (ft)	0.3048	meter (m)
mile (mi)	1.609	kilometer (km)
Radioactivity		
picocurie per liter (pCi/L)	0.037	becquerel per liter (Bq/L)

International System of Units to U.S. customary units

Multiply	By	To obtain
Length		
meter (m)	3.281	foot (ft)
kilometer (km)	0.6214	mile (mi)
kilometer (km)	0.5400	mile, nautical (nmi)
meter (m)	1.094	yard (yd)
Area		
square meter (m ²)	0.0002471	acre
square kilometer (km ²)	247.1	acre
square meter (m ²)	10.76	square foot (ft ²)
square kilometer (km ²)	0.3861	square mile (mi ²)

Temperature in degrees Celsius (°C) may be converted to degrees Fahrenheit (°F) as $^{\circ}\text{F} = (1.8 \times ^{\circ}\text{C}) + 32$.

Temperature in degrees Fahrenheit (°F) may be converted to degrees Celsius (°C) as $^{\circ}\text{C} = (^{\circ}\text{F} - 32) / 1.8$.

Datum

Vertical coordinate information is referenced to the North American Vertical Datum of 1988 (NAVD 88).

Horizontal coordinate information is referenced to the North American Datum of 1983 (NAD 83).

Altitude, as used in this report, refers to distance above the vertical datum.

Supplemental Information

Concentrations of chemical constituents in water are given in either milligrams per liter (mg/L) or micrograms per liter (µg/L).

Activities for radioactive constituents in water are given in picocuries per liter (pCi/L).

Abbreviations

^{12}C	nonradioactive carbon-12
^{14}C	carbon-14
CO_2	carbon dioxide
δD	hydrogen-2/hydrogen-1 (delta deuterium)
$\delta^{18}\text{O}$	oxygen-18/oxygen-16 (delta oxygen-18)
EPA	U.S. Environmental Protection Agency
GMWL	Global Meteoric Water Line
^3H	tritium
LRL	laboratory reporting level
^{14}N	nitrogen-14
NWIS	National Water Information System (U.S. Geological Survey database)
pmc	percent modern carbon
RPD	relative percent difference
R^2	coefficient of determination
$^{87}\text{Sr}/^{86}\text{Sr}$	strontium-87/strontium-86
TAAP	Transboundary Aquifer Assessment Project
TU	tritium unit
USGS	U.S. Geological Survey
WRRI	Water Resources Research Institute

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Abstract

Understanding groundwater quality in transboundary aquifers like the Hueco Bolson is important for the 2.7 million people along the United States and Mexico border living in and near the combined metropolitan areas of Ciudad Juárez, Mexico, and El Paso, Texas, who rely on groundwater for water supply. To better understand water-quality conditions in the Mexico–New Mexico–Texas transboundary area, 23 water-supply wells were sampled in the Hueco Bolson within the United States near El Paso, Tex., during August–September 2016 and May–June 2017. Groundwater samples were analyzed for physical properties, major ions, dissolved solids, nutrients, trace elements, organic compounds, and selected isotopes such as strontium, hydrogen, oxygen, tritium, and carbon-14.

Most of the water samples from the Hueco Bolson water-supply wells were classified as a sodium-chloride type water. Only four wells sampled in the study area had dissolved-solids concentrations greater than 1,000 milligrams per liter (mg/L), with three of those wells closest to the Rio Grande/Río Bravo del Norte (hereinafter referred to as the Rio Grande).

Nitrate concentrations in the groundwater samples collected in the study area ranged from below the long-term method detection level of 0.04 to 6.2 mg/L. Arsenic was the only trace element detected in the wells sampled that had concentrations exceeding the designated drinking-water standard of 10 micrograms per liter ($\mu\text{g/L}$). Four of the 23 wells had arsenic concentrations greater than 10 $\mu\text{g/L}$, and these wells were all located near the Rio Grande. Three of the wells with the highest uranium concentrations (greater than 10 $\mu\text{g/L}$) were also located near the Rio Grande, and two of those wells were the same wells that had arsenic concentrations greater than 10 $\mu\text{g/L}$. Groundwater samples were analyzed for 83 organic compounds, but only 6 were detected—simazine, prometryn, prometon, atrazine, deethylatrazine, and dichloroaniline. All concentrations for the organic compounds detected were less than 0.03 $\mu\text{g/L}$, and the detections were only in five groundwater wells, three of which were located near the Rio Grande.

Strontium, hydrogen, and oxygen isotopic values indicate that recharge water to the central and northern sections of the study area originates from near the Franklin Mountains,

whereas groundwater in the southern section of the study area is likely from the Rio Grande valley. Tritium and carbon-14 values indicate that most of the wells that were sampled contained water that is considered premodern, which means that it is more than several hundred years old. Three wells with modern groundwater (approximately less than 70 years old) are located near the Rio Grande and are the same wells that had elevated arsenic or uranium concentrations and organic compound detections. Most of the results of the geochemical analyses indicate that groundwater near the Rio Grande has higher dissolved-solids concentrations, higher concentrations of several trace elements, and slightly more organic compound detections than the groundwater farther away from the Rio Grande; therefore, the groundwater may be affected by the Rio Grande and surrounding land-use activities.

Introduction

Many communities along the United States and Mexico border rely partially or completely on transboundary aquifers underlying parts of each country for drinking-water, agricultural, and industrial-water supply needs. Little geochemical information is available to help characterize this vital resource (Alley, 2013). Because surface water is scarce along the United States and Mexico border and typically fully appropriated, groundwater from transboundary aquifers is crucial for public supply (Alley, 2013). Among the unique challenges in assessing transboundary aquifers is the ability to provide useful information on the quality of usable water available to meet the diverse needs of residents along the border. Addressing this challenge is critical to provide a foundation for resource management. Some common physical and socioeconomic characteristics shared across the border region between Mexico and the United States near Ciudad Juárez, Mexico, and El Paso, Texas, include a semi-arid climate with little precipitation and large population centers. The combined 2014 population of about 2.7 million in Ciudad Juárez, Mexico, and El Paso, Tex., form the second largest metropolitan area on the Mexico–United States border (National Aeronautics and Space Administration, 2014).

The U.S.-Mexico Transboundary Aquifer Assessment Act (hereinafter referred to as “the act”) was signed into law by the President of the United States in 2006 (Public Law 109-448). The U.S.-Mexico Transboundary Aquifer Assessment Program (TAAP) was established as part of the act to develop and implement an integrated scientific approach to identify and assess priority transboundary aquifers. The area designated by the act includes transboundary aquifers shared between the States of Sonora and Chihuahua in Mexico and the States of Arizona, New Mexico, and Texas in the United States. TAAP collaborators include the U.S. Geological Survey (USGS) Water Science Centers and the Water Resources Research Institutes (WRRIs) of Arizona, New Mexico, and Texas. One of the goals of this act is to complete regional hydrogeologic studies of priority transboundary aquifers in groundwater-dependent border communities subject to stress from development and drought. The regional studies developed under this act were aimed at providing information on groundwater resources in the priority areas. One of the priority aquifer regions stipulated in the act was the Hueco Bolson in New Mexico and Texas. A bolson is an alluvium-floored basin found in arid terrain in northern Mexico and the southwestern United States into which water drains from surrounding mountains (Neuendorf and others, 2005). Understanding the geochemical characteristics of the Hueco Bolson is necessary in developing a plan for long-term management of this groundwater resource.

Purpose and Scope

The purpose of this report is to present the results of analyses of water-quality samples collected in 2016 and 2017 from 23 water-supply wells in a part of the Hueco Bolson; the wells that were sampled were geospatially distributed in New Mexico and Texas near Ciudad Juárez, Mexico, and El Paso, Tex. Water-quality samples from these wells, which belong to Fort Bliss and El Paso Water, were analyzed for major ions, trace elements, nutrients, organic compounds, and selected isotopes (strontium, deuterium, oxygen, tritium, and carbon). Geochemical interpretations of these data were made to provide insights into groundwater quality, sources, and age. Groundwater samples could be not collected in Mexico because of lack of access to that part of the Hueco Bolson; therefore, all water-quality samples were collected in the U.S. part of the Hueco Bolson.

Hydrogeologic Setting

The Hueco Bolson is part of the Hueco-Mesilla Bolsons aquifer and spans a total area of approximately 6,500 square kilometers that includes parts of New Mexico and Texas in the United States and Chihuahua in Mexico (Heywood and Yager, 2003; Hutchison and Hibbs, 2008; George and others, 2011). The Hueco Bolson is bounded by several mountain ranges including the Franklin and Sierra Juárez Mountains to the

west and the Hueco, Sierra Blanca, and Quitman Mountains to the east (White, 1983; Hibbs, 1999; Sheng, 2005; Hutchison and Hibbs, 2008). To the north, the Hueco Bolson is bounded by the Tularosa Basin in New Mexico; the Tularosa Basin is hydraulically connected to the Hueco Bolson (Wilkins, 1986; Heywood and Yager, 2003; Hutchison and Hibbs, 2008; [fig. 1](#)). The Hueco Bolson is considered an intermontane aquifer that is associated with the Rio Grande Rift, which was formed as a result of Cenozoic extensional tectonism that created a horst and graben geological structure (Hutchison, 2006). Over time, the down-dropped graben filled with unconsolidated Tertiary and Quaternary deposits of gravel, sand, silt, and clay that were eroded from the surrounding highlands which may include volcanic rock (White and others, 1997; Heywood and Yager, 2003). These deposits resulted in the alluvial-aquifer region currently known as the Hueco Bolson, which has a maximum thickness of 2,743 meters (White, 1983; Heywood and Yager, 2003; Sheng, 2005). The Rio Grande/Río Bravo or Río Bravo del Norte (hereinafter referred to as the Rio Grande) is the major surface-water feature in the study area and has eroded a valley through the basin-fill deposits of the Hueco Bolson (White and others, 1997).

The Hueco Bolson has been known as a good source of freshwater since the late 1800s and has become the primary source of fresh groundwater for drinking water and for agricultural and industrial use in the rapidly growing transboundary region near Ciudad Juárez, Mexico, and El Paso, Tex. (White, 1983; White and others, 1997; Hibbs, 1999). By the end of the 20th century, the total binational population in the El Paso metropolitan area (including Ciudad Juárez) had grown to approximately 2 million (Heywood and Yager, 2003); as the population grew, groundwater pumping increased over time (White, 1983). Total groundwater drawdown was observed to exceed 60 meters in some areas (Heywood and Yager, 2003), and the increased pumping has led to concerns with brackish water intrusion—in some cases water-supply wells have even been abandoned because of deteriorating water quality (Heywood and Yager, 2003; Hutchison, 2006). In this report, dissolved-solids concentrations less than or equal to 1,000 milligrams per liter (mg/L) are considered indicative of freshwater, whereas dissolved-solids concentrations greater than 1,000 mg/L and less than 10,000 mg/L are considered indicative of brackish water. Groundwater management in the area is centered on the interrelated issues of declining groundwater levels and brackish groundwater intrusion (Hutchison, 2006).

Previous Studies

Most of the previous studies done in the Hueco Bolson near the Ciudad Juárez, Mexico, and El Paso, Tex., area focused on hydrogeology and groundwater flow, especially near Fort Bliss (Abeyta, 1996; Abeyta and Thomas, 1996; Frenzel and Abeyta, 1999). Orr and Risser (1992) summarize previous studies regarding hydrologic data in the Ciudad Juárez/El Paso region of the Hueco Bolson. Few reports

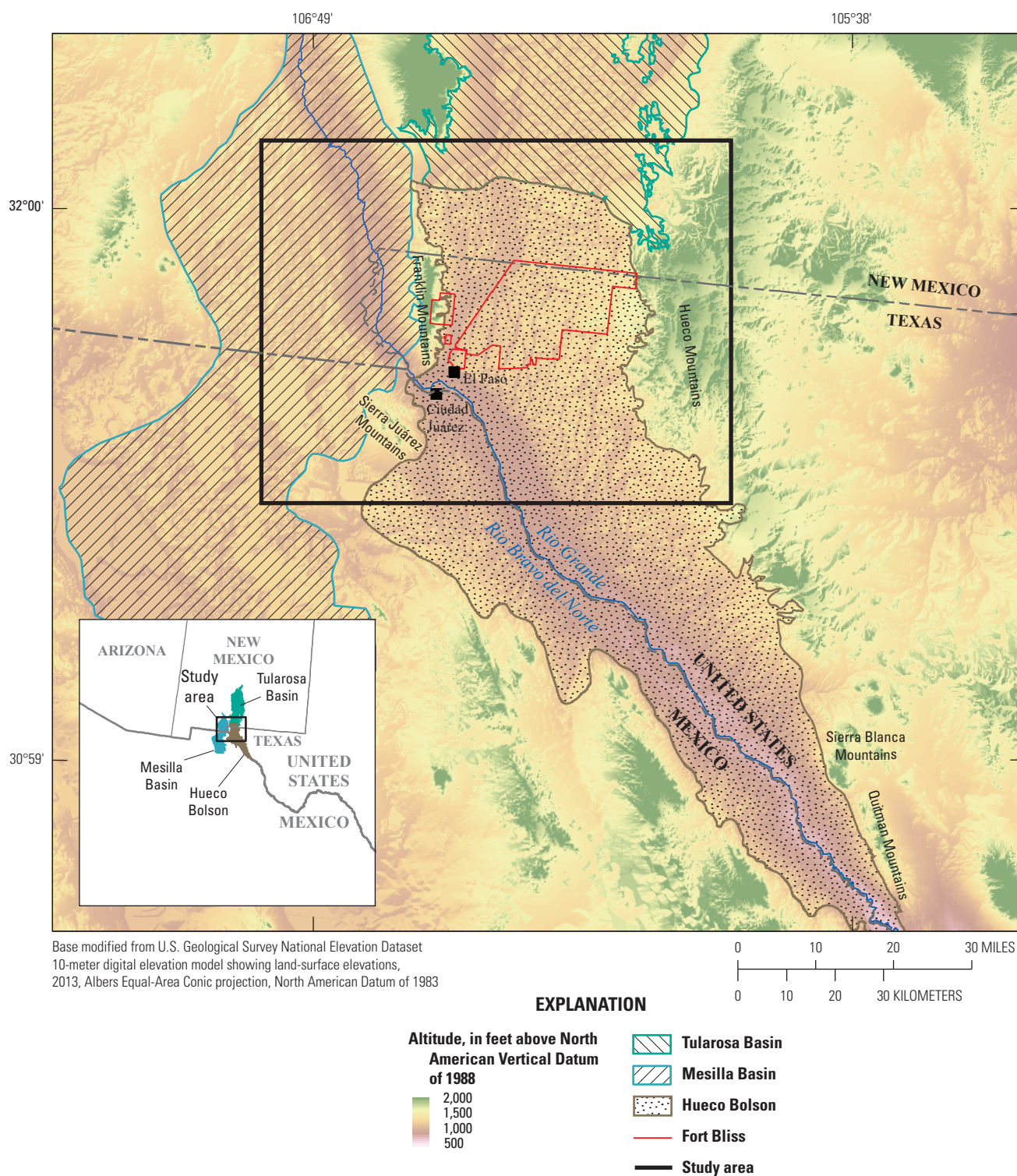


Figure 1. The Hueco Bolson study area, New Mexico and Texas, United States, and Mexico, 2016–17.

discuss geochemistry or water quality in the Ciudad Juárez/El Paso region of the Hueco Bolson. Buszka and others (1994) discuss selected water-quality aspects of the Hueco Bolson near the Hueco Bolson Recharge Project Area near Ciudad Juárez, Mexico, and El Paso, Tex., where groundwater

samples were collected near the recharge project site in 1990 and analyzed for major ions, trace elements, nutrients, dissolved organic carbon, volatile organic compounds, semi-volatile organic compounds, bacteria, and stable-isotopic ratios of oxygen, hydrogen, and carbon. Results indicated that

the principal source of recharge to the aquifer by humans is reclaimed water injection. Anderholm and Heywood (2003) discuss groundwater chemistry in the southwestern part of the Hueco Bolson in a study area similar to the one described in this report. Groundwater samples in the Anderholm and Heywood study were analyzed for major ions, nutrients, total organic carbon, trace elements, and stable and radioactive isotopes. Results indicated that infiltration of precipitation and runoff from the Franklin Mountains and leakage from the Rio Grande Valley are important sources of recharge to the Hueco Bolson. In addition, isotopic and environmental tracer analysis results along the Rio Grande and in the Hueco Bolson were reported by Phillips and others (2003) and Eastoe and others (2008) who distinguished different recharge areas based on the results of deuterium and oxygen isotopes in water-quality samples.

Sample Collection and Analysis

During August and September 2016, 20 water-supply wells were sampled in the western part of Texas just east of the Franklin Mountains as part of the geochemical assessment of the Hueco Bolson (fig. 2). In May and June 2017, three additional water-supply wells were sampled—one well in the northern section of the Hueco Bolson and two wells north of the Hueco Bolson in the southern part of New Mexico. Physical properties (dissolved oxygen, pH, specific conductance, water temperature, turbidity, and alkalinity) along with barometric pressure, groundwater pumping rates, and depth to water were measured in the field at the time of sample collection. Water samples were collected and shipped for laboratory analysis of major ions, nutrients, trace elements, organic compounds, and stable isotope ratios of strontium (strontium-87/strontium-86, $^{87}\text{Sr}/^{86}\text{Sr}$), hydrogen (hydrogen-2/hydrogen-1, δD), oxygen (oxygen-18/oxygen-16, $\delta^{18}\text{O}$), tritium (^3H), and carbon-14 (^{14}C). All water-quality results were reviewed for completeness and accuracy and are stored in the National Water Information System (NWIS) (USGS, 2019) and are also published in a companion data release (Ging and others, 2019).

Field Procedures

The field procedures used to collect groundwater samples are described in the USGS “National Field Manual for the Collection of Water-Quality Data” (USGS, variously dated). All wells sampled were water-supply wells with pumps already installed that were used to purge the water and to collect the water-quality samples. Prior to sample collection, each well was pumped until one to three casing volumes were purged to remove any stagnant water. The number of casing volumes that were purged depended on depth of the well, well casing diameter, and the frequency of pumping performed at the well. After the required one to three casing volumes were

purged, the wells were pumped continually until steady-state measurements for all physical properties were obtained to ensure representative samples of the water in aquifer were collected (USGS, variously dated). When steady-state measurements indicating the system had reached equilibrium were obtained, the water samples were collected from the well through fluoropolymer tubing and stored in new, precleaned bottles. Samples were collected prior to well water entering any pressure tanks or being filtered or undergoing other forms of treatment. Samples were processed onsite according to each laboratory’s protocols to minimize chemical changes or contamination. In addition, samples were preserved by adding the appropriate acid (when necessary), chilled to 4 degrees Celsius ($^{\circ}\text{C}$), or both before being shipped to the laboratory for analysis. Time-sensitive samples were shipped overnight to the analyzing laboratories, and the remaining samples were shipped to the analyzing laboratories upon return from the field. After sample collection and processing, the sampling equipment was cleaned according to the established protocols prior to use at the next well (Wilde, 2004).

Analytical Methods

Major ions, nutrients, trace elements, and organic compounds were analyzed by the USGS National Water Quality Laboratory in Denver, Colorado, by using published methods. Methods for major ions are published in Fishman and Friedman (1989) and Fishman (1993). Nutrients methods are published in Patton and Truitt (2000) and Patton and Kryskalla (2003). Trace-element methods are published in Fishman and Friedman (1989), Struzeski and others (1996), Garbarino (1999), and Garbarino and others (2006). Pesticide analysis was done by solid-phase extraction and gas chromatography/mass spectrometry following the methods published in Zaugg and others (1995), Lindley and others (1996), Sandstrom and others (2001), and Madsen and others (2003). The $^{87}\text{Sr}/^{86}\text{Sr}$ isotopic ratios were analyzed at the USGS Isotope Laboratory in Menlo Park, California, in accordance with methods described by Kendall and McDonnell (1998). Analyses for δD and $\delta^{18}\text{O}$ were done at the USGS Stable Isotope Laboratory in Reston, Virginia. Analytical methods for δD are described in Révész and Coplen (2008a), and analytical methods for $\delta^{18}\text{O}$ are described in Révész and Coplen (2008b). ^3H was analyzed by internal gas proportional counting at the University of Miami Tritium Laboratory in Miami, Florida. Analytical methods for ^3H are documented in Östlund and Werner (1962) and Thatcher and others (1977). ^{14}C was analyzed at the National Ocean Sciences Accelerator Mass Spectrometry Facility at the Woods Hole Oceanographic Institution in Woods Hole, Massachusetts, by accelerator mass spectrometry. Methods for analyzing accelerator mass spectrometry results are described in Roberts and others (2010), and methods for determining and reporting ^{14}C ages are described in Karlen and others (1964), Olsson and Klasson (1970), Stuiver and Polach (1977), and Stuiver (1980).

Environmental Tracers

Environmental tracers, such as $^{87}\text{Sr}/^{86}\text{Sr}$, δD , $\delta^{18}\text{O}$, ^3H , and ^{14}C concentrations in groundwater, are useful for understanding where and when groundwater recharge occurred in an aquifer system. $^{87}\text{Sr}/^{86}\text{Sr}$ can be a useful tool for helping determine the source of dissolved constituents in groundwater, and δD and $\delta^{18}\text{O}$ are useful indicators of conditions at the time and place of groundwater recharge. Lastly, ^3H and ^{14}C can provide information on the apparent age of the groundwater.

Strontium Isotopic Ratios

Strontium isotopic ratios, specifically the ratio of $^{87}\text{Sr}/^{86}\text{Sr}$, are useful in describing the source of groundwater and possible mixing of source waters (Kendall and McDonnell, 1998). When $^{87}\text{Sr}/^{86}\text{Sr}$ values increase or decrease from one location to the next along a flow path, mixing of geochemically different sources of water or mixing of water from different aquifer units could be occurring. Strontium can substitute for calcium, especially in carbonate rocks that are commonly found in subsurface geologic units in the Hueco Bolson (Hem, 1985; Banner, 2004; Musgrove and others, 2010; Bumgarner and others, 2012). As a result of this rock-water interaction, $^{87}\text{Sr}/^{86}\text{Sr}$ values can be used to evaluate sources of dissolved constituents in groundwater and to determine possible groundwater mixing (McNutt and others, 1990; Musgrove and Banner, 1993; Banner and others, 1994; Uliana and others, 2007; Musgrove and others, 2010). Water in specific geologic units is expected to have $^{87}\text{Sr}/^{86}\text{Sr}$ values that reflect the isotopic ratio of minerals in that specific aquifer unit; therefore, $^{87}\text{Sr}/^{86}\text{Sr}$ values can be used as a geochemical tracer of source waters originating from different geologic units (Kendall and McDonnell, 1998). By using $^{87}\text{Sr}/^{86}\text{Sr}$ values obtained from previous studies such as Teeple (2017), $^{87}\text{Sr}/^{86}\text{Sr}$ values measured in samples from Hueco Bolson wells can be compared to $^{87}\text{Sr}/^{86}\text{Sr}$ values in water collected from various areas within the Hueco Bolson region such as near the Franklin Mountains and the Rio Grande.

Hydrogen and Oxygen Isotopic Ratios

Ratios of the stable isotopes of the water molecule (hydrogen and oxygen) can yield isotopic signatures that are useful indicators of the regional recharge regimes of a hydrogeologic system (Faure, 1986). Plotting the ratio of hydrogen-2/hydrogen-1 (referred to as delta deuterium, or δD , in per mil) to the ratio of oxygen-18/oxygen-16 isotopes (referred to as delta oxygen-18 or $\delta^{18}\text{O}$, in per mil) can aid in analyzing when and from where the groundwater was initially recharged into the system (Faure, 1986; Uliana and others, 2007; Bumgarner and others, 2012). Craig (1961) used δD and $\delta^{18}\text{O}$ isotopic analyses from multiple precipitation samples collected around the world to create a Global Meteoric Water Line (GMWL), a linear regression line calculated as $\delta\text{D} =$

$8 \times \delta^{18}\text{O} + 10$. Changes along this line can be attributed to multiple factors including altitude, storm intensity, latitude, seasons, and continental climate (Fontes, 1980). Precipitation with larger amounts of the elevated δD and $\delta^{18}\text{O}$ values (isotopically heavier) generally occurs in lower altitudes, lower latitudes, warmer weather, and closer to the coasts (Witcher and others, 2004). Values that deviate from the GMWL can be a result of two processes: (1) evaporation prior to recharge, and (2) oxygen isotope exchange with rocks (Witcher and others, 2004). Evaporation can cause preferential loss of water molecules containing the lighter stable isotopes of hydrogen and oxygen which can be seen with elevated δD and $\delta^{18}\text{O}$ values. Water samples that indicate gains or losses of oxygen atoms from rock-water interaction tend to deviate from the GMWL in the lateral position because there is the gain or loss of only the oxygen element (Teeple, 2017).

Tritium

^3H is a radioactive isotope of hydrogen with a half-life of 12.32 years and usually has two sources: natural cosmogenic ^3H and ^3H produced by the atmospheric testing of nuclear weapons (Clark and Fritz, 1997; Lucas and Unterweger, 2000). The release of excess ^3H into the atmosphere occurred during widespread nuclear weapons testing from about 1950 to about 1970 (Motzer, 2008). Before nuclear weapons testing, the naturally occurring concentration of ^3H in the atmosphere ranged from about 2 to 8 tritium units (TU) (Motzer, 2008). From about 1950 to about 1970, widespread atomic bomb testing resulted in a substantial increase (more than 1.1×10^9 TU) of ^3H in the atmosphere of the Northern Hemisphere (Motzer, 2008). Concentrations of ^3H in precipitation since 2006 have globally decreased to approximately pre-bomb background levels of 2 to 10 TU (Clark and Fritz, 1997; Phillips and Castro, 2003). The elevated ^3H concentrations in the atmosphere beginning in about 1950 resulted in groundwater recharge containing appreciably higher ^3H concentrations compared to groundwater recharged before 1950. Consequently, ^3H is a good tracer for groundwater that was recharged after about 1950. The use of ^3H to analyze groundwater results in an apparent age in that definitive ages of groundwater cannot be determined, but rather, differences in ^3H concentrations can potentially distinguish if the groundwater was recharged before, during, or after widespread atomic bomb testing began in the 1950s. As noted by Hinkle (1996, p. 5), “the definition of modern water is a function of the dating tool used. Although different dating tools rely on different dates in defining the boundary between modern and old water, the range of these dates is small.” The determination of groundwater age by using ^3H is relative to ^3H concentrations when samples were collected. ^3H is commonly measured in picocuries per liter (pCi/L) or in tritium units, where 3.22 pCi/L is equivalent to 1 TU or 1 part ^3H in 10^{18} parts hydrogen (Lucas and Unterweger, 2000).

Carbon-14

^{14}C is the radioactive isotope of carbon and is naturally produced in the upper atmosphere (Plummer and Busenberg, 2000). Kalin (2000) notes that the half-life used for calculating the radiocarbon age of most geologic and some hydrogeologic samples is the Libby half-life (Libby, 1955), which is 5,568 years. Because ^{14}C has a long radioactive half-life, it is useful for dating groundwater that is thousands to tens of thousands of years old (Kalin, 2000; Banner, 2004; Oden and Truini, 2013). Citing the work of Kalin (2000), Nishikawa and others (2004, p. 39) explained “carbon-14 data are expressed as percent modern carbon (pmc) by comparing ^{14}C activities to the specific activity of National Bureau of Standards [now the National Institute of Standards and Technology] oxalic acid: 13.56 disintegrations per minute per gram of carbon in the year 1950 equals 100 pmc (Kalin, 2000).”

Groundwater recharged after 1950 likely results in a ^{14}C activity value of 100 pmc or greater because atmospheric ^{14}C concentrations increased by as much as 20 percent from widespread atomic bomb testing in the 1950s and 1960s (Plummer and Busenberg, 2000). ^{14}C typically moves into groundwater through dissolved carbon dioxide (CO_2) in precipitation or in organic carbon dissolved in surface water and soil-pore water (Ingebritsen and Sanford, 1999; Raymond and Bauer, 2001). ^{14}C can enter surface water directly as water flows over the land towards stream channels (overland flow) or indirectly as the result of soil-pore water moving through the soil zone and discharging to a surface-water body (Linsley and others, 1982). Surface water in turn can provide a source of groundwater recharge through surface water-groundwater interactions. Along the groundwater’s flow path, ^{14}C concentrations slowly begin to decrease as ^{14}C decays to nitrogen-14 (^{14}N). Dilution of ^{14}C through geochemical processes, such as the dissolution of carbonates or CO_2 from rocks and soil, can substantially alter the original ^{14}C concentration (Lemay, 2002). ^{14}C concentrations in groundwater may be altered, therefore, by the introduction of nonradioactive carbon-12 (^{12}C) from exchange with carbon in rocks and soils that are millions of years old, resulting in apparent ^{14}C groundwater ages that are falsely old. Various types of geochemical modeling are used to correct for these effects to obtain better estimates of groundwater age (Plummer and others, 1994).

Quality-Assurance and Quality-Control Procedures

Quality-control data were collected during sampling to assess the variability and bias that may exist within the sample-collection procedures and laboratory analyses (USGS, variously dated). To test for this variability and bias, three field-blank samples, three sequential-replicate samples, and one matrix-spiked sample for organic compounds were

collected in conjunction with environmental samples. All three field-blank samples were analyzed for inorganic constituents, and two of the field-blank samples were analyzed for organic compounds. In addition, two source-blank samples were collected in conjunction with two field-blank samples for inorganic constituent analysis.

Field-Blank Analyses

Field-blank samples were collected and processed at three well locations prior to the collection of environmental samples at those locations to ensure that equipment cleaning conducted in the field between the collection of samples from different wells was adequate and that the collection, processing, or transporting procedures in the field did not contaminate the environmental samples. In one field-blank sample, low concentrations of barium (0.15 microgram per liter [$\mu\text{g/L}$]), cobalt (0.040 $\mu\text{g/L}$), copper (0.55 $\mu\text{g/L}$), and thallium (0.02 $\mu\text{g/L}$) were detected. Aluminum (3 $\mu\text{g/L}$), cobalt (0.104 $\mu\text{g/L}$), copper (0.51 $\mu\text{g/L}$), manganese (0.44 $\mu\text{g/L}$), and nickel (0.24 $\mu\text{g/L}$) were detected in another field-blank sample. Concentrations of barium in the field-blank samples were small (approximately 0.2 percent of the barium concentrations measured in the environmental samples), but most of the other inorganic constituents detected in the field-blank samples were measured at similar concentrations in the environmental samples. The cause for low-level concentrations of some inorganic constituents in the field-blank samples is unknown. To avoid possible bias, values for constituents measured in environmental samples at concentrations that were less than or equal to those measured in field-blank samples were not included for interpretive purposes.

Calcium was also detected in all three field-blank samples, but concentrations in field-blank samples were considered negligible (less than 0.06 mg/L) compared to concentrations in all the environmental samples (greater than 5 mg/L). An aluminum concentration of 3 $\mu\text{g/L}$ was detected in one source-blank sample, which would account for the aluminum concentration of 3 $\mu\text{g/L}$ detected in the one field-blank sample. No organic compounds were detected in either of the field-blank samples for organic analyses.

Sequential-Replicate Analyses

Three sequential-replicate samples were collected to measure the variability in results originating from sampling procedures and analytical methods. Inorganic constituents were measured in replicate samples that were collected by using a new, preconditioned 0.45-micron capsule filter. Capsule filters were replaced prior to collecting the sequential-replicate samples to prevent the possibility of filter loading, which might reduce the effective pore size of the filter (Horowitz and others, 1996).

To evaluate the potential variability introduced during sample collection, processing, or laboratory analysis, the analytical results measured in an environmental sample were compared with those measured in the associated replicate sample by computing the relative percent difference (RPD) for each constituent. The RPD was computed by using the following equation:

$$RPD = \frac{|C_1 - C_2|}{(C_1 + C_2)/2} \times 100 \quad (1)$$

where

C_1 is the concentration from the environmental sample, and

C_2 is the concentration from the replicate sample.

RPDs of 10 percent or less indicate good agreement between the paired results if the concentrations were sufficiently large compared to their associated laboratory reporting levels (LRLs) (Childress and others, 1999; Oden and others, 2011). An RPD was not computed if either of the paired results was reported as an estimated concentration or below the detection level. Most RPDs did not exceed 10 percent for constituents analyzed in the three sequential-replicate sample pairs collected during this study, indicating generally good agreement between the environmental and replicate sample concentrations. RPDs exceeded 10 percent (but were less than 20 percent) for seven trace elements (aluminum, antimony, cobalt, copper, iron, lithium, and uranium). Differences between the concentrations in paired samples where each sample concentration is low can result in large RPD values. RPDs for nutrients in one environmental-replicate pair were greater than 100 percent because nutrient concentrations in sample pairs were both very low (less than 0.4 mg/L). In addition, RPDs were between 10 and 20 percent for two organic constituents (3,4-dichloroaniline and prometon) because concentrations were low (less than 0.02 µg/L).

Matrix-Spike Analysis

A spiked environmental sample is an environmental-replicate sample to which a known volume containing known concentrations of target constituents is added in the field (Wilde and others, 2004; Martin and others, 2009). Water was collected from the well and processed following standard procedures to produce two samples (USGS, variously dated; Shelton, 1994; Koterba and others, 1995). Spike solution is added to only one of the two water samples, resulting in spiked and unspiked samples (the matrix spike and the “background” sample, respectively). Matrix spikes are usually collected to help determine any matrix interference and the analyzing laboratory’s ability to recover constituent concentrations (Zaugg and others, 1995; Menheer and Brigham, 1997; Mueller and others, 1997).

Unspiked and spiked environmental samples were used to assess bias and variability from possible degradation of pesticide constituents resulting in lower concentrations during

sample processing, storage, and analysis (Mueller and others, 2015). Analytical recoveries of the spiked target constituents are expressed as percentages of expected (theoretical) concentrations. The percent recoveries of constituents in the spiked environmental sample was compared to laboratory recovery spiked samples to evaluate matrix interferences or degradation of organic compounds. Percent recovery is computed as follows:

$$\text{Percent recovery} = [(C_{\text{spiked}} - C_{\text{unspiked}}) \times 100] / C_{\text{expected}} \quad (2)$$

where

C_{spiked} is the measured concentration in the spiked environmental sample, in micrograms per liter;

C_{unspiked} is the measured concentration in the unspiked environmental sample, in micrograms per liter; and

C_{expected} is the theoretical concentration in the spiked environmental sample, in micrograms per liter, and is computed as follows:

$$C_{\text{expected}} = (C_{\text{solution}} \times V_{\text{spike}}) / V_{\text{sample}} \quad (3)$$

where

C_{solution} is the concentration of constituent in the spike solution, in micrograms per liter;

V_{spike} is the volume of spike added to the environmental sample, in milliliters; and

V_{sample} is the volume of the environmental sample, in liters.

Constituent concentrations less than the LRL were set to zero for the purpose of calculating percent recovery.

A mixture of target constituents was added to one of the environmental-replicate samples for spike analysis. Percent recoveries were computed for each of the constituents, with the optimum value being 100 percent (Mueller and others, 2015; Shoda and others, 2017). Depending on the constituent, overall percent recoveries for this study ranged from approximately 54 to 96 percent, with each organic constituent detected in this study having a different range in percent recovery. For example, simazine, atrazine, prometon, and prometryn had percent recoveries in the range of 73 to 96 percent for spiked environmental samples, but deethylatrazine had a percent recovery from 60 to 70 percent, and 3,4-dichloroaniline had a percent recovery from 54 to 60 percent. If a selected constituent has a substantially high or low recovery, the environmental sample results of the pesticide constituents could be affected. Because recoveries for deethylatrazine and 3,4-dichloroaniline were consistently low in laboratory recovery spiked samples (less than 75 percent), all concentration results for those constituent detections are reported as estimated. Concentrations of selected organic compounds measured in the unspiked environmental samples that were less than their respective LRLs were considered irrelevant, and their recoveries were not evaluated in the matrix spike results.

Geochemical Assessment

To better understand general water quality and possible sources and recharge areas for groundwater in the Hueco Bolson, water-quality samples were collected in 2016 and 2017 from 23 water-supply wells near El Paso, Tex. (fig. 2). Water-quality samples from 20 wells were analyzed for physical properties, major ions, nutrients, trace elements,

and organic compounds in 2016. Additional analyses also included selected isotopes such as $^{87}\text{Sr}/^{86}\text{Sr}$, δD , ^{18}O , ^3H , and ^{14}C . Three additional groundwater wells were sampled in 2017 for the same constituent groups minus nutrients and organic compounds.

Physical properties and other constituents were used to evaluate general water quality and potential sources of groundwater in the Hueco Bolson system by examining and

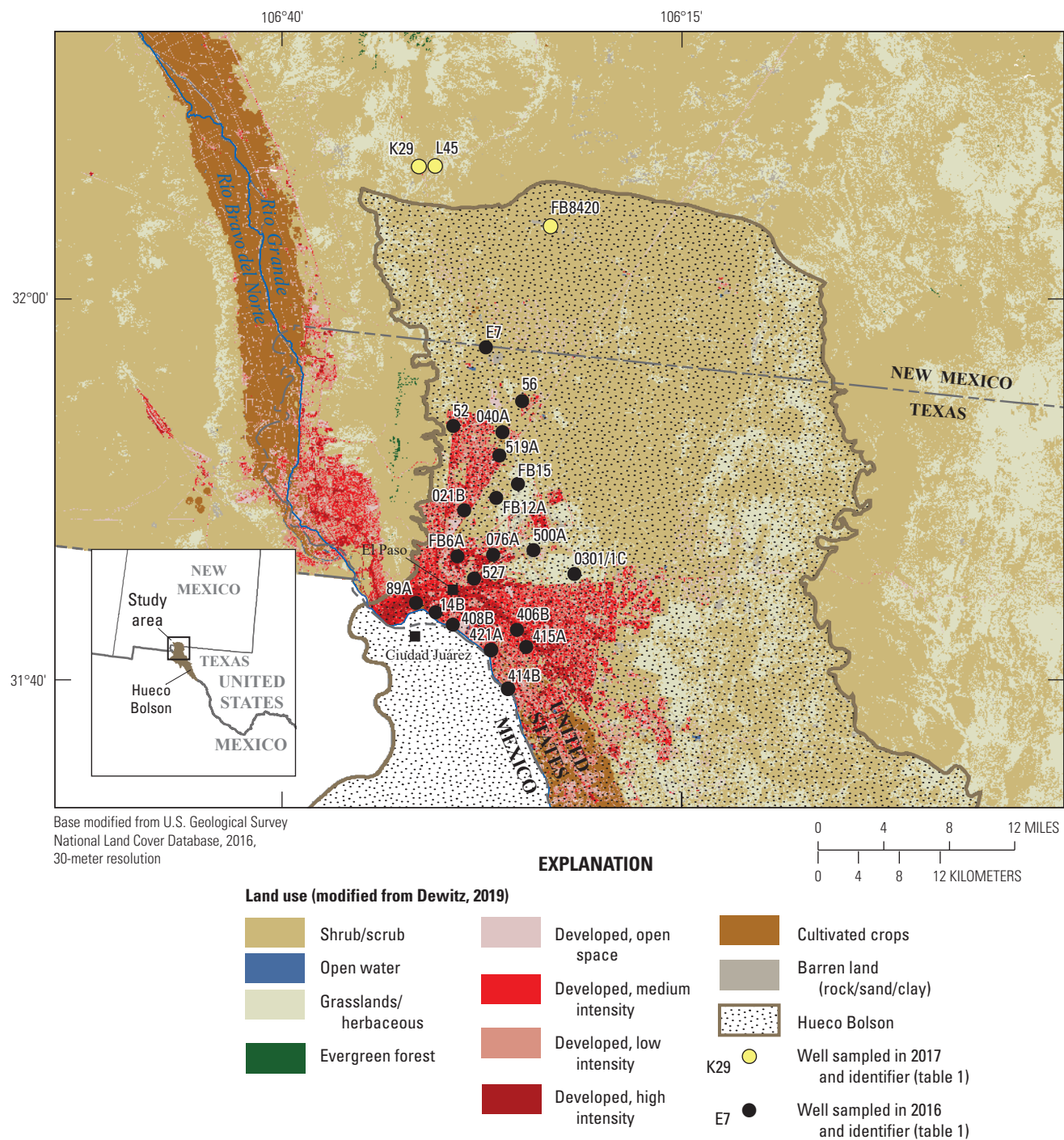


Figure 2. Land use in the Hueco Bolson study area in New Mexico and Texas, with locations of wells sampled in 2016 or 2017.

comparing hydrochemical facies, dissolved solids, nutrients, trace elements, organic compounds, and environmental tracers such as $^{87}\text{Sr}/^{86}\text{Sr}$, δD , ^{18}O , ^3H , and ^{14}C concentrations. These results were used in combination to identify the chemical characteristics of water in the Hueco Bolson and possible insights into potential recharge and sources areas for groundwater in the study area (Plummer and others, 2004). The qualitative geochemical analysis does not include a quantitative evaluation of residence times in the aquifer nor does it include geochemical flow-path modeling of the groundwater system.

Hydrochemical Facies

The composition of groundwater principally is controlled by the composition of recharge water, rock-water interaction, and the mixing of water from different sources. The term “hydrochemical facies” refers to a classification scheme used to describe water in terms of the major cation and anion milliequivalents composition. A trilinear diagram (Piper, 1944) is a useful tool for evaluating the relative abundance of major cations and anions and classifying hydrochemical facies or water types (fig. 3). Most of the water sampled from the Hueco Bolson wells were classified as sodium-chloride type water (within the yellow diamond in fig. 3). Higher magnesium and bicarbonate concentrations were measured in the water samples collected from four of the wells (K29, FB8420, 52, and FB6A) than other wells in the study area, resulting in water types different from those of typical sodium-chloride type waters. The sodium-chloride type water may be more a function of the region rather than land-use activities because the sodium-chloride type water is associated with wells representing different land-use types (Musgrove and Bexfield, 2017). The land use within the study area is predominantly urban near Ciudad Juárez, Mexico, and El Paso, Tex., with land-use types of shrub/scrub and cultivated crops mostly in areas along the Rio Grande (Dewitz, 2019; fig. 2).

Dissolved Solids

Dissolved-solids concentrations are a measure of how much dissolved constituents are in a sample. Sodium and chloride are often the primary constituents that contribute to elevated dissolved-solids concentrations (Hem, 1985). In this report, dissolved-solids concentrations of less than or equal to 1,000 mg/L were considered indicative of fresh-water, whereas dissolved-solids concentrations greater than 1,000 mg/L and less than 10,000 mg/L were considered indicative of brackish water. Dissolved-solids concentrations greater than 1,000 mg/L were measured in samples collected only from four wells in the study area (Ging and others, 2019). Three of the four wells from which samples with the highest dissolved-solids concentrations were measured (wells 414B, 415A, and 421A; fig. 4B) were near the Rio Grande (figs. 2

and 5). In a similar study where water-quality samples were collected in 1997, the highest dissolved-solids concentrations were also measured in the samples collected from wells near the Rio Grande (Anderholm and Heywood, 2003). In the current study, dissolved-solids concentrations ranging from 501 to 1,000 mg/L were measured in samples collected from most of the wells in the study area (fig. 4A and 5). The U.S. Environmental Protection Agency (EPA) secondary drinking-water standard for dissolved solids is 500 mg/L for color, taste, and odor issues (EPA, 2009); dissolved-solids concentrations of 500 mg/L or less were measured in the samples collected from nine wells (Ging and others, 2019). Dissolved-solids concentrations in groundwater can increase with increasing well depth because more minerals dissolve into the water as it progresses farther below land surface (Hem, 1985), but the opposite pattern was observed in the water-quality samples collected during this study. This unusual pattern of decreasing dissolved-solids concentrations with increasing well depth is probably a function of the spatial distribution of the wells, where the shallower wells with the higher dissolved-solids concentrations are the wells closest to the Rio Grande (fig. 4B and 5; table 1).

Relatively high sodium concentrations have been documented in surface-water samples collected from the Rio Grande near El Paso, Tex. (Lurry and others, 1998) and may be contributing to the relatively high sodium concentrations measured in groundwater samples collected from wells near the river. A large coefficient of determination (R^2) value (Helsel and Hirsch, 2002) of 0.7742 for a regression line fitted to the sodium and dissolved-solids concentrations indicates that sodium concentrations increase with increasing dissolved-solids concentrations (fig. 6A); this relation is consistent with sodium being a large component of the dissolved-solids concentration. The hydrochemical facies diagram also indicates that samples from most of the wells contain sodium-chloride type water (fig. 3). Samples from two wells (wells FB6A and FB8420) were outliers on the sodium and dissolved-solids graph, and those two wells were outside the sodium-chloride type water on the trilinear diagram (figs. 3 and 6A). The molar ratio of sodium and chloride in groundwater from wells in this study is variable compared to the one-to-one ratio line, which is indicative of a natural salt source such as halite. Higher sodium than chloride molar concentrations were measured in the samples collected from about 70 percent of the wells, consistent with sodium being the major component of the dissolved-solids concentration in most of the wells that were sampled (fig. 6B). Anderholm and Heywood (2003) reported similar results from analyses of samples from wells in an area similar to the Hueco Bolson in 2017; sodium concentrations generally increased linearly with increasing chloride concentrations, thus indicating that dilute recharge water is likely mixing with sodium-chloride brine water as the groundwater migrates away from the recharge area.

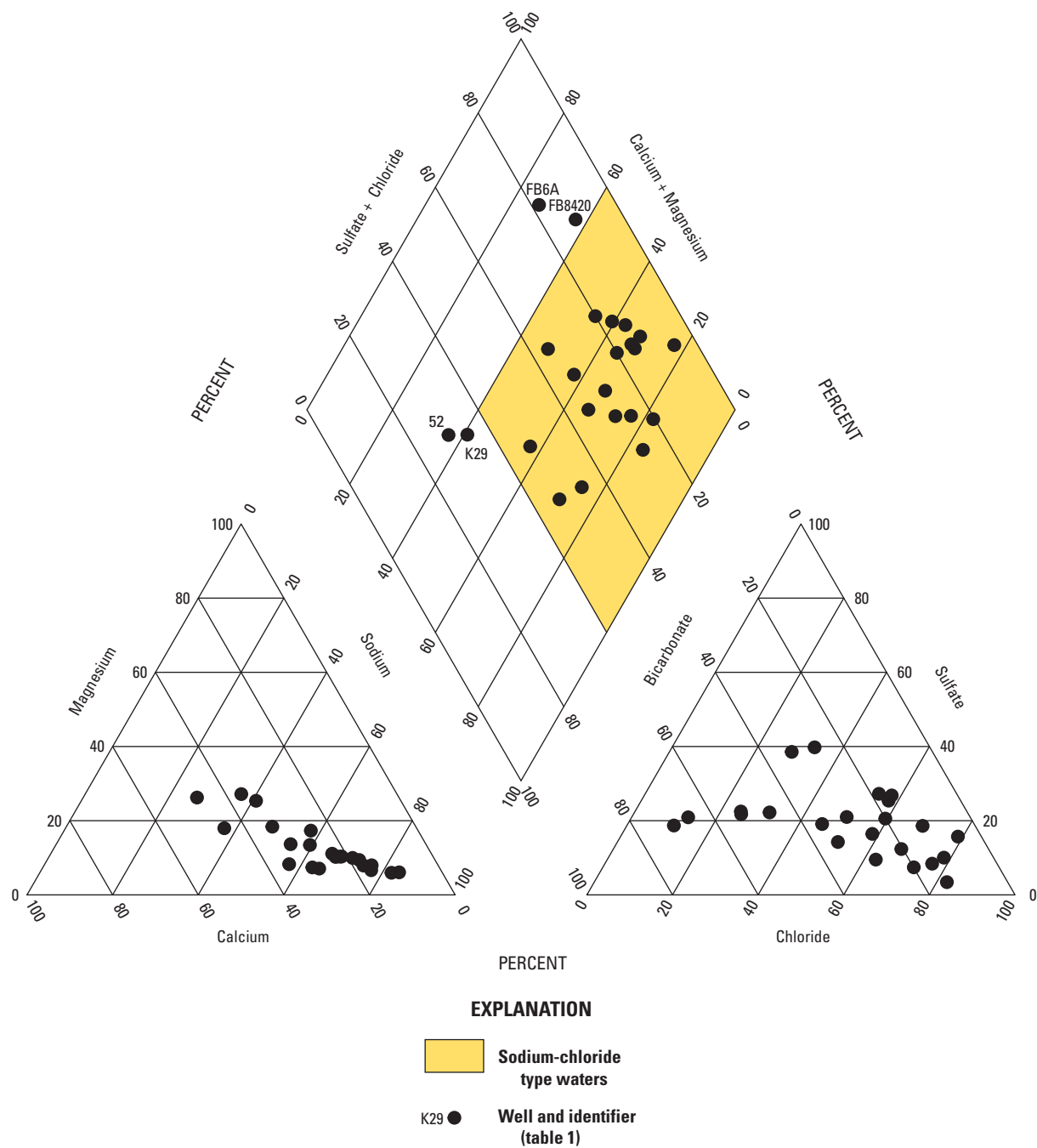


Figure 3. The relative abundance of major cations and anions in groundwater samples collected in New Mexico and Texas in the Hueco Bolson study area and identification of sodium-chloride type waters, 2016–17.

Nutrients

Nitrogen and phosphorus are the most common nutrients in groundwater. Elevated nitrogen and phosphorus concentrations in groundwater frequently result from surface-water infiltration in agricultural or municipal areas where nutrient sources typically include livestock manure, septic systems, wastewater treatment systems, and fertilizers (Dubrovsky and others, 2010). National background concentrations of

nitrate, the most common form of nitrogen in groundwater, are estimated to be 1 mg/L (Dubrovsky and others, 2010). Samples collected for this study were analyzed for nitrogen as nitrate plus nitrite and nitrite. Nitrite concentrations in the study area were low, with detectable concentrations less than 0.1 mg/L (Ging and others, 2019). Because nitrite concentrations were low, concentrations for nitrate plus nitrite analyses were considered equivalent to nitrate concentrations and are referred to in this report simply as nitrate concentrations.

Table 1. Wells sampled in New Mexico and Texas in the Hueco Bolson study area, 2016–17.

[USGS, U.S. Geological Survey; n/a, not available]

Well identifier	USGS station number (USGS, 2019)	State	Date sampled	Well depth, in feet below land surface
E7	320003106250401	Texas	08-29-2016	875
56	315724106222501	Texas	08-29-2016	670
52	315543106263501	Texas	08-30-2016	1,152
040A	315541106232901	Texas	08-30-2016	870
519A	315425106233101	Texas	08-31-2016	1,140
500A	314939106204401	Texas	08-31-2016	720
021B	315120106252001	Texas	09-01-2016	1,155
406B	314522106211301	Texas	09-01-2016	620
076A	314910106231101	Texas	09-02-2016	940
527	314749106241401	Texas	09-02-2016	n/a
414B	314214106212101	Texas	09-19-2016	425
421A	314409106224001	Texas	09-19-2016	564
0301/1C	314836106180301	Texas	09-20-2016	480
FB6A	314853106252301	Texas	09-20-2016	806
FB12A	315211106232202	Texas	09-21-2016	1,140
FB15	315305106222001	Texas	09-21-2016	819
408B	314516106251601	Texas	09-22-2016	n/a
415A	314432106203101	Texas	09-22-2016	465
14B	314612106273901	Texas	09-23-2016	950
89A	314548106262401	Texas	09-23-2016	866
K29	320906106302901	New Mexico	05-31-2017	800
L45	320914106292701	New Mexico	05-31-2017	1,100
FB8420	320645106215101	New Mexico	06-01-2017	n/a

Nitrate concentrations in the groundwater samples collected in the study area ranged from less than the long-term method detection level of 0.04 mg/L to 6.2 mg/L (Ging and others, 2019). No samples collected from the Hueco Bolson wells had nitrate concentrations greater than 10 mg/L, which is the national drinking-water standard for nitrate (fig. 7A; EPA, 2009). Three samples from three wells (wells 52, 040A, and FB6A) were the only samples that had nitrate concentrations greater than 2 mg/L (figs. 2 and 7B). In about 50 percent of the samples collected, nitrate concentrations were between 1 and 2 mg/L, and the highest nitrate concentration (6.2 mg/L) was measured in the sample collected from well FB6A (fig. 7B). Nitrate concentrations tend to increase with increasing dissolved-oxygen concentrations indicating that most of the elevated nitrate concentrations (greater than 1 mg/L) are associated with dissolved-oxygen concentrations greater than 1 mg/L (fig. 7B). Potential sources of nitrate could be related to urban development in Ciudad Juárez, Mexico, and El Paso, Tex., or cultivated-crop land along the Rio Grande (fig. 2). Orthophosphate was the only phosphorus constituent analyzed in samples collected for this study. All orthophosphate

concentrations were less than 0.1 mg/L in the groundwater samples; therefore, most of the nutrients detected in the study were primarily composed of nitrogen, particularly nitrate (Ging and others, 2019).

Trace Elements

Trace elements are present in small amounts in the environment and can be from natural and manmade sources (Ayotte and others, 2011). Concentrations of trace elements are more likely to be higher in groundwater than in surface water because of the movement of water through the rocks underground that make up the aquifers. Groundwater that has been in an aquifer for a long time has had more time to interact with the rocks and aquifer materials, thereby causing potential increases in trace element concentrations. Human activities also can affect concentrations of trace elements in groundwater (Ayotte and others, 2011).

The most commonly detected trace elements in samples from the Hueco Bolson wells with concentrations greater than 1 µg/L were arsenic, barium, boron, chromium, copper,

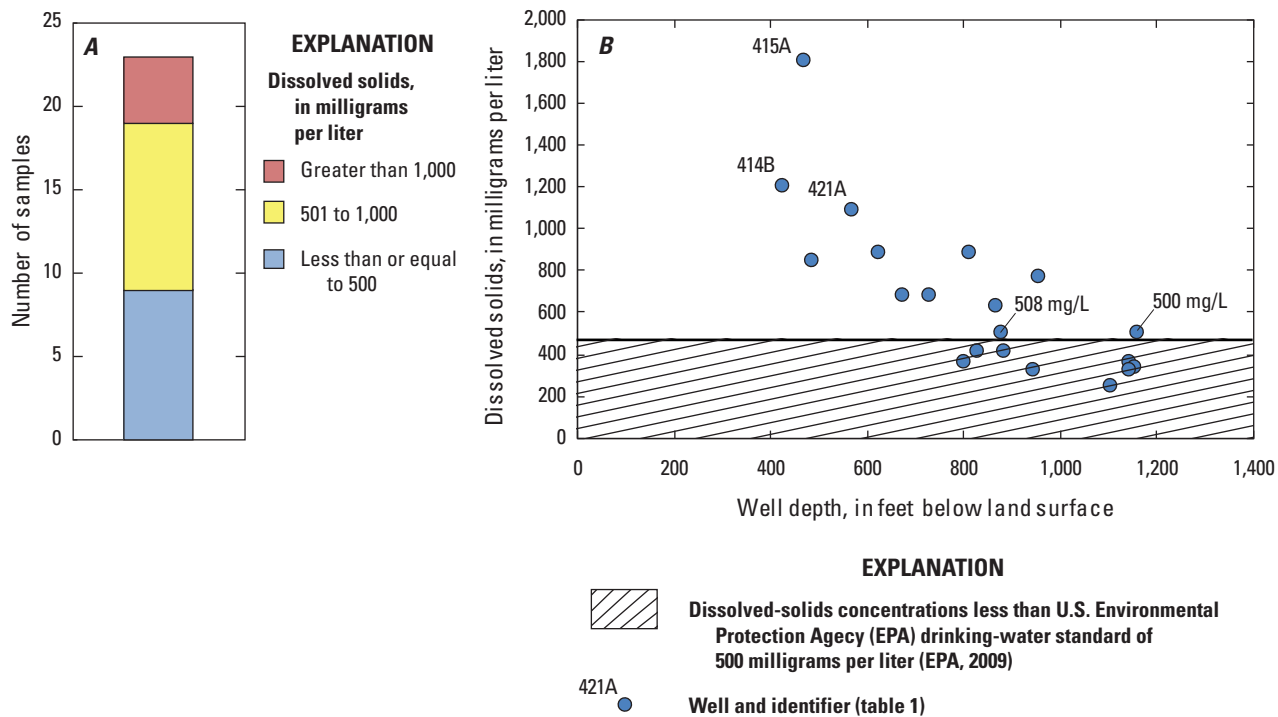


Figure 4. Dissolved-solids concentrations measured in samples collected from wells in New Mexico and Texas in the Hueco Bolson study area during 2016–17: *A*, numbers of samples containing specified ranges of dissolved-solids concentrations, and *B*, relation between dissolved-solids concentration and well depth.

iron, lithium, manganese, molybdenum, selenium, uranium, vanadium, and zinc (Ging and others, 2019). Some of the higher iron and manganese concentrations (greater than 10 $\mu\text{g/L}$) were associated with wells with lower dissolved-oxygen concentrations (less than or equal to 0.2 mg/L), indicating that the iron and manganese concentrations could be affected by oxidation and reduction conditions (Ayotte and others, 2011; Ging and others, 2019). Similar findings were discussed in a previous study by Anderholm and Heywood (2003).

Of all trace elements measured in the groundwater samples obtained in this study, only arsenic concentrations exceeded the EPA-designated drinking-water standard of 10 $\mu\text{g/L}$ (EPA, 2009) in samples from 4 of 23 wells (17 percent); these 4 wells were located near the Rio Grande (table 2; fig. 8). Three of the wells where samples with the highest uranium concentrations (greater than 10 $\mu\text{g/L}$) measured were also near the Rio Grande, and two of those wells were the same wells from which samples with high arsenic concentrations were obtained (figs. 8 and 9). The most common anthropogenic sources of arsenic include arsenic-based pesticides, coal combustion, and ore smelting (Hem, 1985). Uranium is a naturally occurring metal in the environment and can be mined in areas with large deposits. Anthropogenic sources of uranium concentrations include abandoned uranium mines, dissolution of mine tailings, emissions from nuclear industries, and combustion of coal (Szabo and others, 2012). Arsenic and

uranium can naturally occur in certain types of sediments and bedrock, such as rocks of volcanic origin (Scanlon and others, 2005). The Hueco Bolson is part of the Rio Grande aquifer system, and concentrations of arsenic and uranium exceeding 5 $\mu\text{g/L}$ have been measured in groundwater of the Rio Grande aquifer system (Musgrove and Bexfield, 2017). Because other trace elements such as molybdenum and boron that are associated with volcanic rocks were detected in the study area, the primary sources of the arsenic and uranium detected in the samples collected for this study may be geologic (volcanic) rather than anthropogenic in origin (Scanlon and others, 2005). Arsenic and uranium are more soluble in oxygen-rich environments such as surface water, and the higher dissolved-oxygen concentrations in the Rio Grande allow arsenic and uranium to be transported within the river (Robertson, 1991; Levings and others, 1998). In addition, arsenic and uranium are frequently detected in surface-water samples collected from the Rio Grande upstream from Ciudad Juárez, Mexico, and El Paso, Tex., which could indicate that these trace elements are being transported downstream from areas with volcanic rock (Levings and other, 1998). According to Heywood and Yager (2003), the Rio Grande is hydraulically connected to the Hueco Bolson, and water from the river can seep through the alluvium into shallow parts of the aquifer system in the Rio Grande valley, thus possibly accounting for the arsenic and uranium detections in the groundwater.

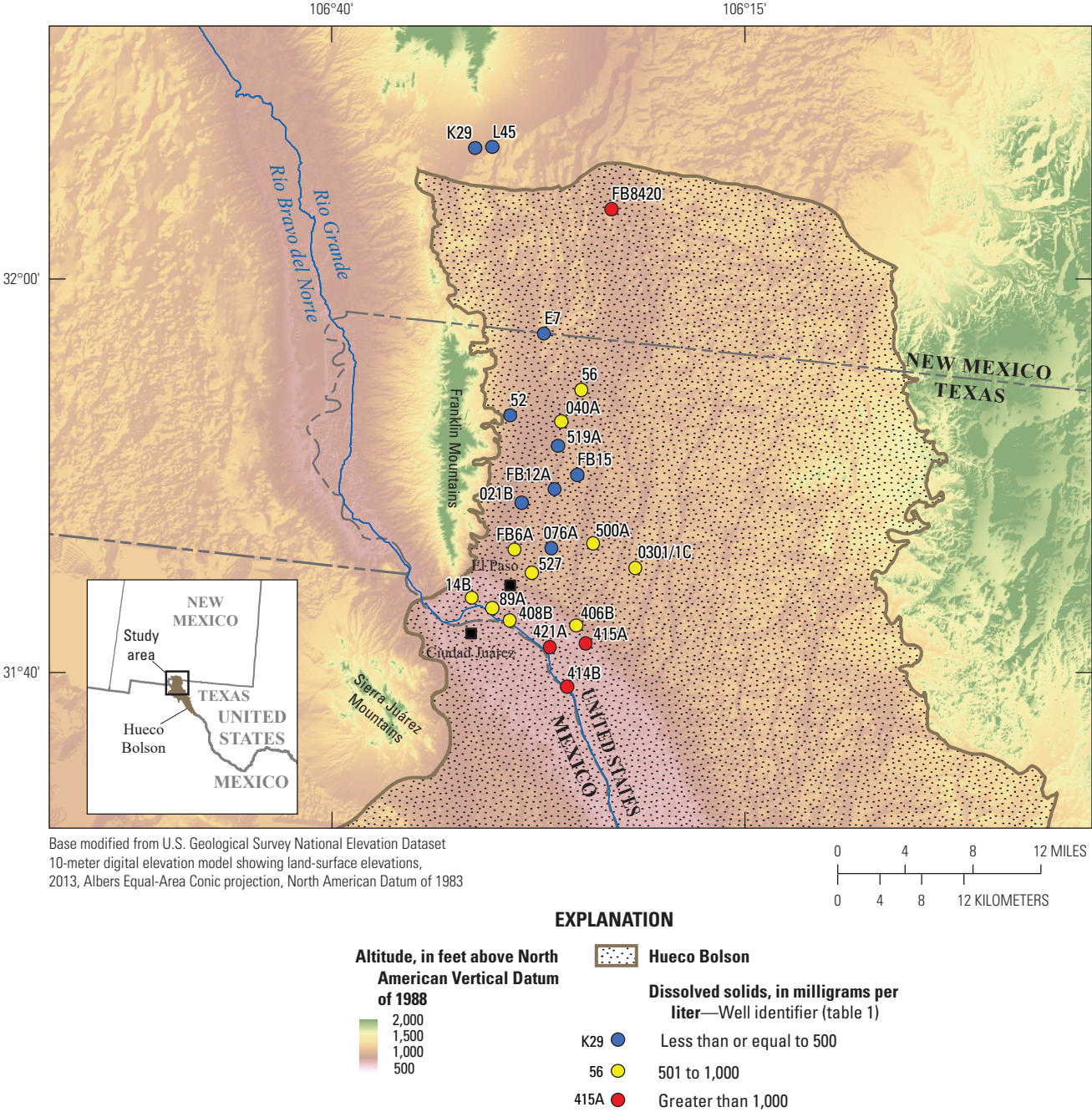


Figure 5. Concentrations of dissolved solids measured in groundwater samples collected from wells in New Mexico and Texas in the Hueco Bolson study area, 2016–17.

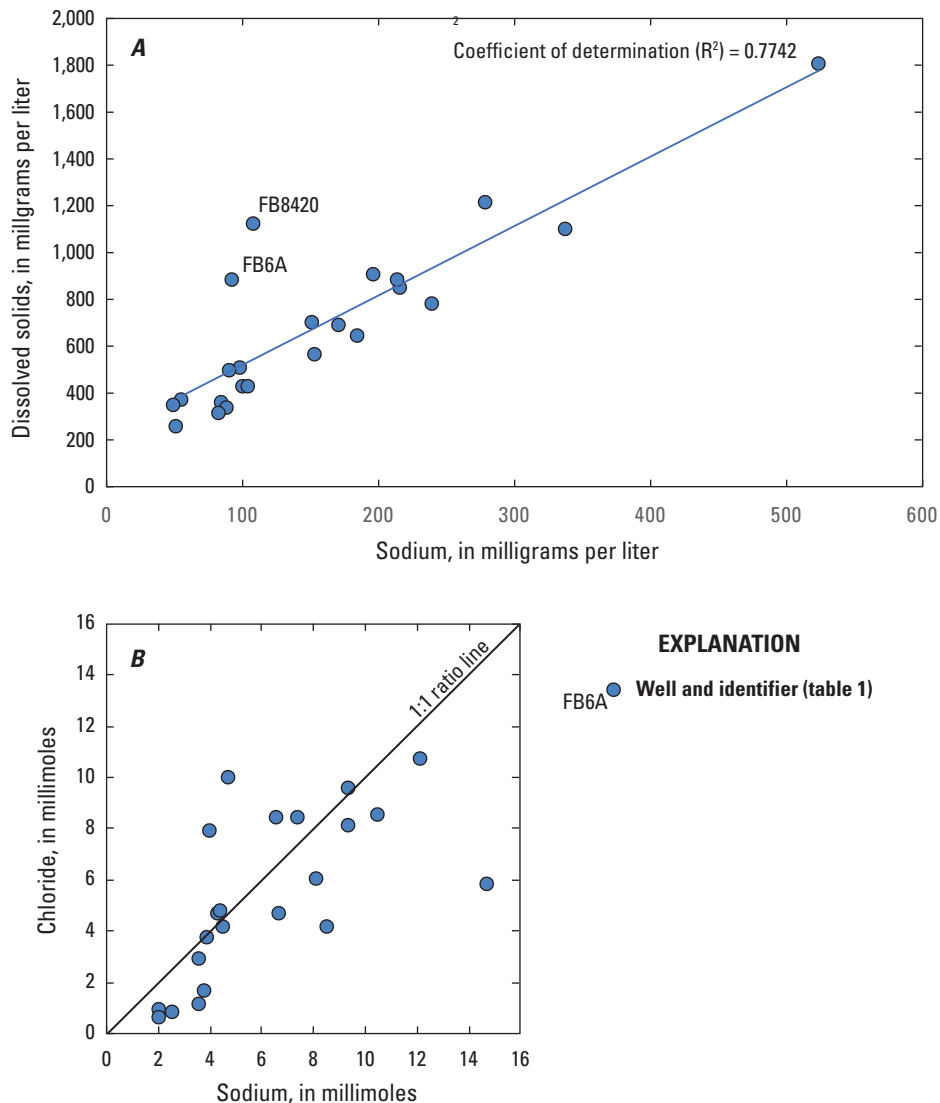


Figure 6. Concentrations of *A*, dissolved solids and sodium and *B*, chloride and sodium measured in groundwater samples collected from wells in New Mexico and Texas in the Hueco Bolson study area, 2016–17.

Organic Compounds

Detections of organic compounds such as pesticides in groundwater samples are potential indicators of anthropogenic effects on water quality. Organic compounds detected in groundwater samples likely result from surface water containing pesticides seeping into the groundwater in the study area. Groundwater samples were analyzed for 83 organic compounds. Of the 23 wells that were sampled, organic compounds were detected in samples from 5 wells. Three of the five groundwater samples with detected amounts of organic compounds were obtained from wells near the Rio Grande (fig. 10). The organic compounds that were detected in samples in this study were simazine, prometryn, prometon,

atrazine, deethylatrazine, and 3,4-dichloroaniline (Ging and others, 2019). All the organic compounds detected are herbicides except for deethylatrazine and 3,4-dichloroaniline, which are degradates of herbicide compounds. Herbicide use may be associated with urban development in Ciudad Juárez, Mexico, and El Paso, Tex., or cultivated-crop land along the Rio Grande (fig. 2). All concentrations for these organic compounds were low (less than 0.03 µg/L). Multiple organic compounds are often detected in the samples collected from a single well; two or three organic compounds were measured in each of the samples collected from four of the five wells (wells 408B, 421A, FB6A, and 040A) with detected amounts of any organic compounds (Ging and others, 2019; fig. 10).

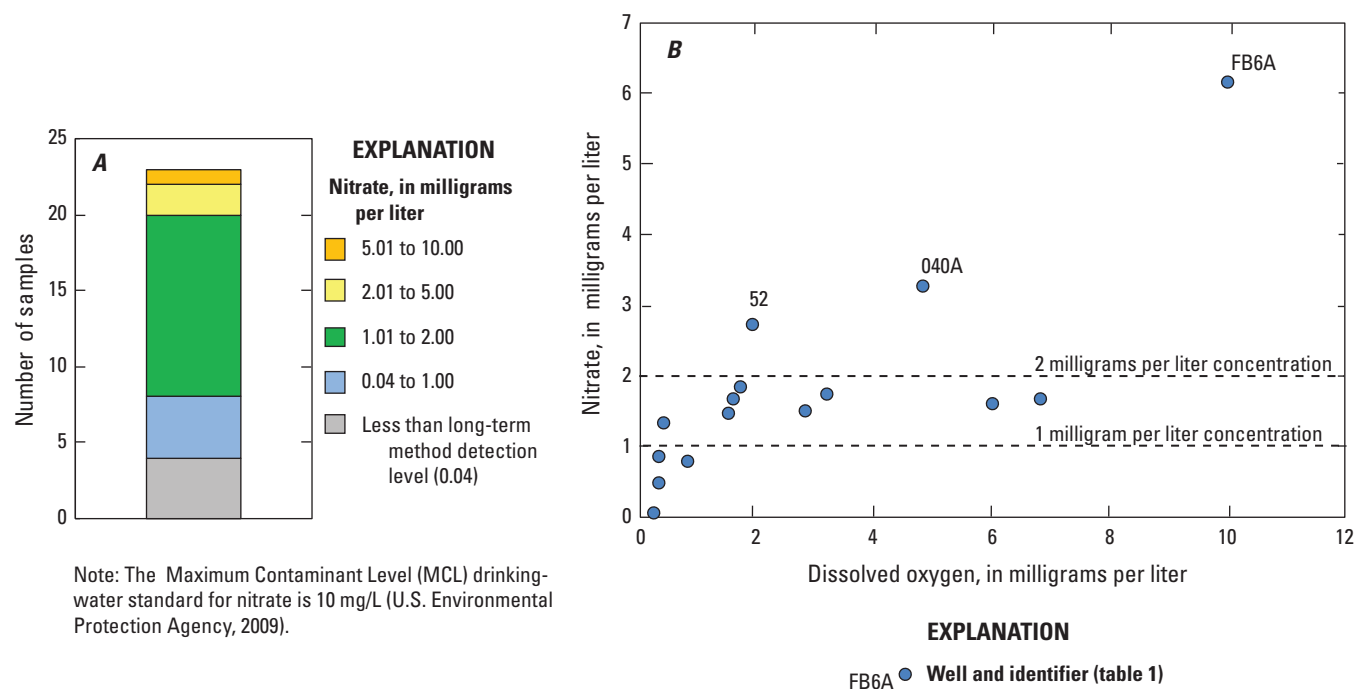


Figure 7. Nitrate concentrations measured in samples collected from wells in New Mexico and Texas in the Hueco Bolson study area during 2016–17: *A*, numbers of samples containing specified ranges of nitrate concentrations, and *B*, relation between nitrate concentration and dissolved-oxygen concentration.

Table 2. Trace elements detected in groundwater samples collected from wells in New Mexico and Texas in the Hueco Bolson study area, with U.S. Environmental Protection Agency designated drinking-water standards for trace elements, and percentage of wells where the collected samples exceeded the standard for selected trace elements, 2016–17.

[µg/L, micrograms per liter]

Trace element	Drinking-water standard, ¹ in µg/L	Percentage of wells with detections	Detected concentrations that exceeded the applicable drinking-water standard, in percent
Antimony	6	87	0
Arsenic	10	100	17
Barium	2,000	100	0
Boron	6,000	100	0
Chromium	100	70	0
Lead	15	96	0
Manganese	300	70	0
Molybdenum	40	100	0
Selenium	50	91	0
Uranium	30	100	0

¹U.S. Environmental Protection Agency, 2009.

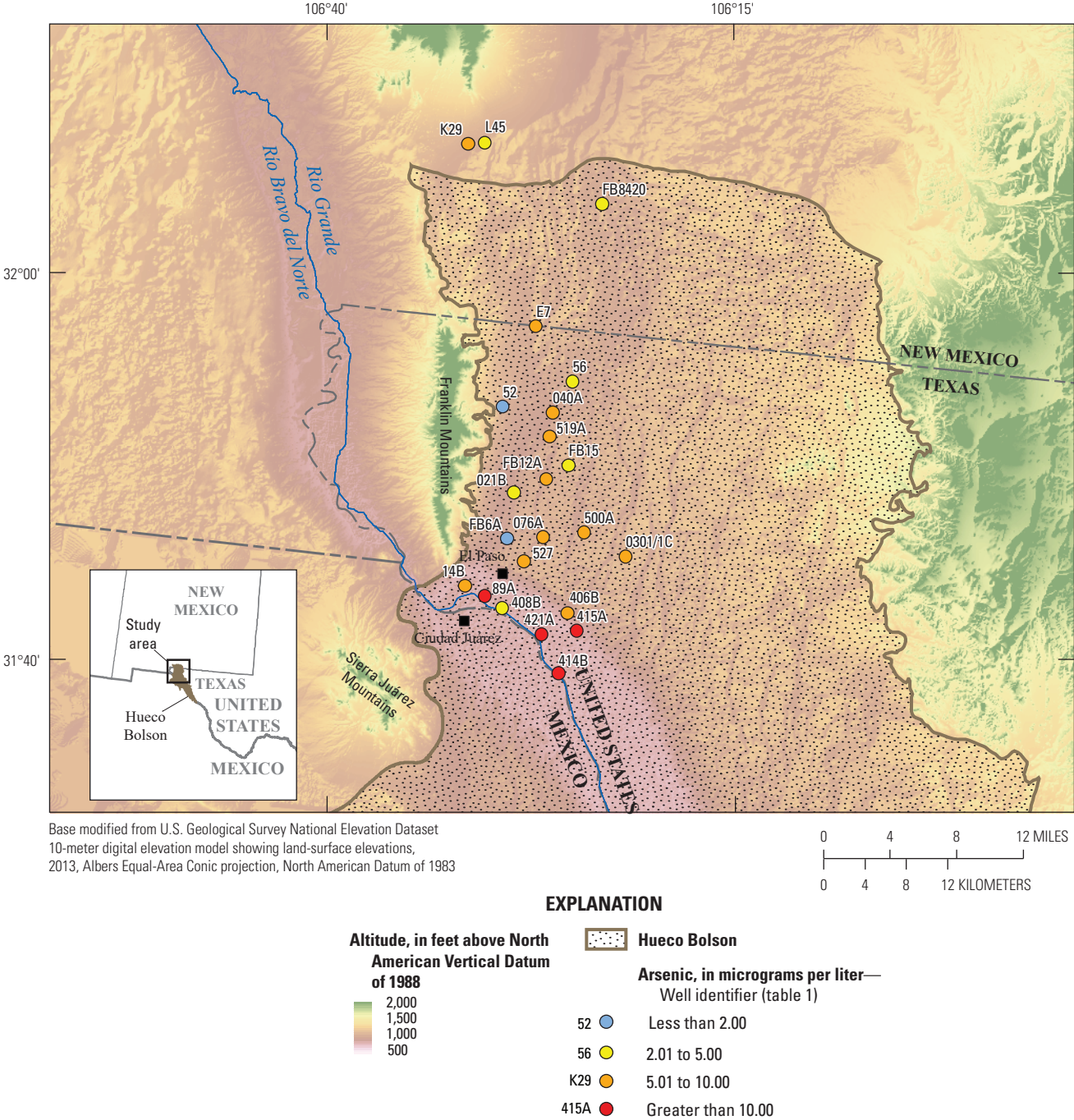


Figure 8. Concentrations of arsenic measured in groundwater samples collected from wells in New Mexico and Texas in the Hueco Bolson study area, 2016–17.

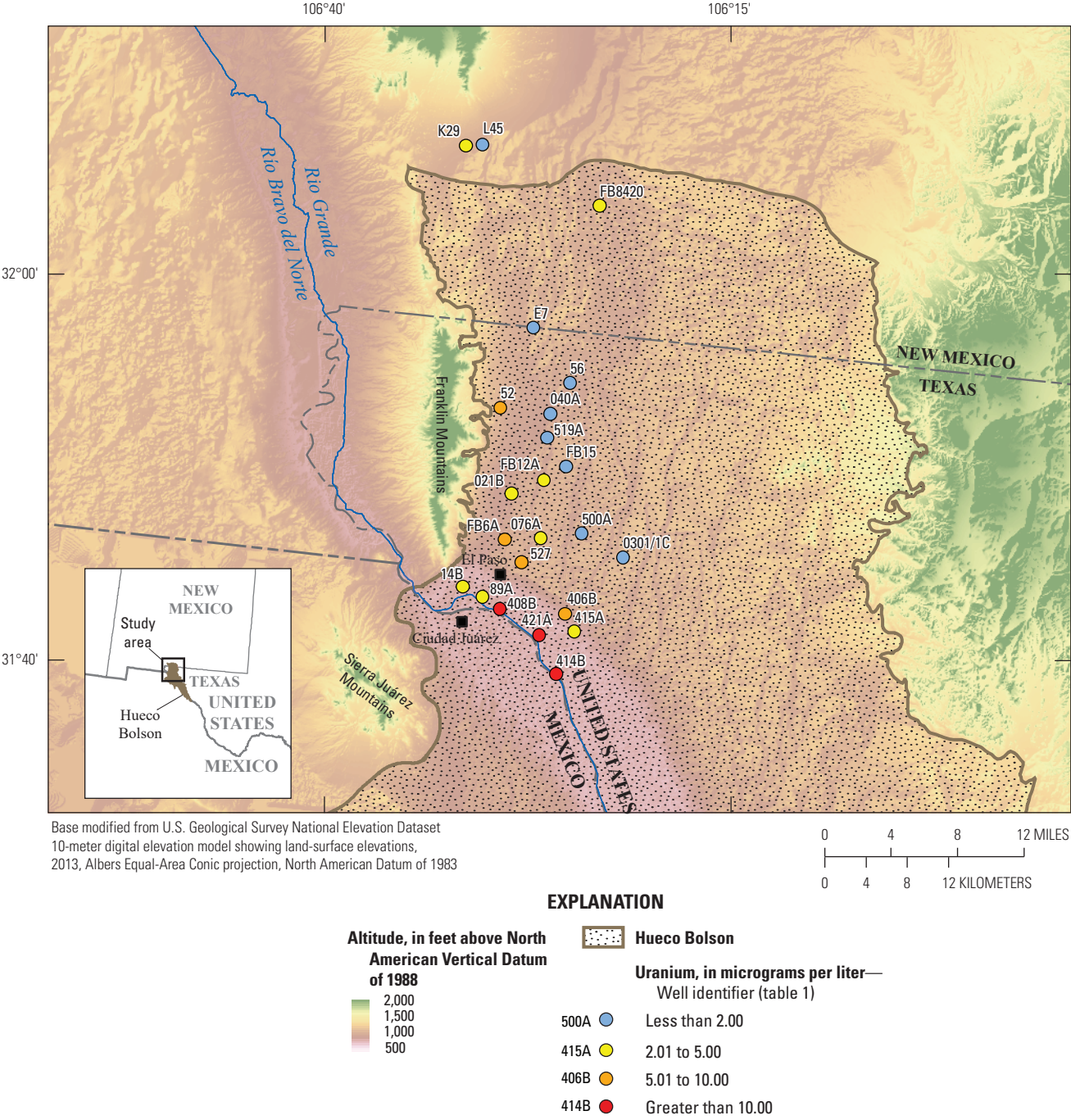


Figure 9. Concentrations of uranium measured in groundwater samples collected from wells in New Mexico and Texas in the Hueco Bolson study area, 2016–17.

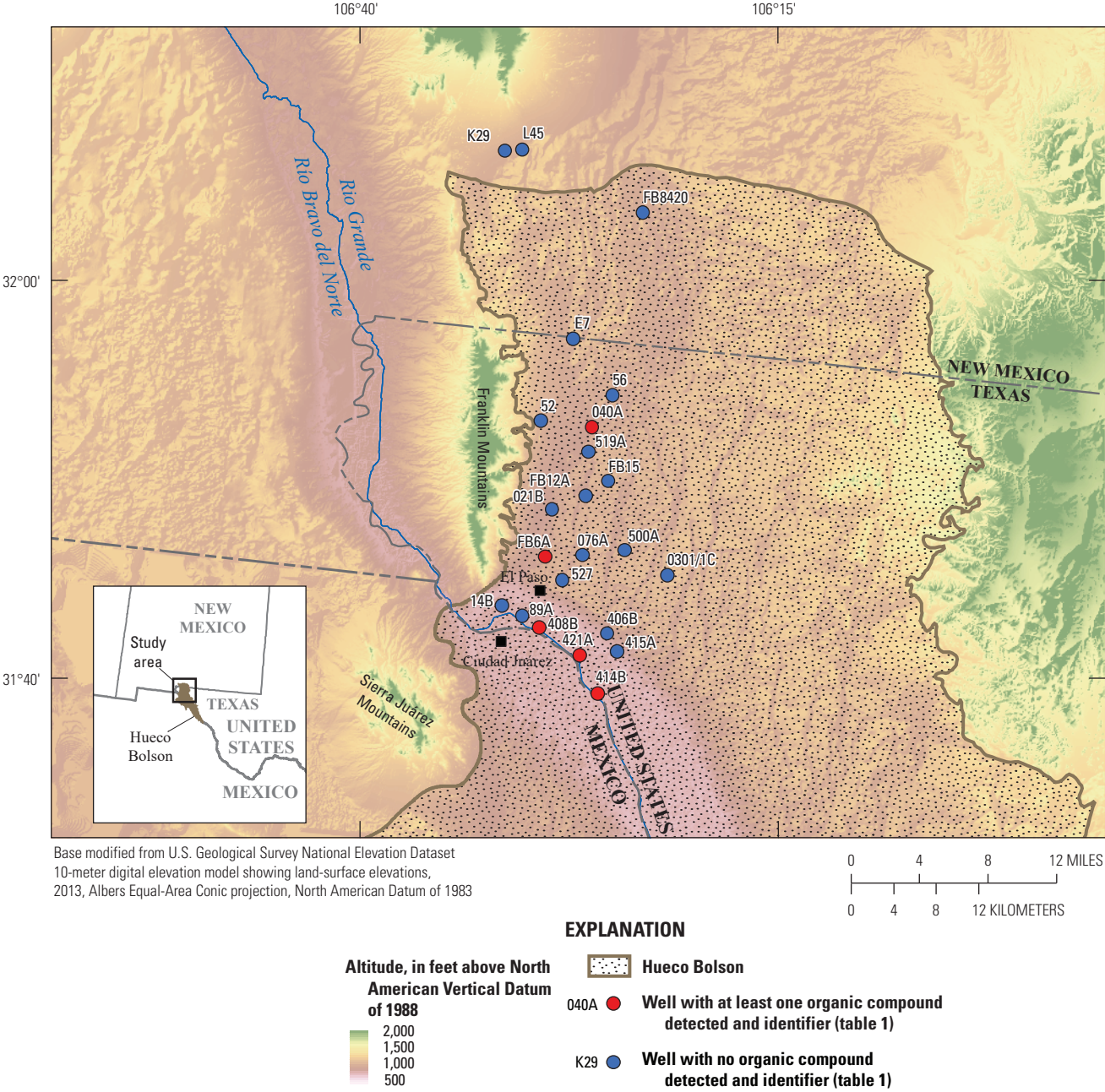


Figure 10. Wells with detections of organic compounds in groundwater samples in New Mexico and Texas in the Hueco Bolson study area, 2016–17.

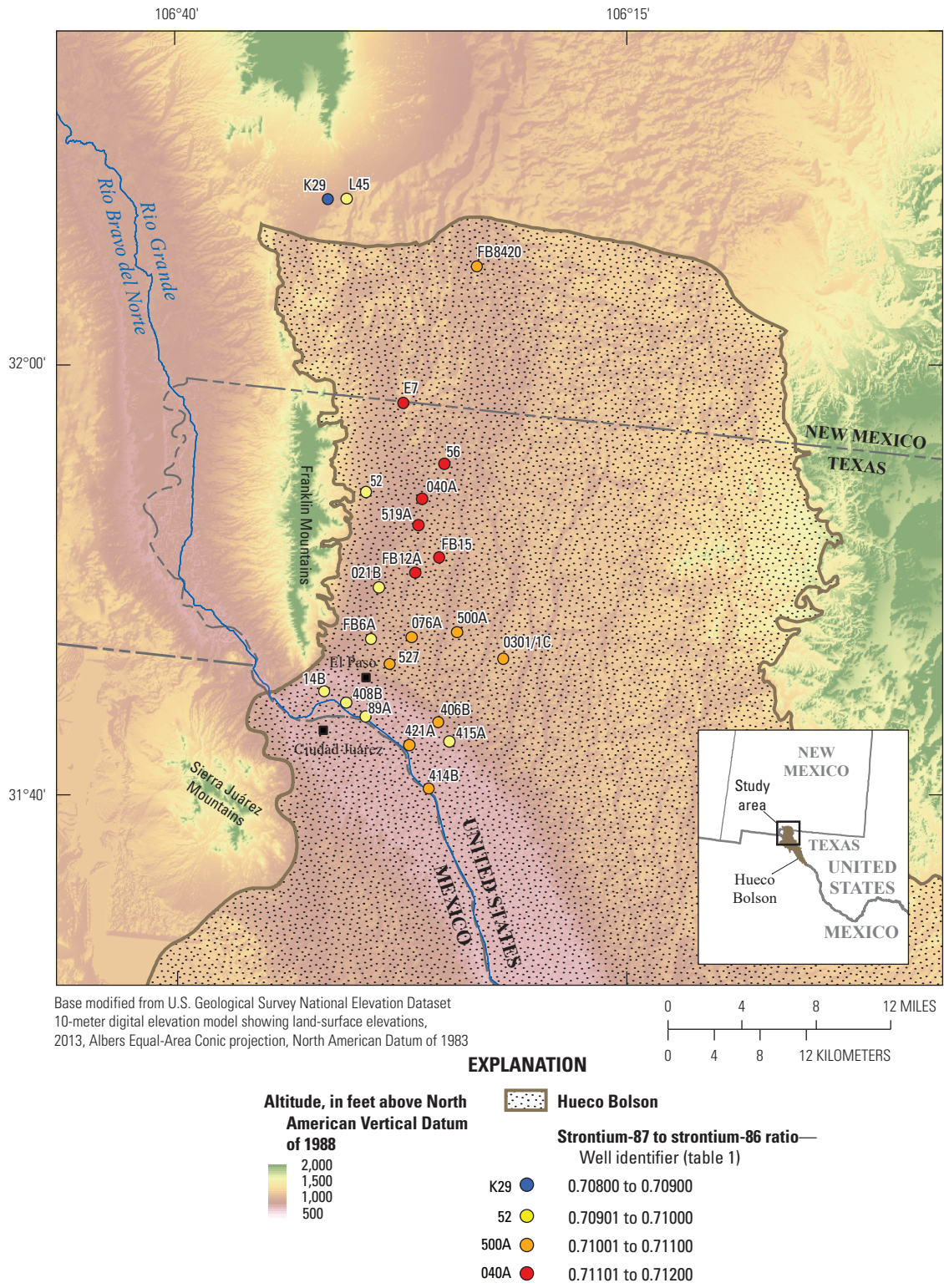


Figure 11. Strontium-87 to strontium-86 ratios in groundwater samples collected from wells in New Mexico and Texas in the Hueco Bolson study area, 2016–17.

Environmental Tracers

Environmental tracers, such as $^{87}\text{Sr}/^{86}\text{Sr}$, δD , $\delta^{18}\text{O}$, ^3H , and ^{14}C concentrations in groundwater, are useful for understanding where and when groundwater recharge occurred in the aquifer system. The isotopic ratio of $^{87}\text{Sr}/^{86}\text{Sr}$ can provide a useful tool for helping determine the source of dissolved constituents in water because the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio undergoes negligible fractionation during mineral-solution reactions (Banner, 2004; Bumgarner and others, 2012). Therefore, $^{87}\text{Sr}/^{86}\text{Sr}$ values in water are expected to reflect the isotopic ratio of minerals in the aquifer system from rock-water interaction because fractionation is limited. The $^{87}\text{Sr}/^{86}\text{Sr}$ values in samples from five wells near the Rio Grande ranged from 0.70950 to 0.71011 (fig. 11), which is similar to the mean $^{87}\text{Sr}/^{86}\text{Sr}$ value (0.71019) that Teeple (2017, p. 67) reported for groundwater samples collected from the Rio Grande alluvium (Ging and others, 2019). In addition, $^{87}\text{Sr}/^{86}\text{Sr}$ values (ranging from 0.71102 to 0.71164) were slightly higher in groundwater samples from six wells collected in the central and northern part of study area, east of the Franklin Mountains, compared to $^{87}\text{Sr}/^{86}\text{Sr}$ values measured in groundwater samples collected from wells near the Rio Grande (Ging and others, 2019; fig. 11). Teeple (2017) reported similar $^{87}\text{Sr}/^{86}\text{Sr}$ values in samples from the Mesilla Basin near the Franklin Mountains, and citing the work of others, stated that the samples may represent groundwater originating from the uplift areas surrounding the Mesilla Basin, which were formed from Tertiary volcanic activity (Witcher and others, 2004). The lower $^{87}\text{Sr}/^{86}\text{Sr}$ values (0.70996 and 0.70925) measured in the samples collected from two wells near the Franklin Mountains (wells 52 and 021B, respectively) may indicate recharge water from a different, deeper geologic area compared to the groundwater obtained from other, shallower wells east of the Franklin Mountains (Ging and others, 2019; fig. 11). Wells 52 and 021B are more than 1,150 feet deep (about 351 meters), whereas other wells east of the Franklin Mountains range from 670 to 1,140 feet deep (about 204 to 347 meters) (Ging and others, 2019; fig. 11; table 1). From the $^{87}\text{Sr}/^{86}\text{Sr}$ values in this study, it appears that groundwater from the central and northern parts of the study area may predominantly receive recharge water from precipitation that falls in the Franklin Mountains area, whereas groundwater in the southern part of the study area may predominantly receive recharge water from the Rio Grande valley.

Groundwater samples in the study area also were analyzed for δD and $\delta^{18}\text{O}$ to help with the determination of source and recharge areas. The ratios of δD to $\delta^{18}\text{O}$ are useful indicators of conditions present at the time and place of groundwater recharge (Faure, 1986; Uliana and others, 2007).

A comparison of δD and $\delta^{18}\text{O}$ in groundwater samples can be used to evaluate the evaporation process along a flow path because evaporation causes the preferential loss of water molecules containing the lighter stable isotopes of hydrogen (hydrogen-1) and oxygen (oxygen-16) and therefore deviation from the GWML (Witcher and others, 2004). The relation of δD and $\delta^{18}\text{O}$ values measured in groundwater samples to the GMWL can help determine changes to groundwater chemistry caused by precipitation seeping into the aquifer. Evaporation, mixing with nonmeteoric water, or hydrothermal alteration of deeper, older waters can account for δD and $\delta^{18}\text{O}$ values that deviate from the GMWL (Witcher and others, 2004). Most of the δD to $\delta^{18}\text{O}$ ratios for the groundwater samples collected during this study plot near the GMWL (fig. 12A). The δD to $\delta^{18}\text{O}$ ratios for five samples collected from wells near the Rio Grande plotted below the GMWL and were similar to δD to $\delta^{18}\text{O}$ ratios reported in previous studies describing groundwater samples collected from wells near the Rio Grande (Anderholm and Heywood, 2003; Phillips and others, 2003; Eastoe and others, 2008; fig. 12B). The pattern of δD to $\delta^{18}\text{O}$ ratios plotting below the GMWL indicates that the source of recharge for the wells along the Rio Grande is likely different from the source of recharge for the rest of the wells in the study area. This finding is consistent with the recharge information interpreted from differences in $^{87}\text{Sr}/^{86}\text{Sr}$ values. As in previous studies such as Anderholm and Heywood (2003) and Phillips and others (2003), the isotopic composition of groundwater samples obtained from the five wells near the Rio Grande is similar to the isotopic composition of surface water from the Rio Grande. The δD and $\delta^{18}\text{O}$ values measured in samples collected from the wells near the Rio Grande during this study follow the Rio Grande evaporation line published in Phillips and others (2003) (fig. 12A).

Groundwater samples in the study area were analyzed for ^3H and ^{14}C to gain additional insights regarding the age of the groundwater. Given the short half-life of ^3H , the presence of ^3H in groundwater is indicative of groundwater recharge within about the past 70 years. Interpreting groundwater ages with ^3H is qualitative in that it can provide insight into distinguishing water recharged before and after nuclear weapons testing. Because ^{14}C has a longer radioactive half-life compared to ^3H , it is useful for determining the age of groundwater that is thousands to tens of thousands of years old (Oden and Truini, 2013). The age of groundwater is commonly qualified as an “apparent age” because chemical processes affect the environmental tracers used to determine age. Musgrove and others (2010, p. 42) explain that “because it is not possible to identify and account for all physical and chemical processes that might affect groundwater age-tracer results, the apparent age of groundwater is most appropriately reported.”

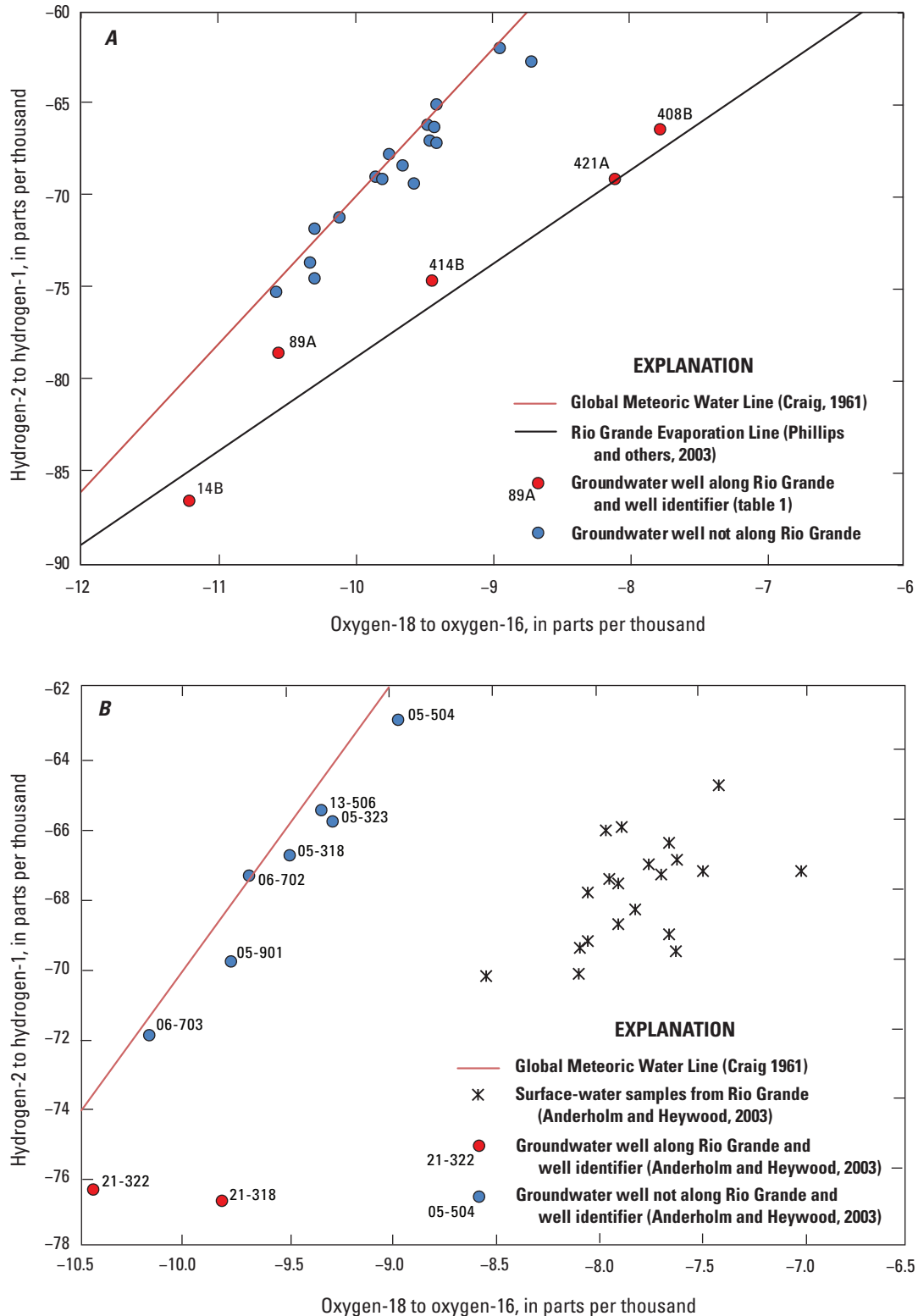


Figure 12. A, The ratio of oxygen-18 to oxygen-16 (delta oxygen-18) and the ratio of hydrogen-2 to hydrogen-1 (delta deuterium) measured in samples collected from wells in New Mexico and Texas in the Hueco Bolson study area, 2016–17; and B, the ratio of oxygen-18 to oxygen-16 (delta oxygen-18) and the ratio of hydrogen-2 to hydrogen-1 (delta deuterium) as reported in previous studies describing groundwater samples collected in the southwestern Hueco Bolson. Modified from Anderholm and Heywood (2003).

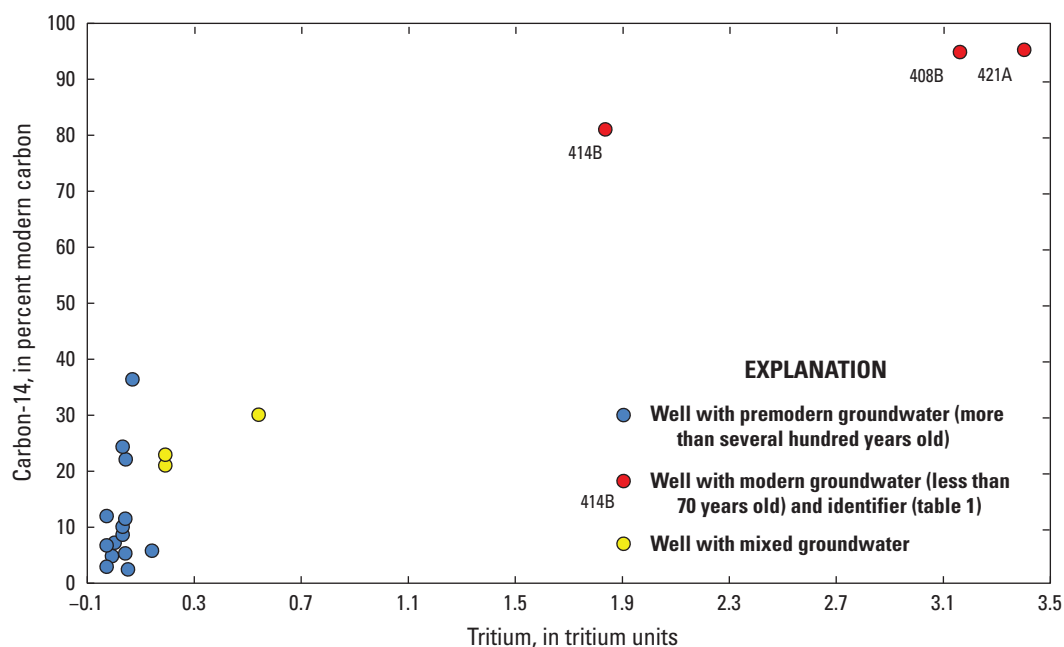


Figure 13. Carbon-14 and tritium concentrations, with apparent age designations for groundwater samples collected from wells in New Mexico and Texas in the Hueco Bolson study area, 2016–17.

By combining the results from ^3H and ^{14}C analyses in water samples and the spatial and temporal variability of ^3H deposition in precipitation, an apparent age can be assigned to the water from a given well (Michel and others, 2018; Lindsey and others, 2019; [figs. 13 and 14](#)). Water that has ^3H concentrations greater than 1.5 TU is considered modern and is less than about 70 years old. Water that has ^{14}C concentrations less than 60 pmc is considered premodern and is more than several hundred years old. Water with ^3H concentrations lower than 1.5 TU and ^{14}C concentrations less than 60 pmc is considered mixed for age-determination purposes and is considered to be a mixture of water less than about 70 years old and water more

than several hundred years old (Lindsey and others, 2019). By using these classifications, 17 of the 23 groundwater samples from the study area are considered premodern ([fig. 14](#)). Wells 408B, 421A, and 414B have relatively young, or modern-age, groundwater. These three wells are located near the Rio Grande and are the same wells from which samples with concentrations of arsenic or uranium of 10 $\mu\text{g/L}$ or greater and with detections of selected organic compounds were collected ([figs. 8, 9, 10, and 14](#)). The modern groundwater and the presence of organic compounds detected in wells near the Rio Grande support potential effects of surrounding land-use activities on groundwater quality in the Rio Grande valley.

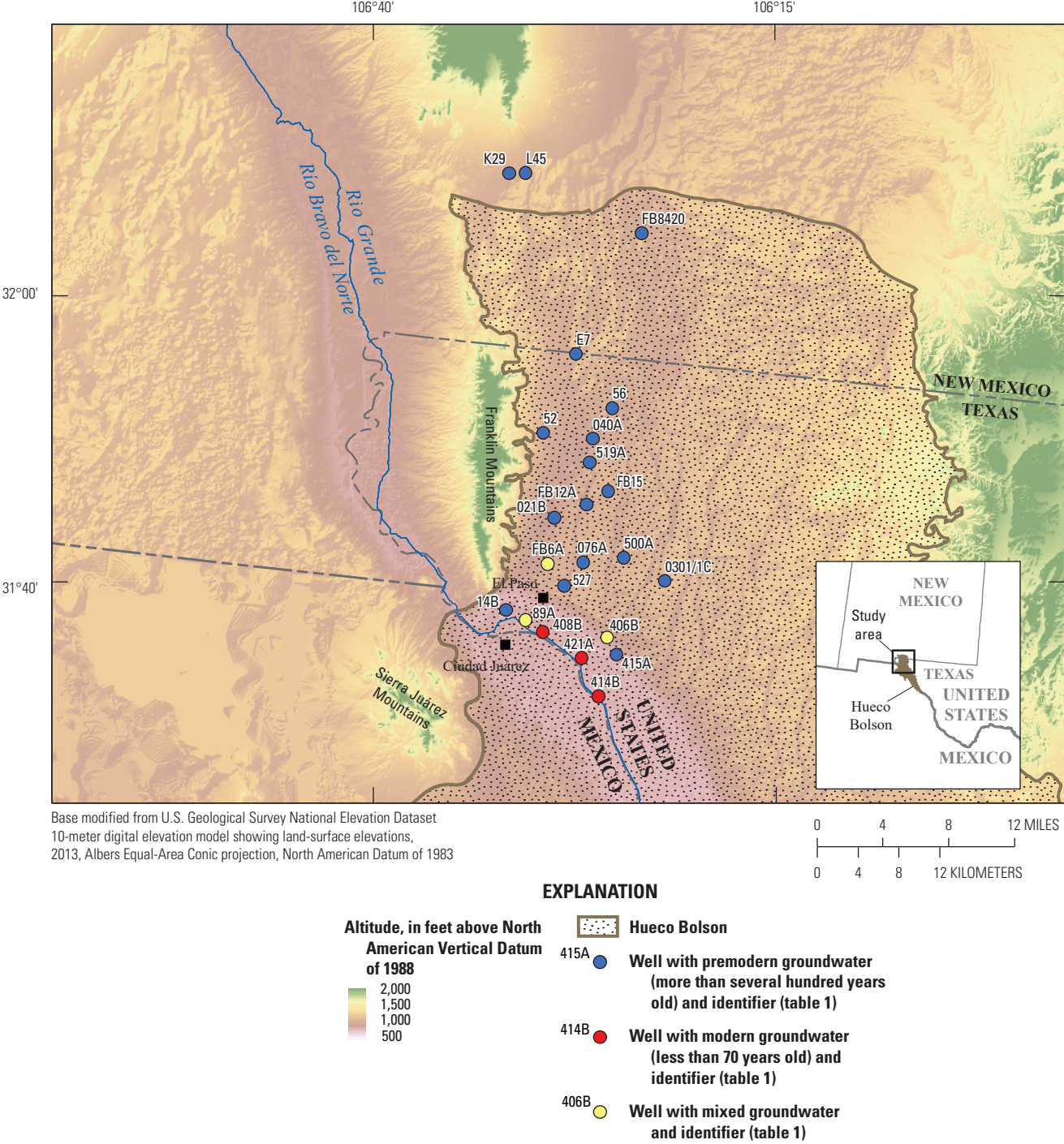


Figure 14. Relative groundwater ages for groundwater samples collected from wells in New Mexico and Texas in the Hueco Bolson study area, 2016–17.

Summary

Twenty-three water-supply wells were sampled in the southern part of New Mexico and western part of Texas for a geochemical assessment of the Hueco Bolson. Water-quality samples from the wells were analyzed for physical properties, major ions, dissolved solids, nutrients, trace elements, organic compounds, and environmental tracers. The environmental tracers included selected isotopes such as strontium, hydrogen, oxygen, tritium, and carbon-14 to help understand potential sources and ages of the water sampled in the wells.

Most of the water samples from the Hueco Bolson wells were classified as sodium-chloride type water. Dissolved-solids concentrations are a measure of how much dissolved constituents such as sodium and chloride are in a sample. Dissolved-solids concentrations greater than 1,000 milligrams per liter (mg/L) (which classifies water as brackish) were measured in samples collected only from four wells in the study area. Three of the four wells from which samples with the highest dissolved-solids concentrations were measured were near the Rio Grande. Dissolved-solids concentrations in groundwater also decreased with increasing well depth below land surface. This unusual pattern of decreasing dissolved-solids concentrations with increasing well depth is probably a function of the spatial distribution of the wells, where the shallower wells with the higher dissolved-solids concentrations are the wells closest to the Rio Grande. A large coefficient of determination for a regression line fitted to the sodium and dissolved-solids concentrations indicates that sodium concentrations increase with increasing dissolved-solids concentrations; this relation is consistent with sodium being a large component of the dissolved-solids concentration.

Nitrate concentrations in the groundwater samples collected in the study area ranged from below the long-term method detection level of 0.04 mg/L to 6.2 mg/L with nitrate concentrations increasing with increasing dissolved-oxygen concentrations.

Of all trace elements measured in the groundwater samples obtained in this study, only arsenic concentrations exceeded U.S. Environmental Protection Agency drinking-water standard of 10 micrograms per liter ($\mu\text{g/L}$) in samples obtained from 4 of 23 wells (17 percent); these 4 wells were located near the Rio Grande. Three of the wells where samples with the highest uranium concentrations (greater than 10 $\mu\text{g/L}$) measured were also near the Rio Grande, and two of those wells were the same wells from which samples with high arsenic concentrations were obtained. The Hueco Bolson is part of the Rio Grande aquifer system, and concentrations of arsenic and uranium exceeding 5 $\mu\text{g/L}$ have been measured in groundwater of the Rio Grande aquifer system. In addition, arsenic and uranium have frequently been detected in surface-water samples collected from the Rio Grande upstream from Ciudad Juárez, Mexico, and El Paso, Texas, which could indicate that these trace elements are being transported downstream because arsenic and uranium are soluble in oxygen-rich environments such as surface water.

Groundwater samples were analyzed for 83 organic compounds, and of the 23 wells sampled in this study, organic compounds were detected only in samples from 5 wells. Three of the five groundwater samples with detected amounts of organic compounds were obtained from wells near the Rio Grande; these detections may be a result of surrounding land-use activities. The organic compounds that were detected in samples in this study were simazine, prometryn, prometon, atrazine, deethylatrazine, and 3,4-dichloroaniline. Multiple organic compounds are often detected in the samples collected from a single well; multiple detections of organic compounds were measured in the samples collected from four of the five of the wells with detected amounts of any organic compounds.

Environmental tracers, such as strontium isotopic ratio (strontium-87 to strontium-86, commonly expressed as $^{87}\text{Sr}/^{86}\text{Sr}$), hydrogen and oxygen isotopic ratio (δD to $\delta^{18}\text{O}$), tritium (^3H), and carbon-14 (^{14}C) concentrations in groundwater, were analyzed in groundwater samples in this study to help with understanding where and when groundwater recharge occurred in the aquifer system. $^{87}\text{Sr}/^{86}\text{Sr}$ is useful in describing the source of groundwater and possible mixing of source waters. The $^{87}\text{Sr}/^{86}\text{Sr}$ values in five wells near the Rio Grande are similar to the mean $^{87}\text{Sr}/^{86}\text{Sr}$ value for groundwater samples collected from the Rio Grande alluvium in a groundwater study in the Mesilla Basin. In addition, $^{87}\text{Sr}/^{86}\text{Sr}$ values were slightly higher in groundwater samples collected from six wells in the central and northern part of study area, east of the Franklin Mountains, compared to $^{87}\text{Sr}/^{86}\text{Sr}$ values measured in groundwater samples collected from wells near the Rio Grande. In the same groundwater study in the Mesilla Basin, similar $^{87}\text{Sr}/^{86}\text{Sr}$ values were reported for groundwater samples from the Mesilla Basin near the Franklin Mountains. Comparison of the ratio of δD to $\delta^{18}\text{O}$ values measured in groundwater samples collected in the study area to the Global Meteoric Water Line (GMWL) can help determine changes to groundwater chemistry from precipitation seeping into the aquifer. Most of the δD to $\delta^{18}\text{O}$ ratios for the groundwater samples collected during this study plot near the GMWL. The δD to $\delta^{18}\text{O}$ ratios for five samples collected from wells near the Rio Grande plotted below the GMWL and were similar to δD to $\delta^{18}\text{O}$ ratios reported in previous studies describing groundwater samples collected from wells near the Rio Grande. The pattern of δD to $\delta^{18}\text{O}$ ratios plotting below the GMWL indicates that the source of recharge for the wells along the Rio Grande is likely different from the source of recharge for the rest of the wells in the study area. This finding is consistent with the recharge information interpreted from differences in $^{87}\text{Sr}/^{86}\text{Sr}$ values.

By combining the results from ^3H and ^{14}C analyses in groundwater samples for this study, an apparent age can be assigned to the water from a given well. Most of the groundwater samples (17 of the 23) in the study area are considered premodern, which means that the water is more than several hundred years old. Three wells with relatively young, or modern-age, groundwater are located near the Rio Grande. Groundwater samples containing arsenic or uranium

concentrations of 10 µg/L or greater were collected from these three wells, along with detections of selected organic compounds. All the environmental tracer results indicate that recharge water to wells closer to the Rio Grande is different from the recharge water to the rest of the wells in the study area.

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