

Prepared in cooperation with the City of Houston

Arsenic and Radionuclide Occurrence and Relation to Geochemistry in Groundwater of the Gulf Coast Aquifer System in Houston, Texas, 2007–11



Scientific Investigations Report 2015–5071

U.S. Department of the Interior
U.S. Geological Survey



Front cover:

Top, Sample collection line attached to spigot near wellhead.

Bottom, U.S. Geological Survey hydrologist collecting a groundwater sample inside a collection chamber while sitting next to spigot near wellhead.

Back cover:

Top, Dedicated mobile water-quality laboratory truck with sample collection line feeding through portal and attached to spigot near wellhead.

Middle, A collection chamber and sampling manifold connected to the sample collection line feeding through portal inside the dedicated mobile water-quality laboratory truck.

Bottom, Municipal supply well in Houston, Texas.

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By Jeannette H. Oden and Zoltan Szabo

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U.S. Department of the Interior
U.S. Geological Survey

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SALLY JEWELL, Secretary

U.S. Geological Survey
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Conversion Factors

Inch/Pound to International System of Units

Multiply	By	To obtain
	Length	
foot (ft)	0.3048	meter (m)
mile (mi)	1.609	kilometer (km)
	Volume	
gallon (gal)	3.785	liter (L)
million gallons (Mgal)	3,785	cubic meter (m ³)
	Flow rate	
gallon per minute (gal/min)	0.06309	liter per second (L/s)
gallon per day (gal/d)	0.003785	cubic meter per day (m ³ /d)
million gallons per day (Mgal/d)	0.04381	cubic meter per second (m ³ /s)
	Pressure	
inch of mercury at 60 °F (in Hg)	3.377	kilopascal (kPa)

International System of Units to Inch/Pound

Multiply	By	To obtain
	Length	
nanometer (nm)	3.937×10^{-8}	inch (in.)
centimeter (cm)	0.3937	inch (in.)
meter (m)	3.281	foot (ft)
kilometer (km)	0.6214	mile (mi)
	Volume	
liter (L)	0.2642	gallon (gal)
	Flow rate	
liter per second (L/s)	15.85	gallon per minute (gal/min)
cubic meter per day (m ³ /d)	264.2	gallon per day (gal/d)
	Mass	
gram (g)	0.03527	ounce, avoirdupois (oz)
kilogram (kg)	2.205	pound avoirdupois (lb)
	Radioactivity	
picocurie per liter (pCi/L)	0.037	becquerel per liter (Bq/L)
becquerel per liter (Bq/L)	27.027	picocurie per liter (pCi/L)
picocurie per liter (pCi/L)	0.3106	tritium units (TU)

Temperature in degrees Celsius (°C) may be converted to degrees Fahrenheit (°F) as follows:

$$^{\circ}\text{F}=(1.8\times^{\circ}\text{C})+32$$

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 1927 (NAD 27).

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

Supplemental Information

Specific conductance is given in microsiemens per centimeter at 25 degrees Celsius ($\mu\text{S}/\text{cm}$ at 25 °C).

Concentrations of chemical constituents in water are given either in milligrams per liter (mg/L) or micrograms per liter ($\mu\text{g}/\text{L}$).

Concentrations of radioactive constituents in water are given in picocuries per liter (pCi/L). One picocurie equals 2.2 radioactive disintegrations per minute.

Arsenic and Radionuclide Occurrence and Relation to Geochemistry in Groundwater of the Gulf Coast Aquifer System in Houston, Texas, 2007–11

By Jeannette H. Oden and Zoltan Szabo

Abstract

The U.S. Geological Survey (USGS), in cooperation with the City of Houston, began a study in 2007 to determine concentrations, spatial extent, and associated geochemical conditions that might be conducive for mobility and transport of selected naturally occurring trace elements and radionuclides in the Gulf Coast aquifer system in Houston, Texas. Water samples were collected from 91 municipal supply wells completed in the Evangeline and Chicot aquifers of the Gulf Coast aquifer system in northeastern, northwestern, and southwestern Houston; hereinafter referred to as northeast, northwest and southwest Houston areas. Wells were sampled in three phases: (1) 28 municipal supply wells were sampled during 2007–8, (2) 60 municipal supply wells during 2010, and (3) 3 municipal supply wells during December 2011. During each phase of sampling, samples were analyzed for major ions, selected trace elements, and radionuclides. At a subset of wells, concentrations of arsenic species and other radionuclides (carbon-14, radium-226, radium-228, radon-222, and tritium) also were analyzed. Selected physicochemical properties were measured in the field at the time each sample was collected, and oxidation-reduction potential and unfiltered sulfides also were measured at selected wells. The source-water (the raw, ambient water withdrawn from municipal supply wells prior to water treatment) samples were collected for assessment of aquifer conditions in order to provide community water-system operators information that could be important when they make decisions about which treatment processes to apply before distributing finished drinking water.

Geochemical conditions of groundwater of the Gulf Coast aquifer system are suitable in some instances for release of arsenic and radionuclides from aquifer materials. Recent changes to the U.S. Environmental Protection Agency (EPA) primary drinking-water regulations for arsenic and a selected number of natural radionuclides have highlighted the necessity for municipal supply system managers to be aware of the occurrence and distribution of these constituents in their source water. Concentrations of arsenic ranged from 0.58 to 23.5 micrograms per liter ($\mu\text{g/L}$), with relatively low median and 75th percentile concentrations (2.7 and 3.6 $\mu\text{g/L}$, respectively). The gross alpha-particle activity completed

within 72 hours after sample collection ranged from R-1.1 (nondetect where the result was below the sample specific critical level) to 39.7 picocuries per liter (pCi/L), with a median of 10.3 pCi/L. After 30 days, the gross alpha-particle activities in the 91 samples ranged from R-0.94 to 25.5 pCi/L, with a median of 5.60 pCi/L. Concentrations of uranium ranged from less than 0.02 to 42.7 $\mu\text{g/L}$, with a median value of 1.69 $\mu\text{g/L}$ and a 75th-percentile value of 6.48 $\mu\text{g/L}$. The maximum concentrations of radium-226 and combined radium (sum of radium-226 plus radium-228) were 4.34 pCi/L and 3.23 pCi/L, respectively.

Aquifer major-ion geochemistry was characterized and shown to contain three chemical types of water as grouped by a simplified predominant cation and anion classification system: (1) calcium- bicarbonate type, (2) sodium-bicarbonate type, and (3) sodium-chloride type. Aquifer geochemistry also was characterized into four reduction-oxidation (redox) categories: (1) oxic, (2) suboxic, (3) mixed, and (4) anoxic. Within the anoxic category, groundwater was further characterized into four presumed predominant reduction processes: (1) iron or sulfate or both $[\text{Fe(III)}/\text{SO}_4]$ reducing, (2) iron $[\text{Fe(III)}]$ reducing, (3) iron and sulfate $[\text{Fe(III)-SO}_4]$ reducing, or (4) methanogenic, as defined by composition of redox species. The oxic category was associated with calcium-bicarbonate-type water, and the methanogenic-anoxic process was associated exclusively with the sodium-bicarbonate-type water. The species of arsenic and the dominant radionuclide present were associated with specific redox categories. Arsenate was associated primarily with oxic water and did not exceed 3.5 $\mu\text{g/L}$, whereas arsenite was associated with iron-reducing, anoxic water samples and, at the highest concentrations, occurred in sulfate-reducing, anoxic; methanogenic-anoxic; or both water samples. Uranium was associated exclusively with the oxic water, whereas the highest concentrations of combined radium were associated with the iron-reducing, anoxic water. The gross alpha-particle activity was greatest in the oxic waters where the source of the radioactivity was the uranium.

Associated geochemical conditions conducive for mobility of arsenic and radionuclides and their spatial and vertical extent in the Gulf Coast aquifer system in Houston are important aspects to the areal management of the municipal

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groundwater supplies in Houston. Ongoing research is seeking to define chemical or geological factors that are the optimal indicators for elevated concentrations of these naturally occurring constituents.

Introduction

Groundwater is used as the source water (the raw, ambient water withdrawn from municipal supply wells prior to water treatment) for a portion of the municipal water-supply needs of Houston, Texas. The primary sources of groundwater for the Houston area are the Evangeline and Chicot aquifers, the top two units of the Gulf Coast aquifer system (figs. 1–2). The city of Houston and the surrounding metropolitan area are hereinafter referred to as Houston in this report. Historically, groundwater withdrawals in Houston have increased over time, primarily for municipal use. Land subsidence caused by the overwithdrawal of groundwater dewatering compressible clay layers underlying Houston has been ongoing throughout the 20th century (Coplin and Galloway, 1999; Ryder and Ardis, 2002). The land subsidence has been accompanied by increased frequency and extent of flooding and fault activity in parts of Houston (Coplin and Galloway, 1999; Ryder and Ardis, 2002). To address these concerns, the Texas legislature created the Harris-Galveston Coastal Subsidence District in 1975 to regulate groundwater withdrawal in the area and increase the use of surface water to prevent future subsidence (Ryder and Ardis, 2002). The Harris-Galveston Subsidence District Regulatory Plan was developed with the overall goal to reduce groundwater withdrawal to no more than 20 percent of total water demand in Harris and Galveston Counties (Harris-Galveston Subsidence District, 2013).

Even though the Regulatory Plan is to reduce groundwater use in Houston, the population of the area is expected to continue to grow rapidly. Maintaining the drinking-water quantity and quality of the municipal water supply is a priority for the water resource managers in the area regardless of the source. Recent changes to the U.S. Environmental Protection Agency (EPA) primary drinking-water regulations for arsenic (As) and a selected number of natural radionuclides (U.S. Environmental Protection Agency, 2000, 2001) have highlighted the necessity for municipal supply system managers to be aware of the occurrence and distribution of these constituents in their source water.

The sediments composing the Gulf Coast aquifer system were deposited under fluvial-deltaic to shallow marine environments during the Tertiary and Quaternary periods (Chowdhury and Turco, 2006). High As concentrations in groundwater are common in Holocene- (Quaternary) age deltaic sediments (sands, silts, and clays) because of a combination of factors related to the young age of the sediments undergoing rapid change from oxidizing to a reducing environment following sediment burial, conditions favorable for As mobilization, and low “flushing rates” that allow As to accumulate in slow-moving groundwater

(Kinniburgh and others, 2003). The Holocene-age deltaic sediments in Bangladesh and other parts of southern Asia are prominent examples of groundwater systems prone to high As concentrations, but similar groundwater systems also are found in many other parts of the world. High concentrations of As and natural radionuclides in groundwater have been documented to occur in several regions of the United States, including parts of Texas (Focazio and others, 2000; Welch and others, 2000; Focazio and others, 2001; DeSimone, 2009; Szabo and others, 2012). Targeted reconnaissance sampling by Focazio and others (2001) has shown that Texas is one of more than a dozen States to have relatively large concentrations of radium (Ra) in water from aquifers used for municipal supply. Chowdhury and others (2006) also analyzed the As and radionuclide data available in the Texas Water Development Board (TWDB) groundwater database for the Gulf Coast aquifer system. Relatively high gross alpha-particle activities (61 to 210 picocuries per liter [pCi/L]) were measured in water from wells screened in the Evangeline aquifer, part of the Gulf Coast aquifer system, in Harris County and other counties in southern Texas (Chowdhury and others, 2006; figs. 5–24). The As concentrations measured from samples obtained from three aquifers (Chicot, Evangeline, Jasper) composing the Gulf Coast aquifer system were highly variable in each aquifer, especially with depth (Chowdhury and others, 2006). Previous studies done in Houston have indicated the presence of occasionally high concentrations of As, radon-222 (Rn-222), and Ra-226 in groundwater (Cech, Howard, and others, 1987; Cech, Lemma, and others, 1987).

Many contaminants in groundwater are derived from aquifer materials and thus occur naturally. Some of the most common naturally occurring contaminants in groundwater are As, uranium (U), and Ra. In a national survey of more than 6,000 domestic wells, naturally occurring contaminants, with the exception of nitrate and fecal indicator bacteria, were many times more prevalent in concentrations exceeding water-quality benchmarks for human health than were organic compounds released to the environment by human activity (DeSimone, 2009). A national study on nitrate in groundwater found that high nitrate concentrations were least common in deep municipal supply wells, with concentrations greater than 1.0 milligrams per liter (mg/L) measured in only 10 percent of the deep municipal supply wells. High nitrate concentrations were also more prevalent in young groundwater (tritium greater than 2.5 pCi/L, recharged post 1963) than in old groundwater (Burrow and others, 2010). Land and others (1999) found that median nitrate concentrations for the Gulf Coast aquifer system were less than the 25th percentile of comparable aquifers nationwide (among the lowest 25 percent nationally). In the Gulf Coast aquifer system, nitrate concentrations were less than 0.5 mg/L in sampled wells ranging in depths from 180 to 490 feet (ft) (Reutter and Dunn, 2000), which were much shallower than most of the wells sampled in this study. On the basis of the information gained from these studies, it is likely that nitrate concentrations were less than 0.5 mg/L for the deep supply wells sampled in this study.

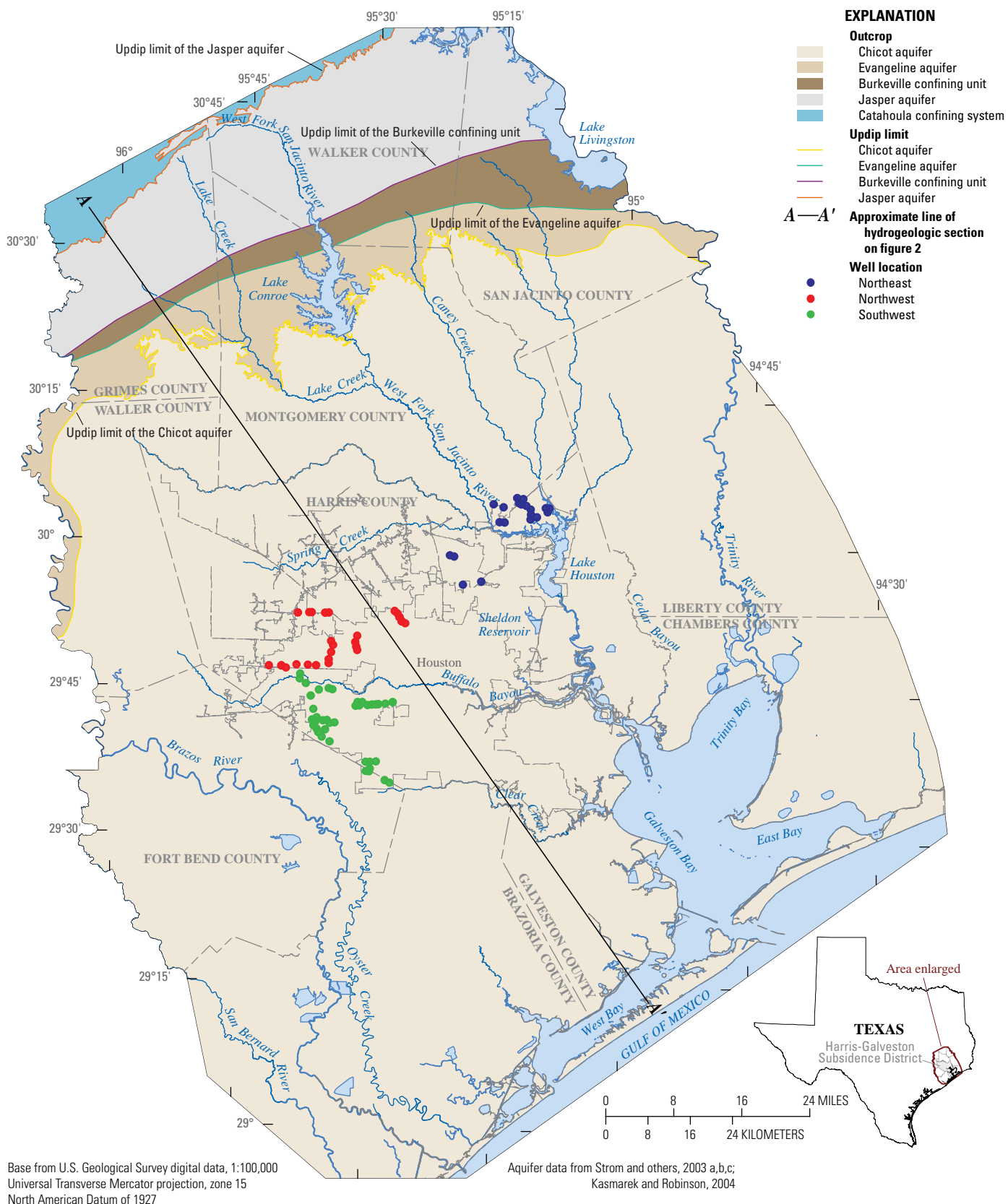


Figure 1. Location of 91 municipal supply wells in Houston, Texas, that were sampled during 2007–11.

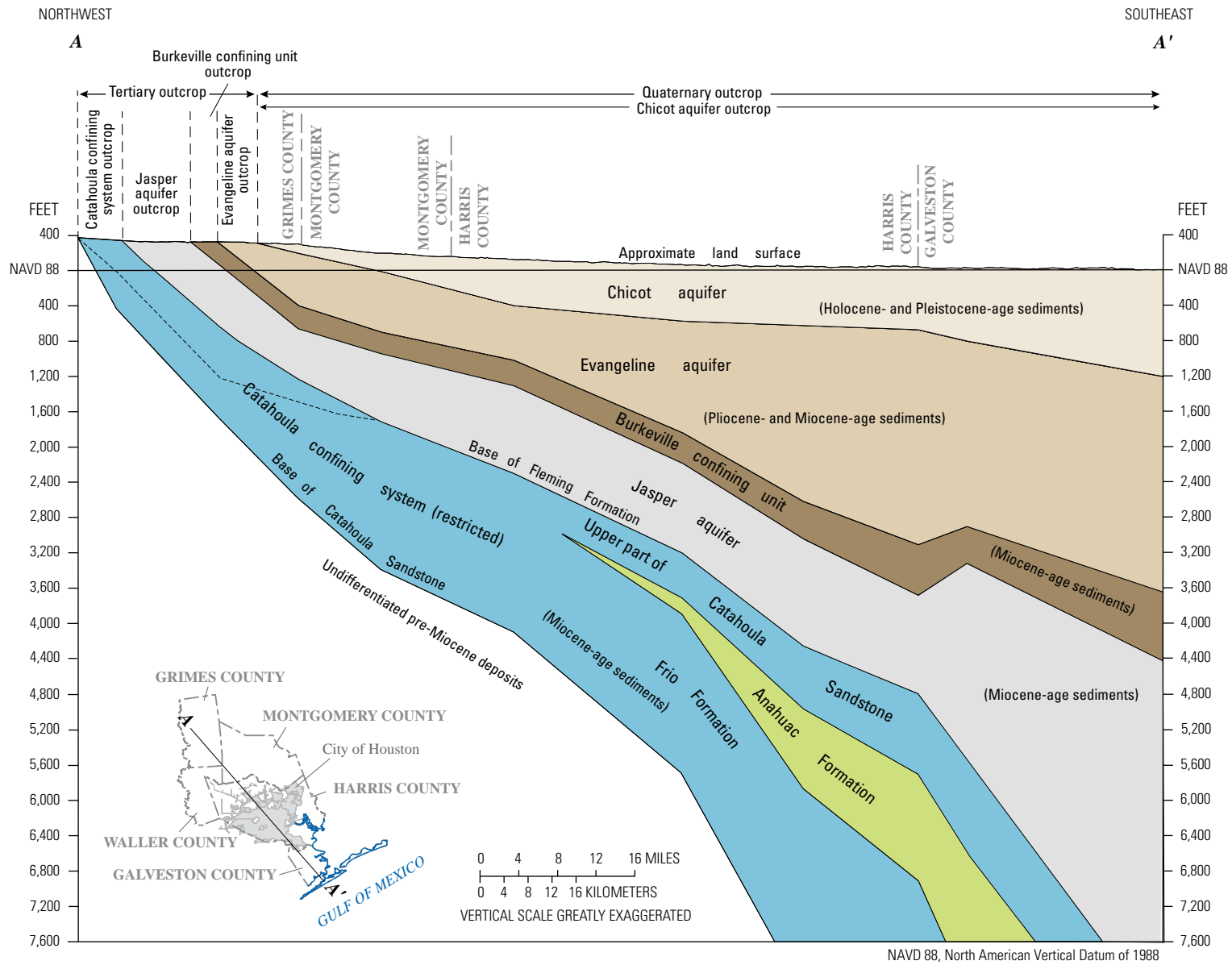


Figure 2. Hydrogeologic section of the Gulf Coast aquifer system in Harris County and adjacent counties, Texas (modified from Baker, 1979, fig. 4).

The natural occurrence of As, U, and Ra are related to aquifer characteristics, mineralogy (including the presence of these constituents in the rocks that compose the aquifer), and geochemical conditions. Chemical inputs also might change the geochemistry of the aquifer and thereby increase the mobility of these compounds (Szabo and others, 1997; Welch and others, 2000; Jurgens, Fram, and others, 2009; Ayotte and others, 2011). Most trace elements' mobility in groundwater, including As and radionuclides, are controlled by geochemical conditions, especially pH, reduction-oxidation (redox) processes, ionic strength (related to total dissolved solids), and major-ion composition by controlling speciation, complexation (Turner and others, 1981), solubility, and electrostatic interactions (sorption/exchange) with the solid matrix (Szabo and others, 1997).

Inorganic As can occur in several forms or species depending upon redox conditions, but among inorganic forms, it primarily occurs as trivalent [As(III)] or pentavalent [As(V)] species in natural waters (Abernathy and Chappell, 1997; National Research Council, 1999; Smedley and Kinniburgh, 2002; Hughes and others, 2011). The solubility of the different inorganic forms of As varies depending on the geochemical conditions of the groundwater system (Hodge and others, 1998; Smedley and Kinniburgh, 2002). Arsenite [As(III)] is the stable form of aqueous arsenic in moderately reduced (oxygen depleted) water, and arsenate [As(V)] is the stable form of arsenic in oxic water (Welch and others, 2000); therefore, speciation of As is of considerable interest in defining the specific geochemical conditions and factors affecting the mobilization of As. The trivalent As(III) form is considered slightly more carcinogenic than the pentavalent As(V) form upon human ingestion, but recent biochemical studies indicate that much of the As(V) is converted to As(III) as the As is metabolized in the human body (Hughes and others, 2011). Similarly, the decay of naturally occurring U-238 and thorium-232 (Th-232) produces other intermediate radioactive elements (progeny) (Faure, 1977; Durrance, 1986), all of which have individually distinct chemistries, resulting in detectable concentrations of these elements over a wide range of geochemical conditions. The most common radionuclides in groundwater are Ra-226, Ra-228, Rn-222, U-238, and U-234 originating from the decay of the long-lived U-238 and Th-232 that are present in all soils and rocks (Szabo and Zapecza, 1991; Wanty and others, 1992); for example, Ra-228 is the direct progeny of Th-232, whereas Ra-226 occurs in the U-238 decay series after the decay of Th-230. A diagram of the U-238 and Th-232 radioactive decay series is provided in figure 3. Radium is most mobile in reducing conditions (Szabo and others, 2012), in chloride-rich mineralized waters (Kraemer and Reid, 1984; Miller and Sutcliffe, 1985), or in acidic conditions (Oden and others, 2000; dePaul and Szabo, 2007). The radionuclide Ra-226 decays to Rn-222, a naturally occurring radioactive gas, which is strongly soluble, and therefore abundant in groundwater (Hall and others, 1985).

Gross (alpha and beta particle) radioactivity measurements represent the total alpha-particle and beta-particle activity of all the radionuclides present in the sample in the given period of time associated with the measurement (Parsa, 1998) and are useful and inexpensive "screening analytes" for the occurrence of radionuclides.

To better understand the occurrence and distribution of As and selected radionuclides in relation to geochemical conditions, the U.S. Geological Survey (USGS), in cooperation with the City of Houston, collected water-quality data during 2007–11 from 91 municipal supply wells completed in the Gulf Coast aquifer system in Houston (fig. 1). These data were collected as part of an ongoing study to determine concentrations, spatial extent, and associated geochemical conditions that might be conducive for mobility and transport of selected naturally occurring trace elements and radionuclides in the Gulf Coast aquifer system in Houston. The wells were sampled in phases, with 28 wells sampled during 2007–8, 60 wells sampled during 2010, and 3 wells sampled during December 2011. The sampled wells are clustered in northeastern, northwestern, and southwestern Houston; hereinafter referred to as northeast, northwest, and southwest Houston areas (fig. 1). Field measurements were made of selected physicochemical properties at each sampling site. The samples were analyzed for major ions, residue on evaporation (dissolved solids), trace elements, and selected radionuclides and measures of radioactivity. Results from 75 of the 91 wells sampled were summarized in Oden and others (2010, 2011). The results from all 91 samples are discussed, and the results from the samples collected from 16 of 91 wells and radionuclide results not published elsewhere are included in appendix 1 of this report.

Purpose and Scope

This report summarizes the ranges of concentrations for As, As species, and selected radionuclides in the Gulf Coast aquifer system in Houston by using analytical results from 91 municipal supply wells sampled by the USGS during 2007–11. Concentrations of these analytes are described with respect to the geochemistry. The spatial and vertical extent of geochemical conditions were considered when evaluating analyte concentrations in order to determine where natural contamination is possibly occurring on the basis of geochemical changes along hydrologic flow paths identified by redox and cation-exchange conditions. Water types were identified on the basis of the dominant cations and anions by using graphical analysis, and redox categories were based on the concentrations of redox sensitive species. The water types and redox categories that co-occur with, and in most cases control, the distributions of As and radionuclides are characterized with respect to sample depth and spatial location in the aquifer system.

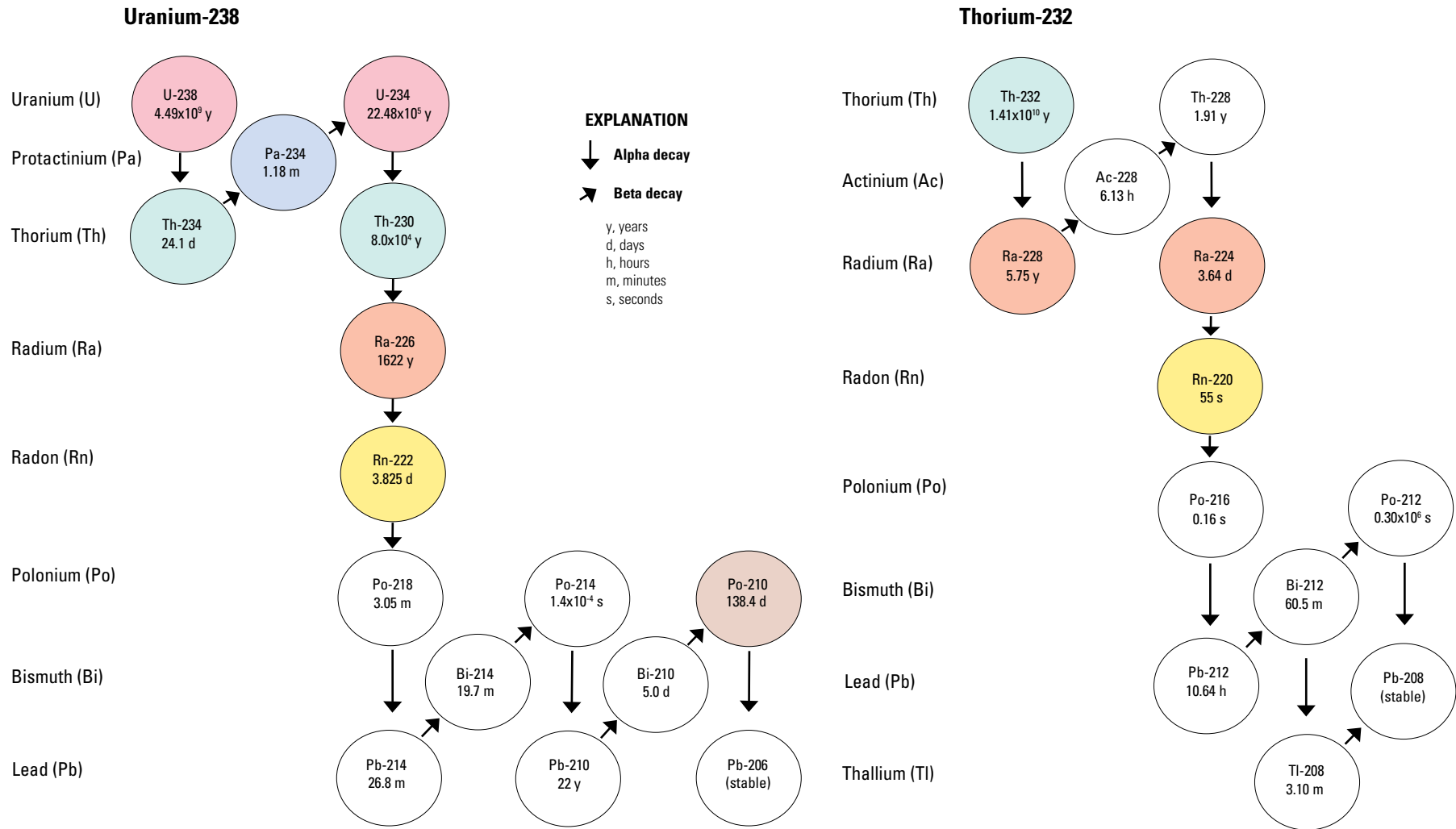


Figure 3. Uranium-238 and thorium-232 radioactive decay series. Colors indicate those radionuclides mentioned in report.

This report also documents source-water (raw ambient groundwater) quality prior to drinking-water treatment, which can differ from the quality of the finished drinking water distributed through municipal water-supply systems. The source-water samples were collected for assessment of aquifer conditions in order to provide community water-system operators information that could be important when they make decisions about which treatment processes to apply before distributing finished drinking water.

Description of Study Area

A detailed description of the study area, including the history of the local water supply and description of the hydrogeology and geologic setting, is provided in Oden and others (2010, 2011). Briefly, Houston is the fourth largest city in the country, with an estimated population of approximately 2,099,451 residents as of April 1, 2010 (U.S. Census Bureau, 2013a). The Houston metropolitan area population of 5.95 million in 2010 is the sixth largest among United States metropolitan statistical areas and represents a 26-percent increase since 2000 (U.S. Census Bureau, 2013b). The source of groundwater for the city of Houston is the Gulf Coast aquifer system, which consists of the Chicot aquifer, Evangeline aquifer, Burkeville confining unit, and the Jasper aquifer (fig. 2). The Chicot and Evangeline aquifers are the primary sources of groundwater used for municipal supply for the city. The Chicot and the underlying Evangeline aquifers are hydraulically connected (not separated by a distinct confining unit) but are classified on the basis of a gradational decrease in grain size with depth.

The Gulf Coast aquifer system consists of a fluvial-deltaic wedge of discontinuous beds of sand, silt, and clay sediments ranging in age from Miocene to Holocene that were deposited in layers that dip and thicken towards the Gulf of Mexico (Ryder, 1996). The sediment deposits are exposed at land surface (crop out) in bands that parallel the Gulf of Mexico. The Gulf Coast aquifer system reflects three depositional environments: (1) continental (alluvial plain), (2) transitional (delta, lagoon, and beach), and (3) marine (continental shelf). Coarser grained nonmarine deposits crop out within and updip from Houston, form the aquifers in the subsurface beneath Houston, and grade laterally downdip into finer grained material that was deposited in marine environments adjacent to the coast. The youngest of these deposits forms the Chicot aquifer, crops out north of Houston, and thickens appreciably towards the Gulf of Mexico (fig. 2). The sediments forming the Chicot aquifer are the coarsest grained. The lenticular sand and clay beds of the aquifer system have lateral and vertical boundaries that are gradational, poorly constrained, and difficult to trace for more than a few miles (Renken, 1998). Cyclical sedimentation facies were formed over geologic time from sea-level transgressions and regressions. During periods of sea-level decline, fluvial-deltaic processes deposited continental

sediments, and as sea level rose, the continental sediments were reworked and marine sediments were deposited, creating a high degree of heterogeneity in lateral and vertical extents (Sellards and others, 1932).

Water with dissolved solids concentrations less than 3,000 mg/L (fresh to slightly saline water) varies with depth within a given aquifer of the Gulf Coast aquifer system and generally becomes more saline with increasing depth and proximity of the Gulf of Mexico (Ryder and Ardis, 2002). Chowdhury and others (2006) analyzed the chemical compositions of about 600 groundwater samples from the TWDB groundwater database and found that concentrations of bicarbonate (HCO_3^-), sodium (Na), and chloride (Cl) increased along flow paths; increased Na-to-Cl ratios from the shallower to deeper aquifers were likely caused either by progressive cation-exchange reactions or mixing of saline water from deeper subsurface with HCO_3^- -rich water penetrating into the subsurface. The spatial increase in salinity is an important water-quality feature in the individual aquifers forming the Gulf Coast aquifer system because it can limit use of the water for drinking purposes and requires treatment or mixing with less mineralized water (Ryder and Ardis, 2002). Three salt-dome basins occur across the area from southern Texas to southern Mississippi penetrating most or all of the overlying strata at any given location (Weiss, 1992). The upward intrusions of the salt domes decrease the thickness of the adjacent aquifer sediments radially and alter the hydraulic characteristics and flow paths in the adjacent aquifer sediments. These distributed salt domes increase the heterogeneity of the hydraulic characteristics of the aquifers (Kasmarek and Robinson, 2004). The effect of these salt domes on groundwater quality is localized with highly mineralized water occurring deep in the aquifer system from salt dissolution (Weiss, 1992). Localized elevated concentrations of Rn-222 and Ra-226 in the groundwater occur near salt domes (Cech, Howard, and others, 1987; Cech, Lemma, and others, 1987), and the concentration of Ra-226 is positively and strongly correlated to increasing salinity (Kraemer and Reid, 1984).

In the Gulf Coast aquifer system, U deposits, called roll-front type U deposits, are located along a belt from east-central to southern Texas in late Eocene- to Pliocene-age sedimentary beds that generally dip towards the Gulf Coast (Eargle and others, 1975; Cook, 1980). The host rocks that contain the roll-front type U deposits in the Houston area are composed of Catahoula Tuff and Oakville Sandstone of Miocene age and Goliad Sand of Pliocene age (Eargle and others, 1975) that generally coincide with the following hydrogeologic units: Catahoula confining system, Jasper aquifer, and Evangeline aquifer of the Gulf Coast aquifer system (Baker, 1979). The sources of these U deposits are volcanic rocks formed in western Texas and northern Mexico in the late Eocene age, which eroded, mixed with sediments, and were eventually deposited on redox boundaries near streams along the Coastal Plain (Eargle and others, 1975).

8 Arsenic and Radionuclide Occurrence and Relation to Geochemistry in Groundwater of the Gulf Coast Aquifer System

In 2004, the USGS developed a numerical finite difference (MODFLOW) model to simulate groundwater flow and land-surface subsidence in the northern part of the Gulf Coast aquifer system in Texas from predevelopment (before 1891) through 2000 (Kasmarek and Robinson, 2004). This model was developed as part of the TWDB Groundwater Availability Modeling (GAM) program. In 2012, the USGS prepared a groundwater model of the Houston area referred to as the “Houston Area Groundwater Model (HAGM)” to meet the need identified by water managers to upgrade the GAM to more accurately reflect recent (2009) conditions (Kasmarek, 2012). The HAGM simulates groundwater flow and land-surface subsidence in the Chicot and Evangeline aquifers and parts of the Jasper aquifer and Burkeville confining unit from predevelopment (before 1891) through 2009 (Kasmarek, 2012). The hydrogeologic units and geological setting of the Gulf Coast aquifer system used in the HAGM coincided with the GAM. Both models consist of 4 layers, 1 for each of the hydrogeologic units of the aquifer system. The hydrogeology of the Gulf Coast aquifer system for both models was based on Baker (1979, 1986) and Ashworth and Hopkins (1995). The estimated altitudes (measured in reference to North American Vertical Datum of 1988 [NAVD 88] or converted to feet below NAVD 88; hereinafter referred to as “datum”) of the bases of the Chicot and Evangeline aquifers were determined for the models from digital data of Strom and others (2003a, b), which were derived from original sources of base-altitude data for the aquifer layers, including Baker (1979, figs. 2, 6, 7; 1986, fig. 7), Carr and others (1985, figs. 4, 5, 6, 7), Kasmarek and Strom (2002, figs. 5, 7), and Jorgensen (1975, figs. 4, 7).

For the model area encompassing 38 counties in Texas, the conceptual model of the Gulf Coast aquifer system is that the fraction of precipitation that does not evaporate, transpire through plants, or run off the land surface to streams enters the groundwater-flow system in topographically high areas where the hydrogeologic units crop out in the northwest part of the study area. Water infiltrates to the saturated zone and flows short distances through shallow zones before much of it discharges to streams; the remainder of the water flows to intermediate and deep zones of the system southeast of the outcrop area where it is discharged by wells and by upward leakage (much less in postdevelopment compared to predevelopment) in topographically low areas near or along the coast (Kasmarek and Robinson, 2004). Water-level maps for the Chicot, Evangeline, and Jasper aquifers show that the regional groundwater-flow direction is east towards the Gulf of Mexico (Chowdhury and others, 2006).

Natural (predevelopment) groundwater flow can be divided into local (shallow, water-table zones with relatively short flow paths and nearby discharge areas), intermediate (intermediate, semiconfined zones with relatively deeper flow paths and downgradient discharge areas), and regional (deep, confined zones with relatively long flow paths and distal discharge areas) flow systems (Tóth, 1963; Johnston, 1999). The actual flow system is more complex than this generalized conceptual description because the heterogeneous nature of

the paleodepositional environment often results in tortuous flow paths. Furthermore, variable groundwater withdrawals from the aquifers that affect the rates of recharge to and discharge from the Chicot, Evangeline, and Jasper aquifers also affect the orientation of the flow paths (Kasmarek and Robinson, 2004).

The aquifer system is under water-table conditions (that is, not confined under pressure) in the uppermost parts of the aquifer system in the outcrop areas. The aquifer system transitions to semiconfined and confined conditions as thickness and depth increase, and the number of interbedded sand and clay layers increases in the subsurface. Because this transition to confined conditions with increasing depth is gradual, assigning specific depth horizons to various (shallow, intermediate, and deep) hydrologic zones or defining the depth where the confined part of the aquifer begins is problematic (Kasmarek and Robinson, 2004).

Oden and Truini (2013) logged eight observation wells with borehole geophysical tools and identified many interbedded silt and clay layers within the water-bearing sands of the Chicot and Evangeline aquifers in Montgomery County, Tex., north of Houston. Clay lenses were identified ranging from a few feet to tens of feet thick in the unsaturated zone or near the land surface that might impede the downward movement of water from the surface to the aquifer and show that, on a local scale, groundwater-flow paths might have a larger lateral extent than previously discussed by others (Oden and Truini, 2013). These clay lenses create localized confinement of the Chicot aquifer. The Evangeline aquifer is considered mostly confined except in the narrow zone where it crops out north of Houston because of the effects of the many interbedded clays in the overlying Chicot aquifer on the flow paths, thereby affecting the hydraulic heads (Gabrysch, 1984).

Because the Chicot and Evangeline aquifers are hydraulically connected, groundwater withdrawals have increased vertical-head gradients and have induced downward flow from local and intermediate flow systems to the regional flow system (Gabrysch, 1979). Initially, Harris and Galveston Counties (a large part of Houston) represent 1 of 3 principal areas of concentrated groundwater withdrawals from the Gulf Coast aquifer system in the model area (Kasmarek and Robinson, 2004; Kasmarek, 2012). The groundwater-withdrawal rate exceeded 450 million gallons per day (Mgal/d) in 1976 (Kasmarek and Robinson, 2004). For 2000–10, the average withdrawal in Harris County was 263.7 Mgal/d, or about a 38-percent reduction compared to withdrawals in 1976, and in Galveston County, where withdrawals have decreased more than any other county in the area, the average withdrawal was about 1.21 Mgal/d, or about a 96-percent reduction compared to withdrawals in 1976 (Kasmarek and Johnson, 2013). Primarily in Houston, groundwater development has caused substantial (as much as 350 ft) declines of the potentiometric surfaces of the aquifers and subsequent land-surface subsidence (Kasmarek and Robinson, 2004). A substantial amount of the total water withdrawn, as much as 19 and 10 percent of the simulated

total water budget of the Chicot and Evangeline aquifers, is derived from dewatering of the clay layers of the aquifers (Kasmarek and Strom, 2002). During 1977–2010, the water-level altitude change of the Chicot aquifer ranged from a 140-ft decline in north-central Harris County to a 200-ft rise in southeastern Harris County, and the water-level altitude change of the Evangeline aquifer ranged from a 320-ft decline to a 220-ft rise in the same areas (Kasmarek and others, 2010). Groundwater withdrawals in Houston result in large cones of depression. Regional groundwater-flow direction from the outcrop areas is towards the center of these cones of depression as opposed to flowing towards the Gulf of Mexico, and with continued groundwater withdrawal, natural discharge areas might decrease, recharge areas might increase, and aquifer storage might decline (Chowdhury and others, 2006).

Well Information

Well data for 75 of the 91 municipal supply wells sampled during 2007–11 were previously published (Oden and others, 2010, 2011), including well depth, depth to top of open interval and bottom of open interval, date of construction, aquifer code, and lithology code. The well data for the remaining 16 wells are included in this report in appendix 2. The USGS National Water Information System (NWIS) aquifer codes assigned to the 91 sampled wells include the Chicot aquifer (112CHCT) for 3 wells, Evangeline aquifer (121EVGL) for 48 wells, and Chicot and Evangeline aquifers (112CEVG) for 40 wells. In order to describe the part of the aquifer or aquifers intersected in detail, the wells were further classified into completion types on the basis of the open interval of each well and the altitude of that interval (table 1). By comparing completion types for the sampled wells, it can be demonstrated that the sampled wells of approximately the

same depth intersect different parts of the aquifer systems, depending upon their spatial location (northeast, northwest, or southwest Houston areas). This difference based on well location is because the aquifer system is a thick wedge of interbedded sand and clay layers thickening and dipping towards the southeast. Consequently, water of differing chemistry in the different areas was likely to have been drawn from wells of approximately similar depths and open intervals.

Before comparing the altitudes of the open intervals, wells were grouped by general location (northeast, northwest, or southwest Houston areas). The altitudes of the top and bottom of the open intervals for the wells sampled are presented graphically in figures 4–6, sorted by area; also shown are the altitudes of the bases of the Chicot and Evangeline aquifers at each well location as estimated in Strom and others (2003a, b). The estimated minimum and maximum altitudes for the base of the Evangeline aquifer in the southwest area are at greater depths below datum than in the northeast and northwest areas (figs. 4–6). When compared across the areas, the ranges of the altitudes of the tops and bottoms of the open intervals for the wells sampled are similar (figs. 4–6). The comparison of the open interval altitudes to the altitudes of the aquifer units at the well locations is useful for determining relations of aquifer units with depth and increases in aquifer thickness towards the south and southeast. A notable difference is shown among these three areas; the open intervals of the wells appear to be of an increasing distance above the base of the Evangeline aquifer (top of the Burkeville confining unit) towards the south, thereby intersecting different parts or layers of the aquifers in the different areas (figs. 4–6). When considering open interval depth below datum, the open intervals overlap with depth throughout the area, but the open intervals are not intercepting the same strata throughout because of the dip and increase in the Gulf Coast aquifer system thickness towards the south.

Table 1. Station number, State well number, land-surface altitude from Groundwater Availability Modeling (GAM) program, depths to top of open interval and bottom of open interval, altitudes of top of open interval and bottom of open interval, altitudes of base of Chicot aquifer and base of Evangeline aquifer, and classification of open interval penetration into aquifer for municipal supply wells sampled in Houston, Texas, 2007–11.

[USGS, U.S. Geological Survey; NAVD 88; North American Vertical Datum of 1988; ft bls, feet below land surface; LJ, Harris County; TS, Montgomery; JY, Fort Bend; CHCT, Chicot aquifer; EVGL, Evangeline aquifer]

USGS station number	State well number	Land-surface altitude from GAM program (feet) (NAVD 88)	Depth to top of open interval (ft bls)	Depth to bottom of open interval (ft bls)	Altitude of top of open interval (feet) (NAVD 88) (figs. 4–6)	Altitude of bottom of open interval (feet) (NAVD 88) (figs. 4–6)	Altitude of base of Chicot (feet) (NAVD 88) (figs. 4–6)	Altitude of base of Evangeline (feet) (NAVD 88) (figs. 4–6)	Completion type ¹	Aquifer designation grouping ²
Northeast area (20 wells)										
295616095170101	LJ-65-06-601	73	440	595	-367	-522	-483	-1,682	lowerCHCT, upperEVGL	lowerCHCT, upperEVGL
300223095142101	LJ-60-63-715	84	364	402	-280	-318	-304	-1,346	lowerCHCT, upperEVGL	lowerCHCT, upperEVGL
295850095201301	LJ-65-06-103	94	660	1,535	-566	-1,441	-446	-1,506	fullyEVGL	fullyEVGL
295855095204301	LJ-65-06-102	97	645	1,520	-548	-1,423	-452	-1,496	fullyEVGL	fullyEVGL
295553095191201	LJ-65-06-528	78	800	1,680	-722	-1,602	-495	-1,660	fullyEVGL	fullyEVGL
300355095093501	LJ-60-63-602	72	744	1,140	-672	-1,068	-323	-1,600	middleEVGL	middleEVGL
300343095090301	LJ-60-63-604	67	748	1,108	-681	-1,041	-331	-1,629	middleEVGL	middleEVGL
300331095092201	LJ-60-63-603	70	752	876	-682	-806	-331	-1,616	middleEVGL	middleEVGL
300446095121901	TS-60-63-507	81	850	1,170	-769	-1,089	-299	-1,466	middleEVGL	middleEVGL
300225095144202	LJ-60-63-709	86	725	953	-639	-867	-304	-1,264	middleEVGL	middleEVGL
300334095113401	LJ-60-63-504	63	657	1,080	-594	-1,017	-316	-1,498	middleEVGL	middleEVGL
300258095145301	TS-60-63-404	89	790	1,036	-701	-947	-301	-1,432	middleEVGL	middleEVGL
300248095105301	LJ-60-63-505	49	730	1,116	-681	-1,067	-338	-1,565	middleEVGL	middleEVGL
300408095115201	LJ-60-63-503	76	860	1,045	-784	-969	-306	-1,483	middleEVGL	middleEVGL
300302095113301	LJ-60-63-511	49	662	1,024	-613	-975	-325	-1,506	middleEVGL	middleEVGL
300231095113701	LJ-60-63-508	45	664	898	-619	-853	-334	-1,519	middleEVGL	middleEVGL
300403095125402	LJ-60-63-502	79	747	828	-668	-749	-303	-1,462	middleEVGL	middleEVGL
300359095122902	LJ-60-63-510	73	782	821	-709	-748	-305	-1,470	middleEVGL	middleEVGL
300426095123902	LJ-60-63-407	84	732	820	-648	-736	-301	-1,463	middleEVGL	middleEVGL
300419095154301	TS-60-62-604	91	1,164	1,450	-1,073	-1,359	-303	-1,417	lowerEVGL	lowerEVGL
Northwest area (29 wells)										
295207095262102	LJ-65-13-221	90	321	556	-231	-466	-537	-1,597	fullyCHCT	lowerCHCT, upperEVGL
294921095312907	LJ-65-12-633	92	372	710	-280	-618	-543	-1,645	lowerCHCT, upperEVGL	lowerCHCT, upperEVGL
294721095361001	LJ-65-12-719	102	558	1,117	-456	-1,015	-576	-1,720	lowerCHCT, upperEVGL	lowerCHCT, upperEVGL
295249095370701	LJ-65-04-729	125	580	1,066	-455	-941	-521	-1,501	lowerCHCT, upperEVGL	lowerCHCT, upperEVGL

Table 1. Station number, State well number, land-surface altitude from Groundwater Availability Modeling (GAM) program, depths to top of open interval and bottom of open interval, altitudes of top of open interval and bottom of open interval, altitudes of base of Chicot aquifer and base of Evangeline aquifer, and classification of open interval penetration into aquifer for municipal supply wells sampled in Houston, Texas, 2007–11.—Continued

[USGS, U.S. Geological Survey; NAVD 88; North American Vertical Datum of 1988; ft bls, feet below land surface; LJ, Harris County; TS, Montgomery; JY, Fort Bend; CHCT, Chicot aquifer; EVGL, Evangeline aquifer]

USGS station number	State well number	Land-surface altitude from GAM program (feet) (NAVD 88)	Depth to top of open interval (ft bls)	Depth to bottom of open interval (ft bls)	Altitude of top of open interval (feet) (NAVD 88) (figs. 4–6)	Altitude of bottom of open interval (feet) (NAVD 88) (figs. 4–6)	Altitude of base of Chicot (feet) (NAVD 88) (figs. 4–6)	Altitude of base of Evangeline (feet) (NAVD 88) (figs. 4–6)	Completion type ¹	Aquifer designation grouping ²
Northwest area (29 wells)—Continued										
294952095342601	LJ-65-12-519	105	634	1,184	-529	-1,079	-550	-1,561	lowerCHCT, upperEVGL	lowerCHCT, upperEVGL
294702095394001	LJ-65-11-917	97	636	1,288	-539	-1,191	-527	-1,723	upperEVGL	lowerCHCT, upperEVGL
295204095261301	LJ-65-13-225	90	714	1,050	-624	-960	-539	-1,594	upperEVGL	lowerCHCT, upperEVGL
294731095414201	LJ-65-11-514	110	796	1,316	-686	-1,206	-547	-1,681	upperEVGL	lowerCHCT, upperEVGL
294800095344101	LJ-65-12-516	101	705	1,150	-604	-1,049	-579	-1,691	upperEVGL	lowerCHCT, upperEVGL
294712095401301	LJ-65-11-803	103	742	1,384	-639	-1,281	-542	-1,709	upperEVGL	lowerCHCT, upperEVGL
294735095344001	LJ-65-12-521	95	804	1,349	-709	-1,254	-586	-1,711	upperEVGL	lowerCHCT, upperEVGL
294723095382601	LJ-65-11-920	102	627	1,238	-525	-1,136	-515	-1,725	upperEVGL	lowerCHCT, upperEVGL
295150095254601	LJ-65-13-214	91	644	1,493	-553	-1,402	-554	-1,597	lowerCHCT, fullyEVGL	lowerCHCT, fullyEVGL
295228095262901	LJ-65-13-220	90	613	1,653	-523	-1,563	-521	-1,602	lowerCHCT, fullyEVGL	lowerCHCT, fullyEVGL
295247095344701	LJ-65-04-811	114	448	1,460	-334	-1,346	-539	-1,390	lowerCHCT, fullyEVGL	lowerCHCT, fullyEVGL
294950095313701	LJ-65-12-622	95	610	1,470	-515	-1,375	-533	-1,580	lowerCHCT, fullyEVGL	lowerCHCT, fullyEVGL
295246095351301	LJ-65-04-723	117	599	1,489	-482	-1,372	-536	-1,407	lowerCHCT, fullyEVGL	lowerCHCT, fullyEVGL
294900095312101	LJ-65-12-619	90	630	1,440	-540	-1,350	-550	-1,699	lowerCHCT, fullyEVGL	lowerCHCT, fullyEVGL
294717095401001	LJ-65-11-804	110	610	1,626	-500	-1,516	-542	-1,707	lowerCHCT, fullyEVGL	lowerCHCT, fullyEVGL
295251095264502	LJ-65-05-814	93	648	1,689	-555	-1,596	-504	-1,610	fullyEVGL	fullyEVGL
295306095270502	LJ-65-05-813	91	601	1,470	-510	-1,379	-482	-1,607	fullyEVGL	fullyEVGL
294723095370501	LJ-65-12-730	102	685	1,692	-583	-1,590	-545	-1,726	fullyEVGL	fullyEVGL
294925095341201	LJ-65-12-520	102	831	1,510	-729	-1,408	-555	-1,595	fullyEVGL	fullyEVGL
294844095342401	LJ-65-12-522	100	847	1,530	-747	-1,430	-566	-1,648	fullyEVGL	fullyEVGL
295243095383101	LJ-65-03-916	127	769	1,354	-642	-1,227	-520	-1,512	fullyEVGL	fullyEVGL
295249095364701	LJ-65-04-728	124	825	1,418	-701	-1,294	-522	-1,499	fullyEVGL	fullyEVGL
295203095261401	LJ-65-13-224	90	1,072	1,610	-982	-1,520	-539	-1,594	lowerEVGL	lowerEVGL
295228095263101	LJ-65-13-222	90	1,168	1,641	-1,078	-1,551	-521	-1,602	lowerEVGL	lowerEVGL
295027095312301	LJ-65-12-328	95	1,062	1,450	-967	-1,355	-522	-1,517	lowerEVGL	lowerEVGL

Table 1. Station number, State well number, land-surface altitude from Groundwater Availability Modeling (GAM) program, depths to top of open interval and bottom of open interval, altitudes of top of open interval and bottom of open interval, altitudes of base of Chicot aquifer and base of Evangeline aquifer, and classification of open interval penetration into aquifer for municipal supply wells sampled in Houston, Texas, 2007–11.—Continued

[USGS, U.S. Geological Survey; NAVD 88; North American Vertical Datum of 1988; ft bls, feet below land surface; LJ, Harris County; TS, Montgomery; JY, Fort Bend; CHCT, Chicot aquifer; EVGL, Evangeline aquifer]

USGS station number	State well number	Land-surface altitude from GAM program (feet) (NAVD 88)	Depth to top of open interval (ft bls)	Depth to bottom of open interval (ft bls)	Altitude of top of open interval (feet) (NAVD 88) (figs. 4–6)	Altitude of bottom of open interval (feet) (NAVD 88) (figs. 4–6)	Altitude of base of Chicot (feet) (NAVD 88) (figs. 4–6)	Altitude of base of Evangeline (feet) (NAVD 88) (figs. 4–6)	Completion type ¹	Aquifer designation grouping ²
Southwest area (42 wells)										
294329095284603	LJ-65-21-150	60	330	631	-270	-571	-664	-2,153	fullyCHCT	lowerCHCT, upperEVGL
294108095324702	LJ-65-20-520	72	565	675	-493	-603	-652	-2,199	fullyCHCT	lowerCHCT, upperEVGL
294519095383201	LJ-65-11-918	93	550	1,152	-457	-1,059	-500	-1,864	lowerCHCT, upperEVGL	lowerCHCT, upperEVGL
294529095371801	LJ-65-12-735	89	622	1,200	-533	-1,111	-599	-1,919	lowerCHCT, upperEVGL	lowerCHCT, upperEVGL
294252095362101	LJ-65-20-125	81	704	1,590	-623	-1,509	-625	-2,092	lowerCHCT, upperEVGL	lowerCHCT, upperEVGL
294456095341101	LJ-65-12-820	76	594	1,345	-518	-1,269	-609	-2,018	lowerCHCT, upperEVGL	lowerCHCT, upperEVGL
294501095343601	LJ-65-12-817	78	597	957	-519	-879	-610	-2,021	lowerCHCT, upperEVGL	lowerCHCT, upperEVGL
294348095303702	LJ-65-20-319	70	630	1,320	-560	-1,250	-633	-2,081	lowerCHCT, upperEVGL	lowerCHCT, upperEVGL
294201095355601	LJ-65-20-405	80	632	1,610	-552	-1,530	-638	-2,161	lowerCHCT, upperEVGL	lowerCHCT, upperEVGL
294131095360701	LJ-65-20-407	83	618	1,634	-535	-1,551	-644	-2,199	lowerCHCT, upperEVGL	lowerCHCT, upperEVGL
294149095363002	LJ-65-20-408	85	643	1,529	-558	-1,444	-636	-2,188	lowerCHCT, upperEVGL	lowerCHCT, upperEVGL
294147095344303	LJ-65-20-513	76	649	1,399	-573	-1,323	-649	-2,178	lowerCHCT, upperEVGL	lowerCHCT, upperEVGL
294144095351002	LJ-65-20-409	78	615	1,222	-537	-1,144	-648	-2,180	lowerCHCT, upperEVGL	lowerCHCT, upperEVGL
294113095361702	LJ-65-20-422	84	660	968	-576	-884	-648	-2,217	lowerCHCT, upperEVGL	lowerCHCT, upperEVGL
294326095293002	LJ-65-21-144	64	652	1,380	-588	-1,316	-652	-2,125	lowerCHCT, upperEVGL	lowerCHCT, upperEVGL
294329095284602	LJ-65-21-148	60	699	1,490	-639	-1,430	-664	-2,153	lowerCHCT, upperEVGL	lowerCHCT, upperEVGL
294319095305901	LJ-65-20-303	70	560	1,445	-490	-1,375	-635	-2,098	lowerCHCT, upperEVGL	lowerCHCT, upperEVGL
294338095270401	LJ-65-21-201	65	554	1,031	-489	-966	-690	-2,229	lowerCHCT, upperEVGL	lowerCHCT, upperEVGL
294029095354301	LJ-65-20-410	84	700	1,180	-616	-1,096	-674	-2,241	lowerCHCT, upperEVGL	lowerCHCT, upperEVGL
294002095351001	LJ-65-20-414	84	709	1,028	-625	-944	-691	-2,253	lowerCHCT, upperEVGL	lowerCHCT, upperEVGL
294047095345601	LJ-65-20-516	83	710	960	-627	-877	-670	-2,234	lowerCHCT, upperEVGL	lowerCHCT, upperEVGL
294050095355501	LJ-65-20-416	84	584	866	-500	-782	-662	-2,231	lowerCHCT, upperEVGL	lowerCHCT, upperEVGL
293934095342201	LJ-65-20-811	82	739	997	-657	-915	-694	-2,279	lowerCHCT, upperEVGL	lowerCHCT, upperEVGL
294333095275602	LJ-65-21-143	60	716	1,492	-656	-1,432	-678	-2,185	lowerCHCT, upperEVGL	lowerCHCT, upperEVGL
294340095311103	LJ-65-20-321	67	659	1,415	-592	-1,348	-628	-2,073	lowerCHCT, upperEVGL	lowerCHCT, upperEVGL

Table 1. Station number, State well number, land-surface altitude from Groundwater Availability Modeling (GAM) program, depths to top of open interval and bottom of open interval, altitudes of top of open interval and bottom of open interval, altitudes of base of Chicot aquifer and base of Evangeline aquifer, and classification of open interval penetration into aquifer for municipal supply wells sampled in Houston, Texas, 2007–11.—Continued

[USGS, U.S. Geological Survey; NAVD 88; North American Vertical Datum of 1988; ft bls, feet below land surface; LJ, Harris County; TS, Montgomery; JY, Fort Bend; CHCT, Chicot aquifer; EVGL, Evangeline aquifer]

USGS station number	State well number	Land-surface altitude from GAM program (feet) (NAVD 88)	Depth to top of open interval (ft bls)	Depth to bottom of open interval (ft bls)	Altitude of top of open interval (feet) (NAVD 88) (figs. 4–6)	Altitude of bottom of open interval (feet) (NAVD 88) (figs. 4–6)	Altitude of base of Chicot (feet) (NAVD 88) (figs. 4–6)	Altitude of base of Evangeline (feet) (NAVD 88) (figs. 4–6)	Completion type ¹	Aquifer designation grouping ²
Southwest area (42 wells)—Continued										
293732095300601	LJ-65-20-911	68	645	1,188	-577	-1,120	-683	-2,500	lowerCHCT, upperEVGL	lowerCHCT, upperEVGL
293734095293701	LJ-65-21-708	63	632	1,182	-569	-1,119	-694	-2,501	lowerCHCT, upperEVGL	lowerCHCT, upperEVGL
293736095285301	LJ-65-21-709	65	644	1,169	-579	-1,104	-702	-2,500	lowerCHCT, upperEVGL	lowerCHCT, upperEVGL
293543095274901	JY-65-29-109	63	650	1,204	-587	-1,141	-624	-2,562	lowerCHCT, upperEVGL	lowerCHCT, upperEVGL
294317095313001	LJ-65-20-304	71	755	1,552	-684	-1,481	-632	-2,095	upperEVGL	lowerCHCT, upperEVGL
294328095290402	LJ-65-21-149	61	796	1,498	-735	-1,437	-659	-2,141	upperEVGL	lowerCHCT, upperEVGL
294323095300102	LJ-65-20-324	67	756	1,174	-689	-1,107	-645	-2,111	upperEVGL	lowerCHCT, upperEVGL
294627095375801	LJ-65-11-914	81	762	1,120	-681	-1,039	-492	-1,767	upperEVGL	lowerCHCT, upperEVGL
293527095271501	JY-65-29-209	66	766	1,035	-700	-969	-629	-2,611	upperEVGL	lowerCHCT, upperEVGL
293635095294101	JY-65-29-107	67	750	1,205	-683	-1,138	-650	-2,512	upperEVGL	lowerCHCT, upperEVGL
293652095293601	LJ-65-29-108	68	750	1,170	-682	-1,102	-673	-2,519	upperEVGL	lowerCHCT, upperEVGL
293636095300401	JY-65-28-309	68	770	1,020	-702	-952	-650	-2,527	upperEVGL	lowerCHCT, upperEVGL
294348095270401	LJ-65-21-202	65	1,069	1,946	-1,004	-1,881	-686	-2,214	middleEVGL	middleEVGL
294113095361701	LJ-65-20-421	84	1,081	1,642	-997	-1,558	-648	-2,218	middleEVGL	middleEVGL
294127095342502	LJ-65-20-519	76	1,146	1,440	-1,070	-1,364	-655	-2,199	middleEVGL	middleEVGL
294452095354501	LJ-65-20-104	77	995	1,435	-918	-1,358	-613	-2,051	middleEVGL	middleEVGL
294414095364202	LJ-65-20-126	82	970	1,322	-888	-1,240	-611	-2,058	middleEVGL	middleEVGL

¹Completion type is specific to an individual well and classifies the wells on the basis of which part or parts of the aquifer or aquifers are penetrated.

²Aquifer designation grouping is a group of comparable wells with similar characteristics based on location of open intervals in the aquifer or aquifers.

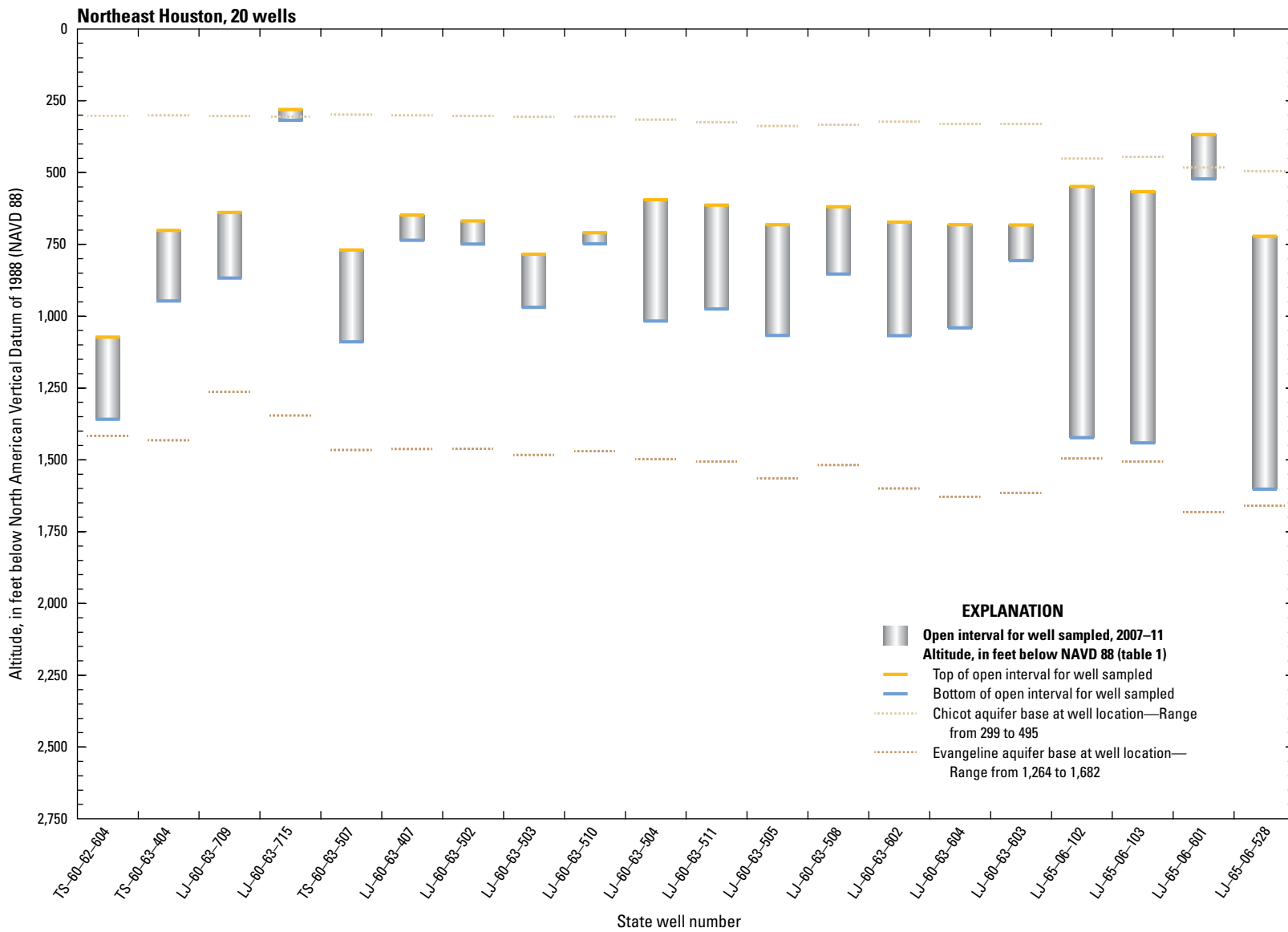


Figure 4. Altitudes of the tops and bottoms of open intervals for municipal supply wells in the northeast Houston, Texas, area that were sampled during 2007–11 and altitudes of bases of the Chicot and Evangeline aquifers at each well location as described by Strom and others (2003a, b).

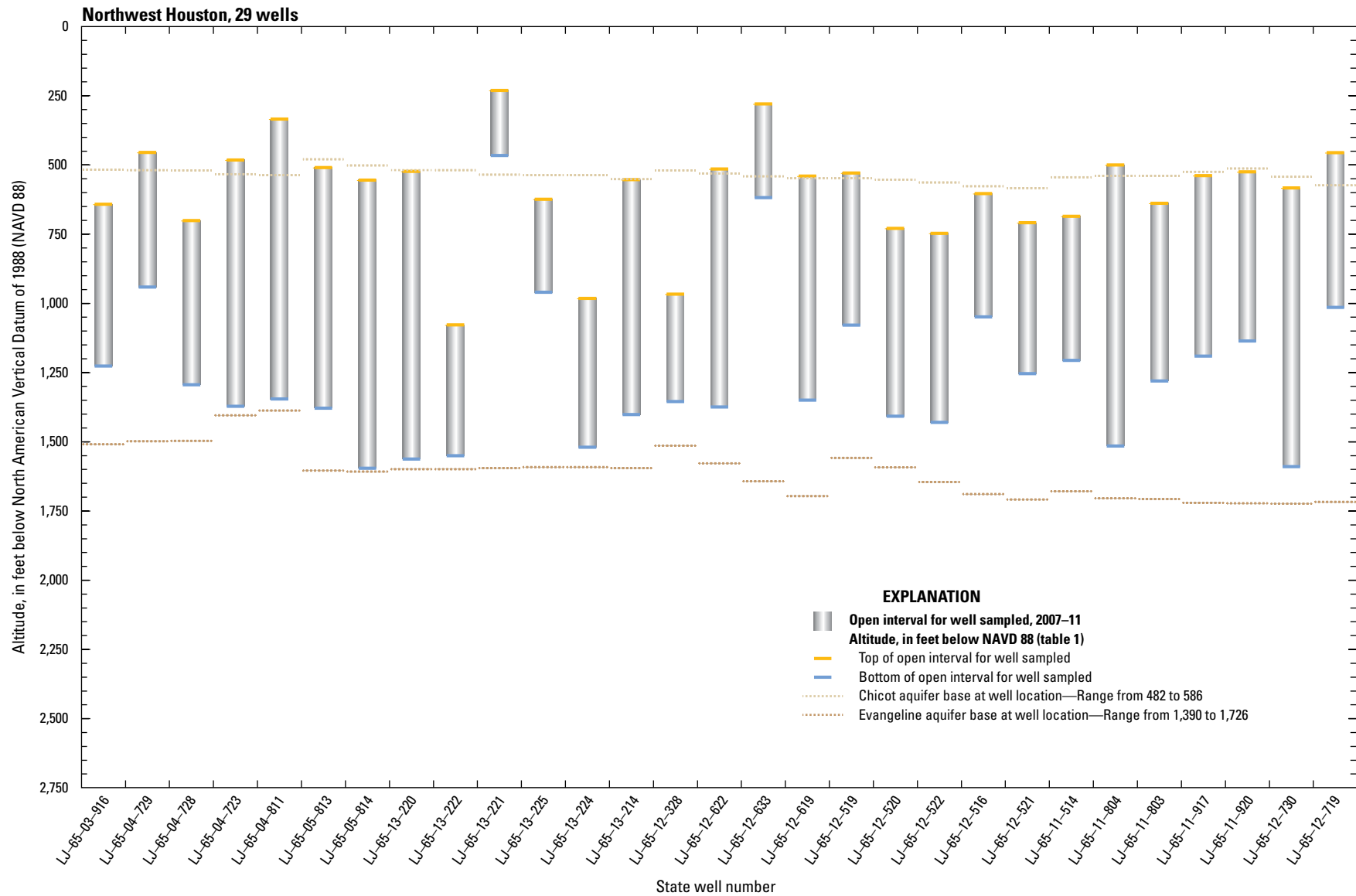


Figure 5. Altitudes of the tops and bottoms of open intervals for municipal supply wells in the northwest Houston, Texas, area that were sampled during 2007–11 and altitudes of bases of the Chicot and Evangeline aquifers at each well location as described by Strom and others (2003a, b).

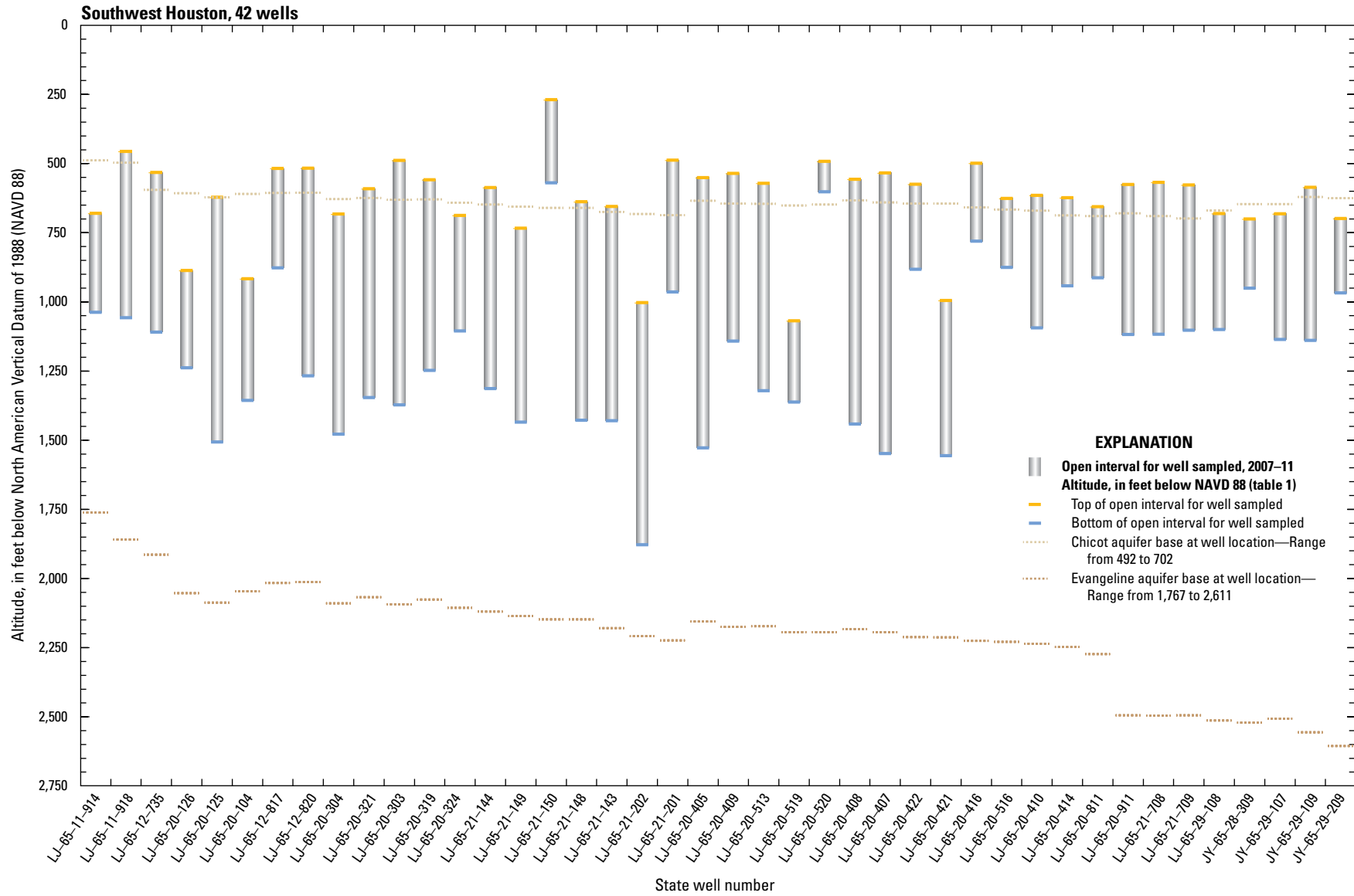


Figure 6. Altitudes of the tops and bottoms of open intervals for municipal supply wells in the southwest Houston, Texas, area that were sampled during 2007–11 and altitudes of bases of the Chicot and Evangeline aquifers at each well location as described by Strom and others (2003a, b).

The sampled wells were classified as partially penetrating or fully penetrating a single aquifer or as partially penetrating a single aquifer or multiple aquifers. When fully penetrating, the upper, middle, and lower parts of the aquifer are penetrated, but not necessarily the entire aquifer thickness. When partially penetrating, the part of the aquifer penetrated was described as the upper, middle, or lower part on the basis of the distance from the open intervals to the estimated base of the Chicot aquifer and the Evangeline aquifer. The completion type is specific to an individual well and classifies the wells on the basis of which part or parts of the aquifer or aquifers are penetrated. As many as seven combinations were used to describe and classify the wells on the basis of which part or parts of the aquifer or aquifers were penetrated. These seven completion types are referred to as (1) “fullyCHCT,” (2) “fullyEVGL,” (3) “lowerCHCT, upperEVGL,” (4) “lowerCHCT, fullyEVGL,” (5) “upperEVGL,” (6) “middleEVGL,” and (7) “lowerEVGL” (table 1). The greatest number of sampled wells, 33 of 91, partially penetrated the lower part of the Chicot aquifer and upper part of the Evangeline aquifer and are therefore classified as “lowerCHCT, upperEVGL” (table 1). To simplify description of the completion types for the sampled wells and to ensure that the sizes of the groups are large enough to allow for statistical calculations, some of the small groups of well-completion types with approximately overlapping open intervals or nearly similar positions in the aquifer system were combined. The new grouping was termed “the aquifer designation grouping” and is used hereinafter as the classification group representing well completion as shown in table 1. The aquifer designation grouping is a group of comparable wells with similar characteristics based on location of open intervals in the aquifer or aquifers. The small groups of the well-completion types of the “fullyCHCT” (3 wells) and the “upperEVGL” (15 wells) were combined with the larger “lowerCHCT, upperEVGL” (33 wells) group into a larger group of 51 wells collectively listed as the larger “lowerCHCT, upperEVGL” aquifer designation grouping in table 1. The overlapping altitudes of the open intervals in the various parts of the aquifers used for water production indicate that the various parts of the aquifer are not defined by specific physical boundaries within a fixed depth interval below datum but rather represent a gradient among depth intervals below datum. For classification purposes, individual wells were assigned to definitive aquifer groups that were defined by the ranges of distances between the altitudes of the tops of the first open intervals to the altitudes of the base of the Chicot aquifer and distances between the altitudes of the bottoms of the last open intervals for each well to the altitudes of the base of the Evangeline aquifer (or top of the Burkeville confining unit) in the northeast, northwest, and southwest areas, not by depth of the interval below datum.

The aquifer designation groupings (table 1) were used for comparing the parts or layers of the aquifers intersected by the open intervals of the sampled wells in each of the three areas. The minimum and maximum distances from the tops of the first open interval to the base of the Chicot aquifer and distances from the bottom of the last open interval to the base of the Evangeline aquifer for each aquifer designation grouping are presented graphically in figure 7 by area (northeast, northwest, or southwest Houston). Of the 51 wells with the “lowerCHCT, upperEVGL” aquifer designation grouping, 37 were in the southwest Houston area, which is consistent with the base of the Evangeline aquifer being at a much deeper altitude than in the other sampled areas in north Houston (fig. 6). None of the wells sampled in the southwest area is deep enough to be assigned an aquifer designation grouping of “lowerEVGL” because freshwater is available at shallower depths in the Chicot aquifer and because the Chicot aquifer is much thicker in this area compared to the northeast and northwest areas, increasing the expense of drilling into the “lowerEVGL” for freshwater.

The majority of the wells in the northeast Houston area either fully penetrated the Evangeline aquifer or partially penetrated parts of this aquifer (fig. 4), such as only the middle or lower parts. Of the 33 sampled wells open only in the Evangeline aquifer, the greatest number of those (19) was classified as partially penetrating the “middleEVGL” group, mostly in northeast Houston (fig. 7). The Chicot aquifer is so thin towards northeast Houston that most open intervals are not open to it but rather to the aquifers below the Chicot aquifer. For the subset of sampled wells composing the “middleEVGL” group, the altitudes of the top and bottom of the open intervals are relatively distant from the estimated bases of either the Chicot or the Evangeline aquifers and intersect isolated zones. Of the remaining 14 sampled wells that are screened only in the Evangeline aquifer, 10 are classified as “fullyEVGL” and 4 are classified as “lowerEVGL”; all 14 are located in the northeast and northwest areas (fig. 7). The open intervals of the four wells classified as “lowerEVGL” are open primarily to the lower part of the Evangeline aquifer; the tops of the open intervals of these four wells are a minimum of 443 ft below the base of the Chicot aquifer, and the bottoms of the open intervals are within a maximum distance of 162 ft above the base of the Evangeline aquifer (fig. 7).

In the northwest area, most of the wells fully penetrate the Evangeline aquifer or partially penetrate multiple aquifers, and wells are classified based on open intervals with the following aquifer designation groupings: “fullyEVGL” (7 wells); “lowerCHCT, upperEVGL” (12 wells); “lowerCHCT, fullyEVGL” (7 wells); or “lowerEVGL” (3 wells) (fig. 7). The estimated altitude of the base of the Chicot aquifer is at a greater depth below land-surface datum than in the northeast area, and the aquifer also is correspondingly thicker, so more wells are completed or partially completed in that aquifer.

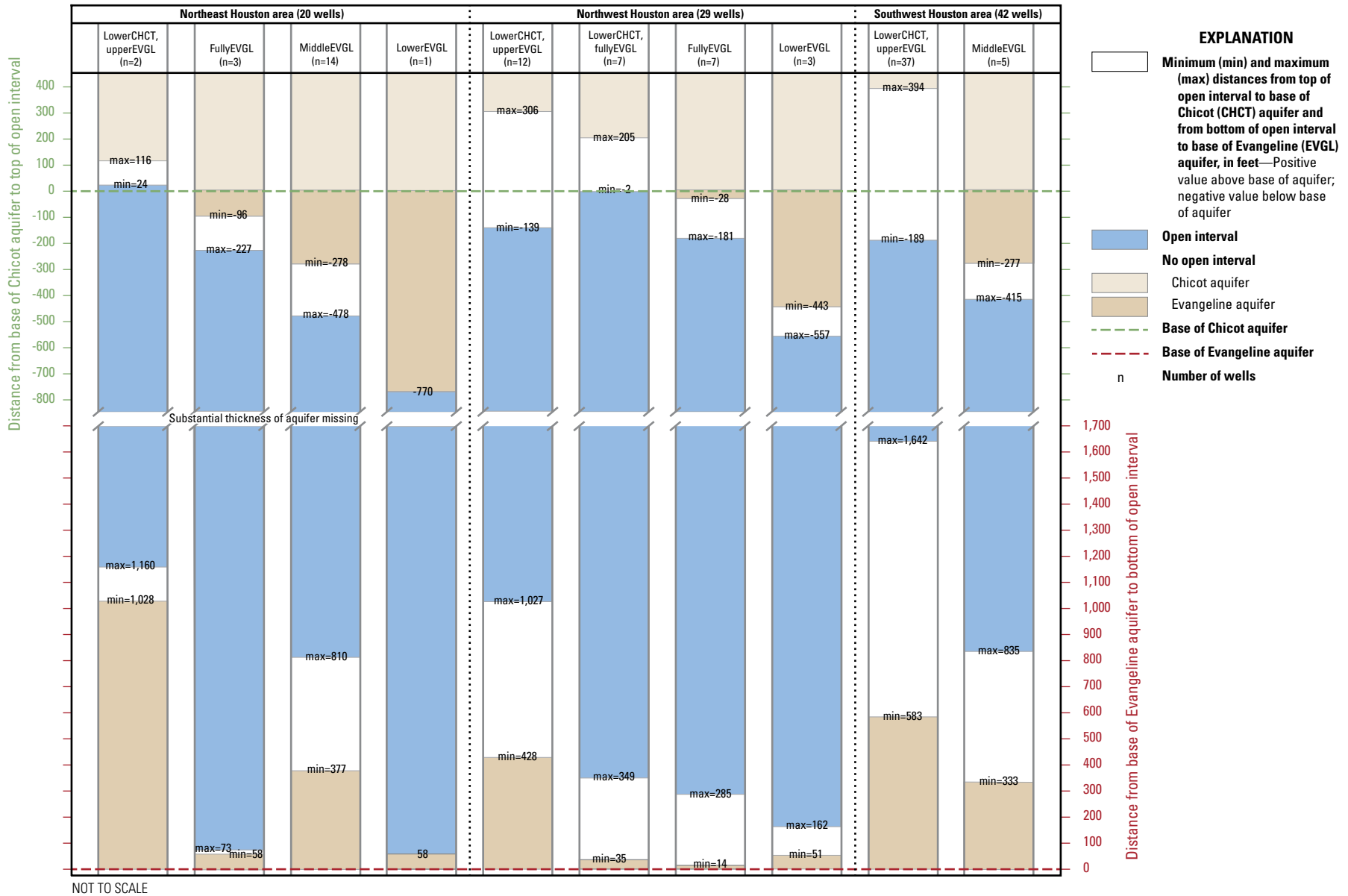


Figure 7. Graphical representation for wells sampled during 2007–11 of the minimum and maximum distances from the top of open intervals to the base of the Chicot aquifer and distances from the bottom of open intervals to the base of the Evangeline aquifer as described by Strom and others (2003a, b). Distances are categorized by aquifer designation grouping and by area (northeast, northwest, and southwest Houston, Texas).

Wells completed to the same depth interval below datum could be classified as belonging to a different part of the aquifer in each area on the basis of the distance between the altitudes of the wells' open intervals to the altitudes of the bases of the aquifers (fig. 7; table 1); for example, well LJ-65-11-804 in the northwest area has an aquifer designation of "lowerCHCT, fullyEVGL"; the altitude of the top of its open interval is 500 ft below datum; and the altitude of the bottom of its open interval is 1,516 ft below datum (fig. 5; table 1). If this well was in the northeast area instead of the northwest area, it would most likely be open only to the Evangeline aquifer because the deepest part of the base of the Chicot aquifer was estimated as 495 ft below datum, and the well would most likely be classified under the "fullyEVGL" designation instead of the "lowerCHCT, fullyEVGL" designation. If this same well was in the southwest area, it would most likely be classified as "lowerCHCT, upperEVGL." The altitudes of the base of the Chicot aquifer for most of the wells sampled in the southwest area are at a greater depth than 500 ft below datum, and the sediments composing the Chicot aquifer were deposited in a much thicker layer in the southwest area compared to the northeast and northwest areas. The bottom of the open interval of a well with an altitude of 1,516 ft below datum is at least 500 ft above the base of the Evangeline aquifer in the southwest area (fig. 6). Consequently, this same well, if located in each of these areas, could potentially withdraw water from different parts of the aquifer system. The spatial location of each well, in addition to its depth, needs to be considered in order to assess the relative position of the well open interval within the aquifer system so that differences in geochemical conditions can be envisioned in a broader context.

Methods

Groundwater samples were collected and processed from 2007 to 2011 from 91 wells in Houston in accordance with protocols established by the USGS National Field Manual for the Collection of Water-Quality Data (U.S. Geological Survey, variously dated). The methods and results for 75 of the 91 wells that were sampled are documented by Oden and others (2010, 2011), including a summary of the methods by which the source-water samples were collected and analyzed for each constituent or constituent group and quality-control results. The 16 samples not published elsewhere were collected by using the same methods described in the previous publications by Oden and others (2010, 2011).

Data Collection and Laboratory Analysis

During each phase of sampling, water temperature, dissolved-oxygen concentration, pH, specific conductance, turbidity, and alkalinity were measured in the field at each sampling site, and oxidation-reduction potential (ORP) and unfiltered sulfides also were measured at selected wells.

Groundwater samples were analyzed for major ions (calcium [Ca], magnesium [Mg], potassium [K], Na, bromide [Br], Cl, fluoride [F], silica, and sulfate [SO₄]), residue on evaporation (dissolved solids), trace elements (As, barium [Ba], boron [B], chromium [Cr], iron [Fe], lithium, manganese [Mn], molybdenum [Mo], selenium [Se], strontium [Sr], and vanadium [V]), and selected radionuclides and measures of radioactivity (U and gross alpha- and beta-particle activity [at 72 hours and 30 days]). At a subset of wells, the As species (As[V], As[III], dimethylarsinate [DMA], and monomethylarsonate [MMA]) and other radionuclides (carbon-14 [¹⁴C], Ra-226, Ra-228, Rn-222, and tritium) also were analyzed. On the basis of the previous work done in the Gulf Coast aquifer system regarding concentrations of nitrate in groundwater (Land and others, 1999; Reutter and Dunn, 2000), samples were not analyzed for nitrate for this study. A detailed description of the sample-collection process, sample analysis, and reporting of results for selected constituents analyzed by using standard methods of the USGS was summarized in Oden and others (2010, 2011). Included in appendix 1 of this report are data from water samples collected from 13 wells in 2010, data from 3 wells sampled in December 2011, and additional radionuclide results that were not included in Oden and others (2011). Those samples were submitted to the USGS National Water Quality Laboratory (NWQL) in Denver, Colorado, and analyzed for the same list of major ions and trace elements (including U) as those samples described in Oden and others (2011). The radionuclide analyses included gross alpha- and beta-particle activity (at 72 hours and 30 days) and, at a select number of wells, Ra-226 was analyzed at the contract laboratory of Eberline Services in Richmond, California. Gross alpha- and beta-particle activities are referred to as filtered, alpha or beta radioactivity, 72-hour or 30-day count in the tables in this report. For the three samples collected in December 2011, As-speciation analysis was done by using the collision-reaction cell inductively coupled plasma-mass spectrometry (cICP-MS) method described in Garbarino and others (2006).

The analytical quantification procedure used by the NWQL for reporting results is based on the long-term method detection level (LT-MDL) and laboratory reporting level (LRL). The LT-MDL concentrations are defined as a censoring limit for most analytical methods at the NWQL, and its purpose is to limit the false positive rate to less than or equal to 1 percent. An LT-MDL is a modification of the EPA 40 Code of Federal Regulations Part 136 definition of the method detection limit (MDL). The LRL is defined as twice the LT-MDL and is established to limit the occurrence of false negative detections to less than or equal to 1 percent (Childress and others, 1999). A constituent concentration is considered estimated by the laboratory when results are greater than the LT-MDL and less than the LRL; that is, a detection is considered likely, but quantification is considered questionable. The remark code of "E" (estimated) is assigned by the laboratory for these results. The presence

of a constituent in the sample that can be verified, but the concentration is not enough to be quantified, is reported as a remark code of "M." Similarly, nonzero concentration values that round to zero are converted to a null value on output and reported by using a remark code of "M" (U.S. Geological Survey, 2009). Beginning in October 2010, the NWQL changed the reporting convention for all inorganic analytes that use the LRL convention. For these constituents, the reporting level was set at the LT-MDL concentration. Concentrations that are less than the LT-MDL are reported as "less than" the LT-MDL concentration (<LT-MDL) and a remark code of "E" would no longer be assigned to results greater than the LT-MDL and less than the LRL (U.S. Geological Survey, 2010). For this report, inorganic analyses are reported using this new convention for samples collected after October 1, 2010.

Quality-control (QC) data were collected throughout the sampling effort from 2007 to 2011 to assess sample-collection procedures and laboratory analyses, and results from 2007 to 2010 were summarized in Oden and others (2010, 2011). Additional QC data collected during 2010–11 that were not previously published are presented in appendix 3A of this report. The equation to compute the relative percent difference (RPD) and the criteria for acceptable differences between paired results are presented in Oden and others (2010, 2011) and are presented as a footnote in appendix 1 of this report. The QC data indicate that the data are reproducible, unbiased, and of sufficient quality to allow for evaluation of variability in the occurrence of small concentrations of trace elements. A discussion of the quality-control data is summarized in appendix 3B.

Data Analysis

For this study, the wells were first classified into completion types by converting the depth to the top of the first open interval and depth to the bottom of the last open interval for each of the 91 wells sampled to altitudes by subtracting the depths in feet below land surface (ft bls) from the altitude of the land surface above datum at the location of each well as described by Strom and others (2003a, b) (table 1). This distance in feet was calculated between the altitudes of the tops of the first open interval and bottoms of the last open interval for each well to the estimated altitudes of the base of the Chicot aquifer and the Evangeline aquifer (or top of the Burkeville confining unit). The assignment for each well-completion type was based on these relative distances. Some of the small groups of well-completion types with approximately overlapping open intervals or nearly similar positions in the aquifer system were combined with the larger "lowerCHCT, upperEVGL" (33 wells) group (table 1).

Those wells are collectively listed as the aquifer designation grouping in table 1 and used as the classification group representing well completion. The well-completion types are included in table 1 because the assigned well-completion type may provide additional information for the interpretation of the results when comparing minor differences among the water-quality results of the samples.

All samples were analyzed for the following constituent groups: major ions, selected trace elements, and selected radionuclides and measures of radioactivity. The specific trace element and radionuclide constituents varied slightly during each of the three sampling rounds. A database was constructed containing the analytical results for all 91 wells that were sampled during 2007–11. Subsets of data were grouped from wells sampled for selected constituents of interest that were not analyzed in all samples (for example, As species, Ra-226, and Rn-222). These groupings were used for the multivariate statistical tests used to determine which variables were related to others in these groupings. Subsets of data also were grouped by the three areas where the wells were located and by aquifer designation grouping. Additional subdatabases were created for primary cation and anion water types and redox categories.

Summary statistics were computed for 33 constituents measured in the water-quality samples collected from the 91 wells (table 2). Also included are summary statistics for six constituents analyzed in samples from a subset of wells: (1) ORP, (2) As(V), (3) As(III), (4) Ra-226, (5) Ra-228, and (6) Rn-222. Summary statistics also were created for the data subsets (app. 4). Of the 39 constituent concentrations analyzed, 11 constituents included a varied number of censored results, with multiple detection limits for 7 of the constituents. To estimate the summary statistics for these constituents, the maximum likelihood estimation statistical method was used and adjusted for transformation bias (Helsel and Cohn, 1988). The regression on order statistics (ROS) of the log-transformed data method was used to estimate the summary statistics for nine constituents with censored results because more than 50 percent of the results were censored, and the sample size was small, factors that limit the application of the approximate maximum likelihood estimation statistical method (Helsel and Cohn, 1988). Summary statistics by location, aquifer designation grouping, or redox category could not be computed for several constituents including As(III) and As(V) because few of the concentration results for these constituents were greater than LRLs in some of the groups. Important thresholds, or "cut points," were established on the basis of the natural occurrence distributions of the constituents of concern; for example, As species and U had notable groupings of specific concentration ranges often associated with a chemical type or redox category.

Table 2. Summary statistics for selected constituents in water samples collected from 91 municipal supply wells sampled in Houston, Texas, during 2007–11.

[nm, nanometer; NTRU, nephelometric turbidity ratio unit; mg/L, milligrams per liter; °C, degrees Celsius; 1st quartile, 25th percentile; 3rd quartile, 75th percentile; CaCO₃, calcium carbonate; <, less than; SiO₂, silicon dioxide µg/L, micrograms per liter; µg-As/L, micrograms arsenic per liter; pCi/L, picocuries per liter; Th, thorium; Cs, cesium; R, nondetect, result below sample specific critical level (ssLc)]

	Oxidation reduction potential, reference electrode not specified (millivolts)	Turbidity, water, unfiltered, broad band light source (400–680 nm), detectors at multiple angles including 90 degrees, ratiometric correction (NTRU)	Dissolved oxygen, water, unfiltered (mg/L)	pH, water, unfiltered, field (standard units)	Specific conductance, water, unfiltered (microsiemens per centimeter at 25 °C)	Temperature, water (°C)	Calcium, water, filtered (mg/L)	Magnesium, water, filtered (mg/L)
Number of samples	71	91	91	91	91	90	91	91
Minimum	-212	0.1	<0.10	7.2	314	22.7	8.23	1.99
1st quartile	-135	0.1	0.04 (<0.10)*	7.4	476	25.0	35.3	5.22
Median	-54.3	0.2	0.39	7.5	501	25.5	41.8	7.34
3rd quartile	112	0.4	2.0	7.6	531	25.9	49.8	8.73
Maximum	466	2.0	4.5	8.1	1,110	29.9	69.9	12.3

	Potassium, water, filtered (mg/L)	Sodium, water, filtered (mg/L)	Alkalinity, water, filtered, inflection-point titration method (incremental titration method), field (mg/L as CaCO ₃)	Bicarbonate, water, filtered, inflection-point titration method (incremental titration method), field (mg/L)	Bromide, water, filtered (mg/L)	Chloride, water, filtered (mg/L)	Fluoride, water, filtered (mg/L)	Silica, water, filtered (mg/L as SiO ₂)
Number of samples	91	91	91	91	91	91	91	91
Minimum	1.47	14.2	126	154	0.06	15.3	0.11	14.2
1st quartile	1.89	33.9	167	203	0.12	33.5	0.20	21.0
Median	2.17	41.6	179	218	0.14	41.1	0.24	23.6
3rd quartile	2.36	58.6	199	242	0.16	47.1	0.34	26.2
Maximum	2.76	182	324	394	0.32	216	1.34	32.1

	Sulfate, water, filtered (mg/L)	Residue on evaporation, dried at 180 °C, water, filtered (mg/L)	Arsenate (H ₂ AsO ₄ ⁻ , As[V]), water, filtered (µg-As/L)	Arsenic, water, filtered (µg/L)	Arsenite (H ₃ AsO ₃ , As[III]), water, filtered (µg-As/L)	Barium, water, filtered (µg/L)	Boron, water, filtered (µg/L)	Chromium, water, filtered (µg/L)
Number of samples	91	91	31	91	31	91	91	91
Minimum	<0.18	175	<0.3	0.58	<0.4	110	20	<0.06
1st quartile	9.18	275	0.4 (<0.8)*	2.2	0.2 (<0.4)*	214	46	0.03 (<0.06)*
Median	12.0	290	0.8	2.7	0.6 (<1.0)*	235	54	0.22
3rd quartile	14.1	307	2.3	3.6	2.1	278	80	1.2
Maximum	17.2	612	3.5	23.5	14.9	472	548	6.1

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Table 2. Summary statistics for selected constituents in water samples collected from 91 municipal supply wells sampled in Houston, Texas, during 2007–11.—Continued

[nm, nanometer; NTRU, nephelometric turbidity ratio unit; mg/L, milligrams per liter; °C, degrees Celsius; 1st quartile, 25th percentile; 3rd quartile, 75th percentile; CaCO₃, calcium carbonate; <, less than; SiO₂, silicon dioxide µg/L, micrograms per liter; µg-As/L, micrograms arsenic per liter; pCi/L, picocuries per liter; Th, thorium; Cs, cesium; R, nondetect, result below sample specific critical level (ssLc)]

	Iron, water, filtered (µg/L)	Lithium, water, filtered (µg/L)	Manganese, water, filtered (µg/L)	Molybdenum, water, filtered (µg/L)	Selenium, water, filtered (µg/L)	Strontium, water, filtered (µg/L)	Vanadium, water, filtered (µg/L)	Alpha radioactivity, 30-day count, water, filtered, Th-230 curve (pCi/L)
Number of samples	91	91	91	91	91	91	91	91
Minimum	<3	5.0	<0.2	<0.2	<0.03	202	<0.04	R-0.94
1st quartile	6 (<8)*	12.5	1.6 (<3.8)*	1.3	0.02 (<0.03)*	372	0.11 (<0.16)*	3.00
Median	32	16.7	7.2	2.1	0.74	498	1.5	5.60
3rd quartile	145	19.7	13.7	2.9	3.8	596	5.0	8.20
Maximum	612	24.6	109	18.1	25.1	738	18.0	25.5

	Alpha radioactivity, 72-hour count, water, filtered, Th-230 curve (pCi/L)	Beta radioactivity, 30-day count, water, filtered, Cs-137 curve (pCi/L)	Beta radioactivity, 72-hour count, water, filtered, Cs-137 curve (pCi/L)	Radium-226, water, filtered, radon method (pCi/L)	Radium-228, water, filtered (pCi/L)	Radon-222, water, unfiltered (pCi/L)	Uranium (natural), water, filtered (µg/L)
Number of samples	91	91	91	41	28	31	91
Minimum	R-1.1	R-1.04	1.48	0.204	R-0.18	161	<0.02
1st quartile	5.70	2.52	2.53	0.406	0.35	370	0.32
Median	10.3	3.48	3.07	0.853	0.47	570	1.69
3rd quartile	13.2	4.75	3.64	1.65	0.66	830	6.48
Maximum	39.7	14.4	6.60	4.34	1.10	2,380	42.7

*Adjusted maximum likelihood estimation statistical method calculates interquartile range below a single reporting level and between multiple reporting levels.

Major-ion chemistry of groundwater was assessed by calculating the percentages of the cations and anions in each sample from their total milliequivalents per liter concentrations, ordering the major ions according to the percentage of total ions that each represents, and assigning the water type, with only those major ions with a percentage of total milliequivalents per liter greater than 10 included (Back, 1966). Simplified water types were then assigned by the dominant cation and dominant anion determining the classes. Dominance was simply defined by the greatest cation and anion percentage of total ions in milliequivalents per liter; it was not required that the dominant dissolved ion must be greater than 50 percent of the total, as is the case with other more complicated classification systems, such as that of Back (1966). Trilinear (piper) diagrams were used to illustrate the composition of the water with respect

to the combination of selected major ions. By using piper diagrams, the dominant water types can be established (Hem, 1985). Piper diagrams consist of two triangular-shaped diagrams (one for cations and another for anions) and a central diamond-shaped field. The percentages of total ions in milliequivalents per liter concentrations are plotted on separate triangular diagrams for cations and anions, and those points are then extended to a point of intersection in the diamond-shaped field (Hem, 1985). The location of the point in the diamond reveals the general composition of the water and may be indicative of a water source or dominant chemical process (Back, 1966). Separate piper diagrams were used to illustrate similarities and differences in the composition of water from each area of Houston, with samples grouped by aquifer designation.

The groundwater samples were grouped into redox categories by using a systematic approach based on sample geochemistry (McMahon and Chapelle, 2008; Chapelle and others, 2009) that can be calculated by using the software of Jurgens, McMahon, and others (2009). The redox state of a groundwater sample was defined by the predominant type of redox process occurring in the sample, as inferred from water-quality data. Classification was based on the concentrations of redox-sensitive species, specifically dissolved oxygen (DO, as the dissolved gaseous oxygen molecule [O_2 , in milligrams per liter]), nitrate (NO_3^- as nitrogen [N]), manganese (Mn^{2+}), iron (Fe^{2+}), sulfate (SO_4^{2-} as SO_4), and total sulfide (sum of dihydrogen sulfide [aqueous H_2S], hydrogen sulfide [HS^-] and sulfide [S^{2-}]; hereinafter referred to as “sulfide”). Samples were not analyzed for nitrate for this study on the basis of previous work done in the Gulf Coast aquifer system (Land and others, 1999; Reutter and Dunn, 2000); on the basis of the results of these previous investigations, it was assumed that nitrate concentrations were less than the threshold concentration of 0.5 mg/L used by McMahon and Chapelle (2008).

All samples with DO concentrations greater than or equal to 0.5 mg/L were classified as oxic, whereas those with DO concentrations less than 0.5 mg/L were classified as either suboxic or anoxic (reduced) on the basis of the presence of concentrations of at least one of the various electron acceptors (Mn^{2+} , Fe^{2+} , and SO_4^{2-}). Some samples were classified as mixed when the criteria for more than one redox process were met; most common in groundwaters of the United States is when samples contain DO concentrations greater than or equal to 0.5 mg/L and elevated concentrations of those of various electron acceptors (McMahon and Chapelle, 2008). Samples from the anoxic category were further subcategorized by predominant reduction process on the basis of concentrations of the various electron acceptors (Mn^{2+} , Fe^{2+} , and SO_4^{2-}) present (McMahon and Chapelle, 2008; Chapelle and others, 2009). The predominant reduction process is considered to represent even more reducing waters on the basis of the succession of terminal electron-accepting processes defined by Lovley and Chapelle (1995); for example, a sample designated as anoxic Fe reducing is less reducing than a sample designated as SO_4 reducing.

Sulfide is the characteristic final product of SO_4 reduction (Chapelle and others, 2009). Sulfide can be used to differentiate between Fe(III)- and SO_4 -reducing redox processes if the concentration of sulfide in water samples is detectable, which is not always the case (even in SO_4 -reducing conditions) because sulfide can be readily sequestered in aquifer sediment (Slowey and Brown, 2007). One of the sequestering agents for sulfide is Fe(II). Typically, amorphous Fe-sulfide precipitate can form in SO_4 -reducing conditions, but consolidation to pyrite or other Fe-sulfur minerals is unlikely in Fe-rich, sulfur-poor conditions (Burton and others, 2011). The Fe(II) itself may be sequestered not only by sulfide but also by adsorption onto available hydroxides (Silvester and others, 2005) or clay minerals (Carroll, 1959) or by

coprecipitation with carbonate, phosphate, and other ligands (Postma, 1981). In some circumstances, therefore, Fe(III)- or SO_4 -reducing, anoxic conditions can be present without high Fe(II) or sulfide concentrations. Furthermore, the reporting levels of the methods used to measure unfiltered sulfide concentrations vary substantially and are generally greater than those for methods used to determine Fe concentrations. During this study, the reporting level of the methods used to measure unfiltered sulfide concentrations ranged considerably from 0.005 mg/L in 2007 to 0.20 mg/L in 2008–11. In 2007, a portable Hach DR 2800 spectrophotometer was used to measure the unfiltered sulfide concentrations in the field by using the methylene blue method of Clesceri and others (1998), as adopted and modified by Hach (Hach Company, 2007). In 2008–11, a V-2000 field photometer with field reagents supplied by CHEMetrics was used for this measurement (CHEMetrics, 2008). In the absence of sulfide data or if sulfide and DO in the water were undetectable, anomalously low SO_4 concentrations (typically less than 4 mg/L) were considered to indicate the possibility that SO_4 reduction to sulfide was taking place. Anomalously low SO_4 concentrations (less than 4 mg/L) may also indicate that the sample was naturally SO_4 poor, and methanogenesis (reduction of low molecular weight carbon compounds to methane) is the dominant anoxic process ongoing after reduction of available Fe(III). This assumption is considered reasonable because SO_4 concentrations in the water from the shallowest wells were greater than 4 mg/L, but concentrations at depth, especially in the Evangeline aquifer, were often less than 4 mg/L, indicating that SO_4 was being removed from solution with increasing penetration depth of the water into the aquifer system.

In the absence of appropriately high Fe(II) concentrations (identified as 100 micrograms per liter [$\mu g/L$] by Chapelle and others, 2009) in water without DO, sample chemistry needs to be examined for possible evidence that Fe(III) reduction may nevertheless be occurring. In the case of this dataset, many samples without measureable DO concentrations and presumably very low nitrate concentrations (less than 0.5 mg/L) lacked appropriately high Mn or Fe(II) concentrations (equal to or greater than 50 and 100 $\mu g/L$, respectively) to indicate dominance of the Mn- or Fe(III)-reduction process (Chapelle and others, 2009). These same samples also contained no detectable sulfide, and the SO_4 concentrations were greater than 4 mg/L. These samples were classified as suboxic by using the categories proposed by McMahon and Chapelle (2008), but many were collected from similar depths as those where Fe(III)- or SO_4 -reducing conditions were typically encountered in other parts of the aquifer system, raising the possibility that those reduction reactions had been initiated or were ongoing for the samples classified as suboxic. Further examination of these samples indicated that Fe(II) concentrations were present, in the range of 29 to 99 $\mu g/L$, but somewhat below the 100 $\mu g/L$ Fe(II)-concentrations threshold set as the classification indicator for Fe reduction by McMahon and Chapelle (2008). On the basis of this presumption, the Fe(II)-concentration threshold that indicated

that Fe reduction was ongoing was considered indicative of the Fe-reduction reaction at 29 $\mu\text{g/L}$, rather than 100 $\mu\text{g/L}$. A case-by-case review indicated that, for samples without measurable DO concentrations and with low SO_4 concentrations (less than 4 mg/L) obtained from great depth or for which methanogenesis could be hypothesized as likely occurring, Fe(II) concentrations were present, typically about 100 $\mu\text{g/L}$, with some less than 100 $\mu\text{g/L}$. Because Fe(II) concentrations were present in solution, Fe(III) reduction was likely to be ongoing in conjunction with the presumed methanogenesis (methanogenic-anoxic conditions); therefore, all the samples containing Fe equal to or greater than 29 $\mu\text{g/L}$ were not routinely classified as suboxic but were generally classified as Fe-reducing anoxic. If, in addition, SO_4 concentrations were less than 4 mg/L, the samples were classified as SO_4 -reducing anoxic, possibly methanogenic anoxic, or both. Only samples containing the soluble (reduced) Fe species in concentrations below this locally identified 29- $\mu\text{g/L}$ threshold value were thus grouped as "suboxic." For the suboxic samples, other than the fact that DO had been consumed, a predominant redox process cannot be defined on the basis of the available concentration of the redox constituents. Thresholds for redox categories can be reset on the basis of geochemical evidence as described by McMahan and Chapelle (2008), and groundwater samples collected from the Gulf Coast aquifer system in Houston appear to meet such revised criteria, as opposed to the generalized thresholds suggested by McMahan and Chapelle (2008).

After determining aquifer designation groupings, simplified water types, and redox categories, statistical analyses were done to evaluate statistically significant differences in constituent concentrations among groups. For these comparative analyses, the censored results for 11 constituents (DO concentration, SO_4 , Cr, Fe, Mn, Mo, Se, V, U, As[V], and As[III]) were first assigned a value of one-half the highest LRL used during 2007–11 for each constituent so that the censored results would be assigned tied ranks for the comparative analyses (Helsel, 2005). Estimated results for constituents analyzed with mass spectrometry (Childress and others, 1999) also were set to one-half the highest LRL value. Nonparametric statistical tests were used to compare the results from different groups of samples, so this method of censoring that data is unlikely to affect the results. For the nonparametric Tukey multiple comparison and Kruskal-Wallis tests, the data were first ranked from smallest to largest, and their ranks (not the original values) were used to compute the test statistic without any assumption on the type of distribution (Helsel and Hirsch, 2002). For the principal components analysis (PCA), the data were first transformed by the fourth root to reduce the right skewness of the data, and then a normalized correlation matrix was used, resulting in dimensionless comparable axes scales (Helsel and Hirsch, 2002). The nonparametric Spearman correlation technique is based on ranks of the data and is resistant to effects of outliers (Helsel and Hirsch, 2002). All correlations presented are significant at a probability value (p -value) of 0.05.

Group-comparison tests such as the Tukey multiple comparison and Kruskal-Wallis tests (Helsel and Hirsch, 2002) were used to determine which group means significantly differed in As species, Ra isotopes, gross alpha-particle activities, or U concentration distributions from among the groups of data. Classification groups included location, redox, and aquifer designation. The statistically significant differences among groups were confirmed by the Kruskal-Wallis test, but discrimination and ranking among the groups were completed with the Tukey test. Results from the group-comparison tests are defined as having statistical significance at the 95-percent confidence level, indicating the probability of the null hypothesis being true is 0.05 or less. The differences among the higher and lower ranked groups reflected the difference in the central tendencies of the data distribution about the mean rank of the groups but did not indicate which group had the highest individual concentration. Results were ranked and coded sequentially, with the group with the highest mean of ranks coded "A," the group with the next highest mean ranks was coded "B," then "C," and so on; overlapping groups were coded with the letter for each overlapping group, "AB," for example, representing overlap with groups "A" and "B." The "A" group is referred to as the "A" Tukey class"; the "B" group is referred to as "B" Tukey class," and so on. A multivariate statistic, PCA, was used to reduce dimensionality of the multiple correlations determined among the concentrations of the chemical constituents by viewing data on new axes (principal components) in directions of maximum data variation. The magnitude of the axes is represented by the eigenvalues and the direction of the axes by the eigenvectors (Davis, 1986). Each constituent within each principal component has a score or the principal component loading, which is a coefficient of the linear equation defined by the eigenvector (Davis, 1986). Concentrations of a number of related geochemical constituent concentrations can be combined by PCA into a single derived component that may be useful to categorize related constituents. The computed single component provides information regarding the degree that the variance in concentrations of those correlated constituents accounts for the overall variability of the larger dataset. The interrelated constituents were grouped into principal components that were then sorted and ranked as principal components 1, 2, 3, and so forth by the amount of the total variability for which they account. High loadings imply a high relationship among original values. References are made to the loading of constituent "A" onto components 1, 2, and 3 (Davis, 1986). The same sign between loadings does not mean that it is actually increasing or decreasing, just that the loadings with the same signs are related in an axis in the same direction representing a portion of the data variance. The statistically most significant components to which constituents of concern correlated, such as As, As species, Ra-226, gross alpha- and beta-particle activities, or U, were of most interest. The PCA was used to determine how the constituents measured in all 91 wells were related in the subdatabases

grouped by well location and constituents (Ra-226 and As species) that were sampled in a small number of wells. For the subdatabase grouped by well location, the distance from the top of open interval to the top of the Burkeville confining unit was added as a component to incorporate the variability of the open interval depths in the aquifer system for the PCA.

The draftsman plot (scatter plot of all pairwise combinations of variables) (Clarke and Warwick, 2001) and the associated calculated Pearson correlation matrix among all pairs of variables were examined for evidence of colinearity with minimal scatter. The draftsman plots and Pearson correlation matrix were used as diagnostic tools before normalizing the environmental data for PCA (Clarke and Warwick, 2001). Highly correlated variable pairs (greater than or equal to 0.95) were identified, and one of the variables among the pair was excluded from the PCA. Correlations using the nonparametric Spearman technique (Helsel and Hirsch, 2002) were compared against results of the PCA to assess consistency. The PCA is used to compare similarities in variability for a group of constituents (perhaps all affected by a similar chemical process), whereas Spearman correlations assess only the similarity in trends of concentrations of the two constituents being compared (Helsel and Hirsch, 2002).

Geochemistry

The physicochemical properties and concentrations of major ions help delineate the distribution of water-quality types within the aquifer. Furthermore, the concentrations of many trace-element constituents, including As and radionuclides, are dependent upon the water chemistry. The spatial distribution of the physicochemical properties and major ions aided in understanding the spatial distribution of elevated concentrations of As and radionuclides (Oden and others, 2011).

The results of physicochemical properties, major ions, As and other trace elements, and radionuclide analyses from samples collected from 3 wells in 2011 and from 13 wells in 2010 (the results from the 16 wells that were not included in Oden and others, 2011) are presented in appendix 1 of this report. For statistical analysis purposes, water-quality results primarily for these same groups of constituents measured in groundwater samples collected previously (Oden and others, 2010, tables 6–8; 2011, tables 4–6) are included in this report. Summary statistics for selected constituents described in this report, including physicochemical properties measured in the field and major-ion concentrations, are presented in table 2 for the 91 wells sampled from 2007 to 2011. Physicochemical properties and major-ion concentrations varied considerably among the northeast, northwest, and southwest Houston areas. The physicochemical properties and constituent concentrations also varied on the basis of the position (location) of the sampling site relative to the outcrop region of the aquifer and by the type of aquifer designation grouping (fully penetrating,

partially penetrating, or partial depth of penetration in the multiple aquifers) at the various positions. The summary statistics for physicochemical properties and constituent concentrations grouped by area (northeast, northwest, or southwest), by primary cation and anion water types, by aquifer designation grouping, and by redox category are presented in appendix 4.

Physicochemical Properties

Physicochemical properties (table 2) can provide insight into the chemical evolution of groundwater, and the relations between physicochemical properties and geochemical constituents can provide insight into the geochemistry and sources of groundwater. Dissolved solids concentrations can indicate the degree of chemical evolution of groundwater in an aquifer system (Plummer and Back, 1980; Hem, 1985; Eberts and George, 2000; Chowdhury and others, 2006). As dissolved solids increase, so does the specific conductance of the water, consistent with the well-defined relation described by Hem (1985). Relations between specific conductance and concentrations of geochemical constituents were examined. Specific conductance and geochemical constituent concentrations increased with increasing mineral dissolution (increasing ionic strength of the water). Specific conductance generally increased as alkalinity increased because both measurements increase as the amount of dissolved minerals (dissolved ions) in solution increases, although increase in alkalinity specifically reflects the increase in acid-neutralizing capability of a solution that is caused by the increase in dissolved mineral matter. In most natural waters, the alkalinity is produced by the dissolved carbon dioxide species bicarbonate and carbonate anions. An increase in alkalinity is mostly caused by increase of these species as a product of weathering reactions (Hem, 1985).

Specific conductance measures the electrical conductivity of the water; specific conductance increases as the amount of ionic constituents in solution increases (Hem, 1985). Specific-conductance measurements ranged from 314 to 1,110 microsiemens per centimeter at 25 degrees Celsius ($\mu\text{S}/\text{cm}$ at 25 °C), with a median of 501 $\mu\text{S}/\text{cm}$. The first and third quartiles of specific conductance were 476 and 531 $\mu\text{S}/\text{cm}$, respectively, indicating that the middle 50 percent (also known as the interquartile range, or IQR) of the waters sampled did not vary by much in terms of dissolved mineral content; however, the minimum and maximum measurements were substantially different from the median and IQRs. The maximum specific conductance (1,110 $\mu\text{S}/\text{cm}$) was measured in the water sample collected from well JY-65-29-109; this well was in the southwest Houston area and was assigned an aquifer designation grouping of “lowerCHCT, upperEVGL.” Conversely, the minimum specific conductance (314 $\mu\text{S}/\text{cm}$) was measured in the northeast Houston area in the water sample collected from well LJ-60-63-602; this well was assigned an aquifer designation grouping of “middleEVGL” (table 1).

Water temperature of a groundwater sample can provide insight into the depth of the source of the sample. Temperatures of geological materials increase with depth below land surface, and subsequently, deeper groundwater can reach substantially higher temperatures compared to water near the land surface (Hem, 1985). Most water temperatures did not vary much, with first and third quartile values of 25.0 and 25.9 °C, respectively, bracketing a median of 25.5 °C, or less than plus or minus 1 °C difference (table 2). The minimum and maximum measurements differed greatly from the median, indicating that the depth of the sources of these few water samples could be different from that of most of the samples. The water from the well LJ-65-06-601, with a minimum water temperature of 22.7 °C (table 2), was classified as part of the aquifer designation grouping “lowerCHCT, upperEVGL” (table 1). Well LJ-65-06-601 was also one of the shallowest of the sampled wells, with a top of open interval of -367 ft below datum and a bottom of open interval of -522 ft below datum. The water from well LJ-65-13-222, with the maximum water temperature of 29.9 °C (table 2), was classified as “lowerEVGL” and was among the deepest of the sampled wells, with a top of open interval of -1,078 ft below datum and a bottom of open interval of -1,551 ft below datum (table 1). These results indicate that the water from these two wells is from different depths that presumably represent differences in groundwater-residence time.

The physicochemical properties of DO and ORP provide an indication of the geochemical conditions from within the part of the aquifer from which the samples are withdrawn. The DO concentrations varied considerably, from less than 0.1 to 4.5 mg/L, with a median of 0.39 mg/L (table 2). In slightly more than half of the wells sampled, the DO concentrations were less than 0.5 mg/L and thereby represented water withdrawn from reducing geochemical conditions. The DO concentrations greater than 0.5 mg/L (indicative of oxidizing conditions) were measured in less than half of the wells sampled (table 3). The ORP was measured in the samples collected from 71 wells in the study area and varied greatly from -212 to 466 millivolts (mV), with a median of -54.3 mV (table 2). As with the DO concentrations, water with a negative ORP measurement was measured in slightly more than half of the wells sampled, indicating reducing geochemical conditions. Except for the samples collected from five wells, the DO concentrations were less than 0.5 mg/L when the ORP measurement was negative.

Differences in pH (hydrogen-ion activities) among water samples can indicate differences in the types of chemical reactions taking place in the water withdrawn from the system because hydrogen ions are produced by various types of chemical reactions and consumed by other reactions and, therefore, alter the pH of the water (Hem, 1985). The median pH was 7.5, indicating that most of the samples represented

slightly alkaline groundwater; that is, the groundwater has slightly more acid-neutralizing capacity than water with a pH of 7.0 that, by definition, is termed “neutral.” In the United States, the pH of most groundwater ranges from 6.0 to about 8.5 (Hem, 1985). The IQR of the pH values in the samples from Houston was about 0.2 pH units, indicating that the pH in most of the samples varied only slightly (table 2). The samples with the minimum (7.2) pH measurements can be described as near neutral, and the samples with the maximum (8.1) pH value can be described as moderately alkaline. The compositional characteristics of the samples with extreme pH values were different compared to each other; the samples with pH values near the minimum were more dilute and Ca rich, whereas the samples with values from the upper end were more mineralized and Na rich. The compositional differences and the difference in pH indicate that these few water samples with pH values near the upper end of the distribution of pH values had likely undergone different geochemical reactions than the majority of samples with pH at or near the median value.

The physicochemical properties measured in the field varied among the northeast, northwest, and southwest areas by sample collection depth and by proximity of the well to the Gulf of Mexico. There was no statistically significant difference in ranges of turbidity, DO concentration, and water-temperature measurements in the water from wells in each of the three areas as determined by the Tukey test (table 4A; app. 4A). The difference in distribution for the ORP, pH, specific conductance, and alkalinity measurements was statistically significant among the three areas (95 percent confidence level among Tukey classes indicated by *p*-value of 0.05 or less; table 4A). The significant differences of at least one group from the others were confirmed by the Kruskal-Wallis test, but discrimination and ranking among the groups were completed with the Tukey test.) The pH ranges in measurements from wells in the northeast area were significantly higher than the southwest area with a higher mean rank, and results were grouped as the “A” Tukey class, compared to the lower mean rank and an assigned “B” Tukey class for the southwest area (table 4A). The pH measurements from wells in the northwest area were not statistically significantly different from those in either the northeast or the southwest area but rather were overlapping with both; the northwest area was classified as group “AB” with respect to the pH, indicating that there was not a significant difference in mean rank for the northwest area compared to the other two areas (table 4A). The ORP ranges in measurements from wells in the southwest area were significantly higher than in the northeast and northwest areas; the highest mean rank in the southwest area was grouped as the “A” Tukey class (table 4A), and the other areas were grouped as the “B” Tukey class. Higher ORP measurements in the water from the wells in the southwest are indicative of oxic conditions.

Table 3. Station number, State well number, predominant cation and anion, concentrations of reduction-oxidation variables and threshold values, general reduction-oxidation category, presumed predominant reduction process, concentration ratios of arsenite to arsenic, and activity ratios of radium-226 to uranium-238 in water samples collected from the Gulf Coast aquifer system, in Houston, Texas, 2007–11.

[USGS, U.S. Geological Survey; mg/L, milligrams per liter; N, nitrogen; µg/L, micrograms per liter; TS, Montgomery County; NE, northeast area; Ca, calcium; HCO₃, bicarbonate; <, less than; Fe(III), iron reduction; -, and; SO₄, sulfate reduction; /, and (or); --, no data available; Na, sodium; CH₄gen, methanogenesis; >, greater than; LJ, Harris County; O₂, oxygen reduction; NW, northwest area; SW, southwest area; E, estimated, result is greater than long-term method detection level (LT-MDL) and less than laboratory reporting level (LRL) (Childress and others, 1999); Cl, chloride. Reduction processes are defined by McMahon and Chapelle (2008) and Chapelle and others (2009) and can be approximately calculated by using software of Jurgens, McMahon, and others (2009)]

USGS station number	State well number	Location	Predominant cation, anion	Reduction-oxidation variables						Reduction-oxidation assignment			Trace contaminant	
				Dissolved oxygen (mg/L)	Nitrate + nitrite (as N) (mg/L)	Manganese (µg/L)	Iron (µg/L)	Sulfate (mg/L)	Sulfide (mg/L)	General reduction-oxidation (redox) category	Presumed pre-dominant reduction process	Ratio, mass, iron to sulfide	Ratio, mass, arsenite to arsenic ²	Ratio, activity, radium-226 to uranium-238
				Threshold values ¹										
				0.5	0.5	50	29	4	none					
Reduction-oxidation variable concentrations														
300446095121901	TS-60-63-507	NE	Ca,HCO ₃	<0.10	<0.5	12.8	69	6.9	0.009	Anoxic(mixed)	Fe(III)-SO ₄	7.67	1.40	68.09
300258095145301	TS-60-63-404	NE	Ca,HCO ₃	<0.10	<0.5	109	265	11.2	<0.005	Anoxic	Fe(III)/SO ₄	--	1.2	8.39
300419095154301	TS-60-62-604	NE	Na,HCO ₃	0.21	<0.5	7.1	165	<0.18	<0.005	Anoxic	CH ₄ gen	--	0.97	>15.00
295616095170101	LJ-65-06-601	NE	Ca,HCO ₃	0.50	<0.5	<3.8	52	10.0	<0.20	Mixed(oxic-anoxic)	O ₂ -Fe(III)/SO ₄	--	--	--
295553095191201	LJ-65-06-528	NE	Na,HCO ₃	<0.10	<0.5	36.4	277	6.4	<0.20	Anoxic	Fe(III)/SO ₄	--	--	--
295850095201301	LJ-65-06-103	NE	Ca,HCO ₃	2.0	<0.5	<3.8	5	6.3	-- ³	Oxic	O ₂	--	--	--
295855095204301	LJ-65-06-102	NE	Ca,HCO ₃	2.1	<0.5	<3.8	4	6.4	--	Oxic	O ₂	--	--	--
300223095142101	LJ-60-63-715	NE	Ca,HCO ₃	<0.10	<0.5	25.1	255	11.5	<0.20	Anoxic	Fe(III)/SO ₄	--	--	--
300225095144202	LJ-60-63-709	NE	Ca,HCO ₃	<0.10	<0.5	3.4	29	10.6	0.008	Anoxic(mixed)	Fe(III)-SO ₄	3.63	0.85	3.80
300343095090301	LJ-60-63-604	NE	Ca,HCO ₃	4.2	<0.5	<0.2	<6	3.2	--	Oxic	O ₂	--	0	2.03
300331095092201	LJ-60-63-603	NE	Ca,HCO ₃	2.4	<0.5	9.2	3	5.6	--	Oxic	O ₂	--	--	--
300355095093501	LJ-60-63-602	NE	Ca,HCO ₃	2.5	<0.5	12.0	E4	5.5	--	Oxic	O ₂	--	0	0.55
300302095113301	LJ-60-63-511	NE	Ca,HCO ₃	<0.10	<0.5	65.7	132	9.4	<0.005	Anoxic	Fe(III)/SO ₄	--	1.00	130.15
300359095122902	LJ-60-63-510	NE	Ca,HCO ₃	<0.10	<0.5	79.4	175	11.7	0.014	Anoxic	Fe(III)	12.50	1.07	>30.88
300231095113701	LJ-60-63-508	NE	Ca,HCO ₃	<0.10	<0.5	77.5	144	10.4	0.006	Anoxic	Fe(III)	24.00	0.96	107.79
300248095105301	LJ-60-63-505	NE	Ca,HCO ₃	<0.10	<0.5	34.4	122	7.3	0.006	Anoxic	Fe(III)	20.33	1.25	>28.02
300334095113401	LJ-60-63-504	NE	Ca,HCO ₃	<0.10	<0.5	55.5	111	7.5	<0.005	Anoxic	Fe(III)/SO ₄	--	0.79	>29.85
300408095115201	LJ-60-63-503	NE	Ca,HCO ₃	<0.10	<0.5	16.3	148	5.6	0.013	Anoxic	Fe(III)	11.38	1.38	112.84
300403095125402	LJ-60-63-502	NE	Ca,HCO ₃	<0.10	<0.5	84.8	230	11.5	0.008	Anoxic	Fe(III)	28.75	1.15	>29.19
300426095123902	LJ-60-63-407	NE	Ca,HCO ₃	<0.10	<0.5	33.3	107	10.2	<0.005	Anoxic	Fe(III)/SO ₄	--	1.25	173.38
295204095261301	LJ-65-13-225	NW	Na,HCO ₃	<0.10	<0.5	8.1	131	10.1	<0.20	Anoxic	Fe(III)/SO ₄	--	1.2	6.72
295203095261401	LJ-65-13-224	NW	Na,HCO ₃	<0.10	<0.5	10.3	112	0.81	<0.20	Anoxic	CH ₄ gen	--	0.9	>39.71
295228095263101	LJ-65-13-222	NW	Na,HCO ₃	<0.10	<0.5	5.9	77	E0.17	<0.20	Anoxic	CH ₄ gen	--	0.92	>41.18

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[USGS, U.S. Geological Survey; mg/L, milligrams per liter; N, nitrogen; µg/L, micrograms per liter; TS, Montgomery County; NE, northeast area; Ca, calcium; HCO₃, bicarbonate; <, less than; Fe(III), iron reduction; -, and; SO₄, sulfate reduction; /, and (or); --, no data available; Na, sodium; CH₄gen, methanogenesis; >, greater than; LJ, Harris County; O₂, oxygen reduction; NW, northwest area; SW, southwest area; E, estimated, result is greater than long-term method detection level (LT-MDL) and less than laboratory reporting level (LRL) (Childress and others, 1999); Cl, chloride. Reduction processes are defined by McMahon and Chapelle (2008) and Chapelle and others (2009) and can be approximately calculated by using software of Jurgens, McMahon, and others (2009)]

USGS station number	State well number	Location	Predominant cation, anion	Reduction-oxidation variables						Reduction-oxidation assignment			Trace contaminant	
				Dissolved oxygen (mg/L)	Nitrate + nitrite (as N) (mg/L)	Manganese (µg/L)	Iron (µg/L)	Sulfate (mg/L)	Sulfide (mg/L)	General reduction-oxidation (redox) category	Presumed predominant reduction process	Ratio, mass, iron to sulfide	Ratio, mass, arsenite to arsenic ²	Ratio, activity, radium-226 to uranium-238
295207095262102	LJ-65-13-221	NW	Ca,HCO ₃	4.3	<0.5	1.6	<8	4.8	--	Oxic	O ₂	--	0	1.00
295228095262901	LJ-65-13-220	NW	Ca,HCO ₃	1.8	<0.5	1.2	8	9.3	--	Oxic	O ₂	--	0	0.16
295150095254601	LJ-65-13-214	NW	Ca,HCO ₃	0.53	<0.5	1.0	<8	11.6	<0.20	Oxic	O ₂	--	0	0.14
294723095370501	LJ-65-12-730	NW	Ca,HCO ₃	<0.10	<0.5	12.7	70	13.3	<0.20	Anoxic	Fe(III)/SO ₄	--	--	--
294721095361001	LJ-65-12-719	NW	Ca,HCO ₃	2.0	<0.5	4.5	27	8.7	--	Oxic	O ₂	--	--	--
294921095312907	LJ-65-12-633	NW	Ca,HCO ₃	3.5	<0.5	<3.8	10	6.4	--	Oxic	O ₂	--	--	--
294950095313701	LJ-65-12-622	NW	Ca,HCO ₃	1.2	<0.5	5.4	31	13.0	--	Mixed(oxic-anoxic)	O ₂ -Fe(III)/SO ₄	--	--	--
294900095312101	LJ-65-12-619	NW	Ca,HCO ₃	1.2	<0.5	5.5	10	12.5	0.40	Mixed(oxic-anoxic)	O ₂ -SO ₄	--	--	--
294844095342401	LJ-65-12-522	NW	Na,HCO ₃	<0.10	<0.5	12.9	183	14.4	<0.20	Anoxic	Fe(III)/SO ₄	--	--	14.71
294735095344001	LJ-65-12-521	NW	Na,HCO ₃	<0.10	<0.5	13.7	117	15.7	<0.20	Anoxic	Fe(III)/SO ₄	--	--	9.52
294925095341201	LJ-65-12-520	NW	Na,HCO ₃	<0.10	<0.5	9.7	145	12.2	<0.20	Anoxic	Fe(III)/SO ₄	--	--	63.48
294952095342601	LJ-65-12-519	NW	Ca,HCO ₃	<0.10	<0.5	13.6	214	15.5	<0.20	Anoxic	Fe(III)/SO ₄	--	--	--
294800095344101	LJ-65-12-516	NW	Na,HCO ₃	<0.10	<0.5	11.0	391	16.8	<0.20	Anoxic	Fe(III)/SO ₄	--	--	--
295027095312301	LJ-65-12-328	NW	Na,HCO ₃	0.88	<0.5	6.7	225	4.9	0.20	Mixed(oxic-anoxic)	O ₂ -Fe(III)-SO ₄	1.13	--	--
294723095382601	LJ-65-11-920	NW	Ca,HCO ₃	<0.10	<0.5	9.6	102	14.6	<0.20	Anoxic	Fe(III)/SO ₄	--	--	--
294702095394001	LJ-65-11-917	NW	Na,HCO ₃	<0.10	<0.5	11.3	115	14.9	<0.20	Anoxic	Fe(III)/SO ₄	--	--	7.96
294717095401001	LJ-65-11-804	NW	Ca,HCO ₃	<0.10	<0.5	13.2	162	14.6	<0.20	Anoxic	Fe(III)/SO ₄	--	--	7.94
294712095401301	LJ-65-11-803	NW	Ca,HCO ₃	<0.10	<0.5	14.9	311	14.1	<0.20	Anoxic	Fe(III)/SO ₄	--	--	3.73
294731095414201	LJ-65-11-514	NW	Na,HCO ₃	<0.10	<0.5	14.5	57	12.3	<0.20	Anoxic	Fe(III)/SO ₄	--	--	--
295251095264502	LJ-65-05-814	NW	Ca,HCO ₃	1.03	<0.5	2.9	31	10.3	<0.20	Mixed(oxic-anoxic)	O ₂ -Fe(III)/SO ₄	--	0.1	0.45
295306095270502	LJ-65-05-813	NW	Ca,HCO ₃	4.5	<0.5	1.1	E8	10.1	--	Oxic	O ₂	--	0	0.20
295247095344701	LJ-65-04-811	NW	Ca,HCO ₃	1.10	<0.5	3.6	13	13.6	--	Oxic	O ₂	--	0	--
295249095370701	LJ-65-04-729	NW	Ca,HCO ₃	1.0	<0.5	10.9	59	13.1	--	Mixed(oxic-anoxic)	O ₂ -Fe(III)/SO ₄	--	--	--

Table 3. Station number, State well number, predominant cation and anion, concentrations of reduction-oxidation variables and threshold values, general reduction-oxidation category, presumed predominant reduction process, concentration ratios of arsenite to arsenic, and activity ratios of radium-226 to uranium-238 in water samples collected from the Gulf Coast aquifer system, in Houston, Texas, 2007–11.—Continued

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USGS station number	State well number	Location	Predominant cation, anion	Reduction-oxidation variables						Reduction-oxidation assignment			Trace contaminant	
				Dissolved oxygen (mg/L)	Nitrate + nitrite (as N) (mg/L)	Manganese (µg/L)	Iron (µg/L)	Sulfate (mg/L)	Sulfide (mg/L)	General reduction-oxidation (redox) category	Presumed pre-dominant reduction process	Ratio, mass, iron to sulfide	Ratio, mass, arsenite to arsenic ²	Ratio, activity, radium-226 to uranium-238
295249095364701	LJ-65-04-728	NW	Na,HCO ₃	<0.10	<0.5	10.7	203	11.8	<0.20	Anoxic	Fe(III)/SO ₄	--	--	--
295246095351301	LJ-65-04-723	NW	Ca,HCO ₃	1.12	<0.5	7.3	44	12.6	<0.20	Mixed(oxic-anoxic)	O ₂ -Fe(III)/SO ₄	--	--	--
295243095383101	LJ-65-03-916	NW	Ca,HCO ₃	0.34	<0.5	9.0	154	13.5	<0.20	Anoxic	Fe(III)/SO ₄	--	--	8.66
293652095293601	LJ-65-29-108	SW	Na,HCO ₃	<0.10	<0.5	42.3	304	15.5	<0.20	Anoxic	Fe(III)/SO ₄	--	--	3.29
293736095285301	LJ-65-21-709	SW	Na,HCO ₃	<0.10	<0.5	14.1	46	14.7	<0.20	Anoxic	Fe(III)/SO ₄	--	--	--
293734095293701	LJ-65-21-708	SW	Na,HCO ₃	<0.10	<0.5	7.0	E4	15.5	<0.20	Suboxic	Suboxic	--	--	--
294348095270401	LJ-65-21-202	SW	Na,HCO ₃	<0.10	<0.5	7.2	22	10.5	<0.20	Suboxic	Suboxic	--	--	--
294338095270401	LJ-65-21-201	SW	Ca,HCO ₃	1.3	<0.5	<0.2	<6	12.3	--	Oxic	O ₂	--	--	--
294329095284603	LJ-65-21-150	SW	Ca,HCO ₃	1.3	<0.5	9.0	108	8.8	--	Mixed(oxic-anoxic)	O ₂ -Fe(III)/SO ₄	--	0	--
294328095290402	LJ-65-21-149	SW	Na,HCO ₃	0.44	<0.5	<3.8	13	14.0	<0.20	Suboxic	Suboxic	--	--	--
294329095284602	LJ-65-21-148	SW	Na,HCO ₃	0.68	<0.5	<3.8	7	12.3	<0.20	Oxic	O ₂	--	--	0.33
294326095293002	LJ-65-21-144	SW	Na,HCO ₃	0.84	<0.5	<3.8	26	13.3	<0.20	Oxic	O ₂	--	--	--
294333095275602	LJ-65-21-143	SW	Na,HCO ₃	0.12	<0.5	4.3	<6	13.0	<0.20	Suboxic	Suboxic	--	--	--
293732095300601	LJ-65-20-911	SW	Na,HCO ₃	0.39	<0.5	4.5	<6	13.4	<0.20	Suboxic	Suboxic	--	--	--
293934095342201	LJ-65-20-811	SW	Ca,HCO ₃	0.47	<0.5	<3.8	<3	13.4	<0.20	Suboxic	Suboxic	--	--	--
294108095324702	LJ-65-20-520	SW	Ca,HCO ₃	1.7	<0.5	1.3	<3	12.6	--	Oxic	O ₂	--	0	--
294127095342502	LJ-65-20-519	SW	Na,HCO ₃	<0.10	<0.5	14.2	114	15.9	<0.20	Anoxic	Fe(III)/SO ₄	--	--	--
294047095345601	LJ-65-20-516	SW	Ca,HCO ₃	2.1	<0.5	<3.8	4	12.1	--	Oxic	O ₂	--	--	--
294147095344303	LJ-65-20-513	SW	Ca,HCO ₃	3.1	<0.5	0.4	<8	10.6	--	Oxic	O ₂	--	0	0.35
294113095361702	LJ-65-20-422	SW	Ca,HCO ₃	3.8	<0.5	E0.2	<8	12.1	--	Oxic	O ₂	--	0	0.28
294113095361701	LJ-65-20-421	SW	Na,HCO ₃	0.39	<0.5	8.9	32	17.2	<0.20	Anoxic	Fe(III)/SO ₄	--	0.88	22.30
294050095355501	LJ-65-20-416	SW	Ca,HCO ₃	4.4	<0.5	<3.8	4	8.8	--	Oxic	O ₂	--	--	--
294002095351001	LJ-65-20-414	SW	Ca,HCO ₃	0.82	<0.5	<3.8	<6	14.1	--	Oxic	O ₂	--	--	--
294029095354301	LJ-65-20-410	SW	Ca,HCO ₃	4.0	<0.5	<3.8	6	9.4	--	Oxic	O ₂	--	--	--
294144095351002	LJ-65-20-409	SW	Ca,HCO ₃	2.4	<0.5	E0.1	<8	8.4	--	Oxic	O ₂	--	0	0.43

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USGS station number	State well number	Location	Predominant cation, anion	Reduction-oxidation variables						Reduction-oxidation assignment			Trace contaminant	
				Dissolved oxygen (mg/L)	Nitrate + nitrite (as N) (mg/L)	Manganese (µg/L)	Iron (µg/L)	Sulfate (mg/L)	Sulfide (mg/L)	General reduction-oxidation (redox) category	Presumed predominant reduction process	Ratio, mass, iron to sulfide	Ratio, mass, arsenite to arsenic ²	Ratio, activity, radium-226 to uranium-238
294149095363002	LJ-65-20-408	SW	Na,HCO ₃	1.33	<0.5	1.9	E6	13.0	--	Oxic	O ₂	--	0	0.61
294131095360701	LJ-65-20-407	SW	Ca,HCO ₃	3.0	<0.5	0.3	<8	9.2	--	Oxic	O ₂	--	0	0.34
294201095355601	LJ-65-20-405	SW	Ca,HCO ₃	2.9	<0.5	<3.8	<6	9.9	--	Oxic	O ₂	--	--	--
294323095300102	LJ-65-20-324	SW	Na,HCO ₃	0.15	<0.5	7.6	57	14.9	<0.20	Anoxic	Fe(III)/SO ₄	--	--	--
294340095311103	LJ-65-20-321	SW	Na,HCO ₃	0.49	<0.5	<3.8	E4	14.6	<0.20	Suboxic	Suboxic	--	--	--
294348095303702	LJ-65-20-319	SW	Na,HCO ₃	0.54	<0.5	<3.8	7	14.8	<0.20	Oxic	O ₂	--	--	--
294317095313001	LJ-65-20-304	SW	Na,HCO ₃	0.2	<0.5	8.3	11	15.5	--	Suboxic	Suboxic	--	--	--
294319095305901	LJ-65-20-303	SW	Ca,HCO ₃	2.5	<0.5	<3.8	<6	9.9	--	Oxic	O ₂	--	--	--
294414095364202	LJ-65-20-126	SW	Na,HCO ₃	<0.10	<0.5	20.8	448	14.9	<0.20	Anoxic	Fe(III)/SO ₄	--	--	--
294252095362101	LJ-65-20-125	SW	Ca,HCO ₃	3.4	<0.5	<3.8	7	10.3	--	Oxic	O ₂	--	--	--
294452095354501	LJ-65-20-104	SW	Na,HCO ₃	<0.10	<0.5	18.6	260	15.4	<0.20	Anoxic	Fe(III)/SO ₄	--	--	--
294456095341101	LJ-65-12-820	SW	Ca,HCO ₃	2.6	<0.5	<3.8	7	12.0	--	Oxic	O ₂	--	--	--
294501095343601	LJ-65-12-817	SW	Ca,HCO ₃	3.5	<0.5	<3.8	E4	10.3	--	Oxic	O ₂	--	--	--
294529095371801	LJ-65-12-735	SW	Ca,HCO ₃	3.5	<0.5	<3.8	<3	9.1	--	Oxic	O ₂	--	--	--
294519095383201	LJ-65-11-918	SW	Ca,HCO ₃	4.2	<0.5	<3.8	<6	8.6	--	Oxic	O ₂	--	--	--
294627095375801	LJ-65-11-914	SW	Na,HCO ₃	<0.10	<0.5	13.5	58	14.5	<0.20	Anoxic	Fe(III)/SO ₄	--	--	--
293527095271501	JY-65-29-209	SW	Na,Cl	<0.10	<0.5	40.9	266	13.5	<0.20	Anoxic	Fe(III)/SO ₄	--	--	9.50
293543095274901	JY-65-29-109	SW	Na,Cl	<0.10	<0.5	45.6	612	14.6	<0.20	Anoxic	Fe(III)/SO ₄	--	--	17.36
293635095294101	JY-65-29-107	SW	Na,HCO ₃	<0.10	<0.5	45.1	183	17.1	<0.20	Anoxic	Fe(III)/SO ₄	--	--	5.16
293636095300401	JY-65-28-309	SW	Ca,HCO ₃	<0.10	<0.5	56.3	404	14.9	<0.20	Anoxic	Fe(III)/SO ₄	--	--	2.56

¹Threshold concentrations were defined by McMahon and Chapelle (2008) and Chapelle and others (2009) to identify the predominant terminal electron acceptor process for the water samples.

²Determined by different analytical methods; may lead to ratios greater than 1.

³When the dissolved oxygen was measured as less than 1.0 mg/L or the oxidation-reduction potential was less than 200 millivolts (mV), unfiltered sulfides also were measured in the field. In 2007, a portable Hach DR 2800 spectrophotometer was used to measure the unfiltered sulfides concentrations in the field by using field supplies and an adapted method described by HACH (Hach Company, 2007). In 2008–11, a V-2000 photometer with CHEMetrics field supplies and method were used for this measurement (CHEMetrics, 2008).

Table 4. Differences among physicochemical properties and constituents by sampling location, reduction-oxidation (redox) category and anoxic process, and aquifer designation grouping as determined by the Tukey multiple comparison test statistic for the 91 groundwater samples that were collected from municipal supply wells in Houston, Texas, 2007–11.

[Group code sequence: highest mean of ranks is “A,” next highest mean ranks, “B,” then “C,” and so on; overlapping groups include the letters for each overlapping group (examples: “AB” and “CD” represent overlap with groups A and B, and C and D, respectively); $\mu\text{S}/\text{cm}$ at 25 °C, microsiemens per centimeter at 25 degrees Celsius; °C, degrees Celsius; NTRU, nephelometric turbidity ratio unit; mg/L, milligrams per liter; CaCO_3 , calcium carbonate; NE, northeast area; *nd*, no difference in concentration range; NW, northwest area; SW, southwest area; SiO_2 , silicon dioxide; $\mu\text{g}/\text{L}$, micrograms per liter; $\mu\text{g}\text{-As}/\text{L}$, micrograms arsenic per liter; pCi/L, picocuries per liter; CH4gen, methanogenic-anoxic process; <, less than; --, no data; CHCT, Chicot aquifer; EVGL, Evangeline aquifer]

Groups										
(A) By location										
Location	Distance from top of open interval to top of Burkeville	Distance from bottom of open interval to top of Burkeville	Dissolved oxygen (mg/L)	pH (standard units)	Specific conductance ($\mu\text{S}/\text{cm}$ at 25 °C)	Temperature, water (°C)	Turbidity (NTRU)	Oxidation reduction potential (millivolts)	Dissolved solids, dried at 180 °C, filtered (mg/L)	
Tukey class, by location, NE	C	B	<i>nd</i>	A	B	<i>nd</i>	<i>nd</i>	B	B	
Tukey class, by location, NW	B	B	<i>nd</i>	AB	A	<i>nd</i>	<i>nd</i>	B	A	
Tukey class, by location, SW	A	A	<i>nd</i>	B	A	<i>nd</i>	<i>nd</i>	A	A	
Probability value of Tukey classification, by location	<0.001	<0.001	0.055	0.049	<0.001	0.66	0.474	<0.001	<0.001	
locationNE,median	896	523	0.05	7.6	337	25.5	0.1	-137	200	
locationNW,median	1,055	228	0.05	7.5	516	25.6	0.2	-90.8	289	
locationSW,median	1,608	845	0.61	7.4	520	25.4	0.2	90.8	306	

Groups										
(A) By location										
Location	Calcium, filtered (mg/L)	Magnesium (mg/L)	Potassium, filtered (mg/L)	Sodium, filtered (mg/L)	Alkalinity (mg/L as CaCO_3)	Bromide, filtered (mg/L)	Chloride, filtered (mg/L)	Fluoride, filtered (mg/L)	Silica, filtered, (mg/L as SiO_2)	Sulfate, filtered (mg/L)
Tukey class, by location, NE	<i>nd</i>	B	A	B	B	C	C	B	B	B
Tukey class, by location, NW	<i>nd</i>	A	A	A	A	A	A	A	AB	A
Tukey class, by location, SW	<i>nd</i>	A	B	A	A	B	B	A	A	A
Probability value of Tukey classification, by location	0.212	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	0.012	<0.001
locationNE,median	39.4	3.91	2.35	24.4	139	0.08	21.2	0.18	24.0	7.40
locationNW,median	42.2	7.68	2.30	43.4	182	0.16	45.5	0.23	22.6	12.5
locationSW,median	47.8	8.11	1.92	48.5	189	0.14	41.3	0.28	25.0	13.2

Table 4. Differences among physicochemical properties and constituents by sampling location, reduction-oxidation (redox) category and anoxic process, and aquifer designation grouping as determined by the Tukey multiple comparison test statistic for the 91 groundwater samples that were collected from municipal supply wells in Houston, Texas, 2007–11.—Continued

[Group code sequence: highest mean of ranks is “A,” next highest mean ranks, “B,” then “C,” and so on; overlapping groups include the letters for each overlapping group (examples: “AB” and “CD” represent overlap with groups A and B, and C and D, respectively); $\mu\text{S}/\text{cm}$ at 25 °C, microsiemens per centimeter at 25 degrees Celsius; °C, degrees Celsius; NTRU, nephelometric turbidity ratio unit; mg/L, milligrams per liter; CaCO_3 , calcium carbonate; NE, northeast area; *nd*, no difference in concentration range; NW, northwest area; SW, southwest area; SiO_2 , silicon dioxide; $\mu\text{g}/\text{L}$, micrograms per liter; $\mu\text{g-As}/\text{L}$, micrograms arsenic per liter; pCi/L, picocuries per liter; CH4gen, methanogenic-anoxic process; <, less than; --, no data; CHCT, Chicot aquifer; EVGL, Evangeline aquifer]

Groups										
(A) By location										
Location	Barium, filtered ($\mu\text{g}/\text{L}$)	Chromium, filtered ($\mu\text{g}/\text{L}$)	Iron, filtered ($\mu\text{g}/\text{L}$)	Lithium, filtered ($\mu\text{g}/\text{L}$)	Manganese, filtered ($\mu\text{g}/\text{L}$)	Molybdenum, filtered ($\mu\text{g}/\text{L}$)	Strontium, filtered ($\mu\text{g}/\text{L}$)	Vanadium, filtered ($\mu\text{g}/\text{L}$)	Arsenate, filtered ($\mu\text{g-As}/\text{L}$)	Arsenic, filtered ($\mu\text{g}/\text{L}$)
Tukey class, by location, NE	A	B	A	B	A	<i>nd</i>	C	B	B	B
Tukey class, by location, NW	B	B	AB	A	AB	<i>nd</i>	A	B	AB	A
Tukey class, by location, SW	B	A	B	A	B	<i>nd</i>	B	A	A	A
Probability value of Tukey classification, by location	<0.001	0.001	0.005	<0.001	0.003	0.568	<0.001	<0.001	0.008	<0.001
locationNE,median	295	0.06	117	8.3	20.7	2.1	289	0.11	0.4	1.75
locationNW,median	230	0.06	77	19.1	9.0	1.9	597	0.17	0.8	2.90
locationSW,median	233	0.94	6.5	16.7	1.9	2.1	512	4.9	2.4	3.05

Groups										
(A) By location										
Location	Arsenite, filtered ($\mu\text{g-As}/\text{L}$)	Boron, filtered ($\mu\text{g}/\text{L}$)	Selenium, filtered ($\mu\text{g}/\text{L}$)	Gross alpha radioactivity, 30-day count, filtered (pCi/L)	Gross alpha radioactivity, 72-hour count, filtered (pCi/L)	Gross beta radioactivity, 30-day count, filtered (pCi/L)	Gross beta radioactivity, 72-hour count, filtered (pCi/L)	Radium-226, filtered (pCi/L)	Radon-222, unfiltered (pCi/L)	Uranium (natural), filtered ($\mu\text{g}/\text{L}$)
Tukey class, by location, NE	<i>nd</i>	B	B	B	B	<i>nd</i>	<i>nd</i>	B	<i>nd</i>	B
Tukey class, by location, NW	<i>nd</i>	A	AB	A	A	<i>nd</i>	<i>nd</i>	AB	<i>nd</i>	A
Tukey class, by location, SW	<i>nd</i>	A	A	A	A	<i>nd</i>	<i>nd</i>	A	<i>nd</i>	A
Probability value of Tukey classification, by location	0.157	<0.001	0.002	<0.001	<0.001	0.268	0.679	0.049	0.485	<0.001
locationNE,median	1.55	38	0.04	1.47	4.93	2.81	3.02	0.442	500	0.095
locationNW,median	0.5	55	0.04	7.2	10.4	3.72	2.22	1.23	715	1.15
locationSW,median	0.5	61	2.35	6.6	12.3	3.78	2.95	1.24	560	4.20

Table 4. Differences among physicochemical properties and constituents by sampling location, reduction-oxidation (redox) category and anoxic process, and aquifer designation grouping as determined by the Tukey multiple comparison test statistic for the 91 groundwater samples that were collected from municipal supply wells in Houston, Texas, 2007–11.—Continued

[Group code sequence: highest mean of ranks is “A,” next highest mean ranks, “B,” then “C,” and so on; overlapping groups include the letters for each overlapping group (examples: “AB” and “CD” represent overlap with groups A and B, and C and D, respectively); $\mu\text{S}/\text{cm}$ at 25 °C, microsiemens per centimeter at 25 degrees Celsius; °C, degrees Celsius; NTRU, nephelometric turbidity ratio unit; mg/L, milligrams per liter; CaCO_3 , calcium carbonate; NE, northeast area; *nd*, no difference in concentration range; NW, northwest area; SW, southwest area; SiO_2 , silicon dioxide; $\mu\text{g}/\text{L}$, micrograms per liter; $\mu\text{g-As}/\text{L}$, micrograms arsenic per liter; pCi/L, picocuries per liter; CH4gen, methanogenic-anoxic process; <, less than; --, no data; CHCT, Chicot aquifer; EVGL, Evangeline aquifer]

Groups										
(B) By redox category and anoxic process										
Redox category	Distance from top of open interval to top of Burkeville	Distance from bottom of open interval to top of Burkeville	Dissolved oxygen (mg/L)	pH (standard units)	Specific conductance ($\mu\text{S}/\text{cm}$ at 25 °C)	Temperature, water (°C)	Turbidity (NTRU)	Oxidation reduction potential (millivolts)	Dissolved solids, dried at 180 °C, filtered (mg/L)	
Tukey class, by redox group 1 (anoxic [Ch4gen])	C	B	CD	A	A	A	nd	D	A	
Tukey class, by redox group 2 (anoxic)	C	AB	D	AB	B	A	nd	C	B	
Tukey class, by redox group 3 (suboxic)	A	A	C	AB	AB	A	nd	B	AB	
Tukey class, by redox group 4 (mixed [oxic-anoxic])	BC	AB	B	BC	AB	B	nd	B	AB	
Tukey class, by redox group 5 (oxic)	AB	A	A	C	AB	B	nd	A	AB	
Probability value of Tukey class by redox group	<0.001	0.006	<0.001	<0.001	0.039	<0.001	0.06	<0.001	0.01	
Redox group 1,median	524	58	0.05	8.0	830	29.7	0.1	-208	486	
Redox group 2,median	1,049	612	0.05	7.5	494	25.9	0.2	-134	280	
Redox group 3,median	1,505	749	0.30	7.6	501	25.6	0.1	-8.9	292	
Redox group 4,median	1,055	349	1.0	7.4	516	25.0	0.7	-33.5	284	
Redox group 5,median	1,502	805	2.5	7.4	515	25.0	0.2	155	301	

Groups										
(B) By redox category and anoxic process										
Redox category	Calcium, filtered (mg/L)	Magnesium, filtered (mg/L)	Potassium, filtered (mg/L)	Sodium, filtered (mg/L)	Alkalinity (mg/L as CaCO_3)	Bromide, filtered (mg/L)	Chloride, filtered (mg/L)	Fluoride, filtered (mg/L)	Silica, filtered (mg/L as SiO_2)	Sulfate, filtered (mg/L)
Tukey class, by redox group 1 (anoxic [Ch4gen])	C	C	AB	A	A	A	A	A	C	C
Tukey class, by redox group 2 (anoxic)	BC	BC	A	BC	B	B	B	B	BC	AB
Tukey class, by redox group 3 (suboxic)	C	BC	B	AB	AB	B	B	A	B	A
Tukey class, by redox group 4 (mixed [oxic-anoxic])	AB	AB	AB	C	AB	AB	AB	B	AB	BC
Tukey class, by redox group 5 (oxic)	A	A	B	C	AB	AB	AB	B	A	C
Probability value of Tukey class by redox group	<0.001	<0.001	0.001	<0.001	0.015	0.002	0.001	<0.001	<0.001	<0.001
Redox group 1,median	8.50	2.09	1.82	178	313	0.27	83.3	1.32	15.1	0.09
Redox group 2,median	38.3	6.97	2.25	45.9	174	0.13	37.0	0.28	22.1	13.8
Redox group 3,median	28.7	5.75	1.88	68.4	195	0.12	34.7	0.44	22.1	13.7
Redox group 4,median	47.2	6.43	2.30	35.0	169	0.16	47.0	0.22	24.5	10.3
Redox group 5,median	49.5	8.64	1.98	38.3	179	0.14	42.9	0.22	26.2	9.88

Table 4. Differences among physicochemical properties and constituents by sampling location, reduction-oxidation (redox) category and anoxic process, and aquifer designation grouping as determined by the Tukey multiple comparison test statistic for the 91 groundwater samples that were collected from municipal supply wells in Houston, Texas, 2007–11.—Continued

[Group code sequence: highest mean of ranks is “A,” next highest mean ranks, “B,” then “C,” and so on; overlapping groups include the letters for each overlapping group (examples: “AB” and “CD” represent overlap with groups A and B, and C and D, respectively); $\mu\text{S}/\text{cm}$ at 25 °C, microsiemens per centimeter at 25 degrees Celsius; °C, degrees Celsius; NTRU, nephelometric turbidity ratio unit; mg/L, milligrams per liter; CaCO_3 , calcium carbonate; NE, northeast area; *nd*, no difference in concentration range; NW, northwest area; SW, southwest area; SiO_2 , silicon dioxide; $\mu\text{g}/\text{L}$, micrograms per liter; $\mu\text{g-As}/\text{L}$, micrograms arsenic per liter; pCi/L, picocuries per liter; CH4gen, methanogenic-anoxic process; <, less than; --, no data; CHCT, Chicot aquifer; EVGL, Evangeline aquifer]

Groups										
(B) By redox category and anoxic process										
Redox category	Barium, filtered ($\mu\text{g}/\text{L}$)	Chromium, filtered ($\mu\text{g}/\text{L}$)	Iron, filtered ($\mu\text{g}/\text{L}$)	Lithium, filtered ($\mu\text{g}/\text{L}$)	Manganese, filtered ($\mu\text{g}/\text{L}$)	Molybdenum, filtered ($\mu\text{g}/\text{L}$)	Strontium, filtered ($\mu\text{g}/\text{L}$)	Vanadium, filtered ($\mu\text{g}/\text{L}$)	Arsenate, filtered ($\mu\text{g-As}/\text{L}$)	Arsenic, filtered ($\mu\text{g}/\text{L}$)
Tukey class, by redox group 1 (anoxic [Ch4gen])	BC	C	AB	<i>nd</i>	B	A	B	BC	B	A
Tukey class, by redox group 2 (anoxic)	A	C	A	<i>nd</i>	A	A	A	C	B	BC
Tukey class, by redox group 3 (suboxic)	ABC	B	C	<i>nd</i>	B	AB	AB	AB	--	AB
Tukey class, by redox group 4 (mixed [oxic-anoxic])	A	B	B	<i>nd</i>	B	B	AB	B	B	C
Tukey class, by redox group 5 (oxic)	A	A	C	<i>nd</i>	C	C	A	A	A	C
Probability value of Tukey class by redox group	0.014	<0.001	<0.001	0.05	<0.001	<0.001	0.018	<0.001	<0.001	0.001
Redox group 1,median	125	0.06	112	23.4	7.1	8.0	216	0.12	0.4	10.1
Redox group 2,median	237	0.06	151	18.3	14.7	2.3	460	0.08	0.4	2.8
Redox group 3,median	210	0.60	4	18.0	4.4	2.7	384	4.7	--	4.0
Redox group 4,median	233	0.27	52	16.5	6.7	1.3	456	0.97	0.4	2.4
Redox group 5,median	237	1.5	4	13.9	0.9	1.1	526	5.1	2.4	2.5

Groups										
(B) By redox category and anoxic process										
Redox category	Arsenite, filtered ($\mu\text{g-As}/\text{L}$)	Boron, filtered ($\mu\text{g}/\text{L}$)	Selenium, filtered ($\mu\text{g}/\text{L}$)	Gross alpha radioactivity, 30-day count, filtered (pCi/L)	Gross alpha radioactivity, 72-hour count, filtered (pCi/L)	Gross beta radioactivity, 30-day count, filtered (pCi/L)	Gross beta radioactivity, 72-hour count, filtered (pCi/L)	Radium-226, filtered (pCi/L)	Radon-222, unfiltered (pCi/L)	Uranium (natural), filtered ($\mu\text{g}/\text{L}$)
Tukey class, by redox group 1 (anoxic [Ch4gen])	A	A	B	B	B	C	B	B	<i>nd</i>	B
Tukey class, by redox group 2 (anoxic)	B	BC	B	AB	B	BC	AB	A	<i>nd</i>	B
Tukey class, by redox group 3 (suboxic)	--	AB	A	AB	AB	AB	AB	--	--	A
Tukey class, by redox group 4 (mixed [oxic-anoxic])	BC	BC	A	A	A	A	A	AB	<i>nd</i>	A
Tukey class, by redox group 5 (oxic)	C	C	A	A	A	A	A	B	<i>nd</i>	A
Probability value of Tukey class by redox group	<0.001	<0.001	<0.001	0.006	<0.001	<0.001	0.001	0.001	0.09	<0.001
Redox group 1,median	9.3	465	0.04	-0.24	1.19	0.81	1.96	0.273	700	0.02
Redox group 2,median	1.6	59.5	0.04	3.8	6.45	3.1	2.98	1.585	730	0.38
Redox group 3,median	--	96.5	2.3	6.6	9.65	4.5	2.65	--	--	3.14
Redox group 4,median	0.5	45.0	2.3	8.2	13.3	4.1	3.73	0.721	815	4.92
Redox group 5,median	0.5	45.0	3.8	6.0	12.5	4.1	3.17	0.733	380	6.48

Table 4. Differences among physicochemical properties and constituents by sampling location, reduction-oxidation (redox) category and anoxic process, and aquifer designation grouping as determined by the Tukey multiple comparison test statistic for the 91 groundwater samples that were collected from municipal supply wells in Houston, Texas, 2007–11.—Continued

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Groups									
(C) By aquifer designation grouping									
Aquifer designation grouping	Distance from top of open interval to top of Burkeville	Distance from bottom of open interval to top of Burkeville	Dissolved oxygen (mg/L)	pH (standard units)	Specific conductance ($\mu\text{S}/\text{cm}$ at 25 °C)	Temperature, water (°C)	Turbidity (NTRU)	Oxidation reduction potential (millivolts)	Dissolved solids, dried at 180 °C, filtered (mg/L)
Tukey class, by aquifer 1 (lowerCHCT, upperEVGL)	A	A	ABC	B	B	ABC	ABC	A	B
Tukey class, by aquifer 2 (lowerCHCT, fullyEVGL)	BC	BC	AB	B	B	BC	AB	A	BC
Tukey class, by aquifer 3 (fullyEVGL)	BCD	BCD	ABC	B	B	AB	AB	AB	B
Tukey class, by aquifer 4 (middleEVGL)	BCD	BCD	BC	A	C	ABC	BC	B	C
Tukey class, by aquifer 5 (lowerEVGL)	CD	CD	ABC	A	A	ABC	ABC	B	A
Probability value of Tukey class by aquifer	<0.001	<0.001	0.026	<0.001	<0.001	0.002	0.007	<0.001	<0.001
aquifer1,median	1,521	831	0.54	7.4	504	25.3	0.2	47.2	298
aquifer2,median	1,065	191	1.12	7.4	515	25.0	0.5	24.0	284
aquifer3,median	939	162	0.19	7.5	503	25.9	0.4	-121	287
aquifer4,median	900	588	0.05	7.6	332	25.7	0.1	-137	200
aquifer5,median	537	66	0.13	8.0	759	28.9	0.2	-206	435

Groups										
(C) By aquifer designation grouping										
Aquifer designation grouping	Calcium, filtered (mg/L)	Magnesium, filtered (mg/L)	Potassium, filtered (mg/L)	Sodium, filtered (mg/L)	Alkalinity (mg/L as CaCO_3)	Bromide, filtered (mg/L)	Chloride, filtered (mg/L)	Fluoride, filtered (mg/L)	Silica, filtered (mg/L as SiO_2)	Sulfate, filtered (mg/L)
Tukey class, by aquifer 1 (lowerCHCT, upperEVGL)	A	A	CD	B	B	B	B	B	A	A
Tukey class, by aquifer 2 (lowerCHCT, fullyEVGL)	A	A	ABCD	BC	BC	AB	AB	BC	A	A
Tukey class, by aquifer 3 (fullyEVGL)	AB	A	A	AB	B	AB	B	BC	AB	AB
Tukey class, by aquifer 4 (middleEVGL)	B	B	ABCD	C	C	C	C	C	AB	AB
Tukey class, by aquifer 5 (lowerEVGL)	B	B	BCD	A	A	A	A	A	B	B
Probability value of Tukey class by aquifer	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	0.001
aquifer1,median	47.8	8.02	1.98	41.6	184	0.14	41.4	0.26	25.1	13.0
aquifer2,median	47.4	8.84	2.30	39.1	172	0.16	47.3	0.21	24.5	12.6
aquifer3,median	40.8	7.54	2.49	46.0	177	0.15	41.9	0.23	21.8	11.1
aquifer4,median	38.0	3.85	2.35	25.7	136	0.08	20.6	0.18	23.1	10.4
aquifer5,median	10.2	2.38	1.87	157	274	0.26	83.2	1.27	15.4	0.45

Table 4. Differences among physicochemical properties and constituents by sampling location, reduction-oxidation (redox) category and anoxic process, and aquifer designation grouping as determined by the Tukey multiple comparison test statistic for the 91 groundwater samples that were collected from municipal supply wells in Houston, Texas, 2007–11.—Continued

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Groups										
(C) By aquifer designation grouping										
Aquifer designation grouping	Barium, filtered (μg/L)	Chromium, filtered (μg/L)	Iron, filtered (μg/L)	Lithium, filtered (μg/L)	Manganese, filtered (μg/L)	Molybdenum, filtered (μg/L)	Strontium, filtered (μg/L)	Vanadium, filtered (μg/L)	Arsenate, filtered (μg-As/L)	Arsenic, filtered (μg/L)
Tukey class, by aquifer 1 (lowerCHCT, upperEVGL)	BC	A	<i>nd</i>	AB	B	B	A	A	A	B
Tukey class, by aquifer 2 (lowerCHCT, fullyEVGL)	ABC	AB	<i>nd</i>	ABC	B	B	A	AB	A	BC
Tukey class, by aquifer 3 (fullyEVGL)	A	AB	<i>nd</i>	AB	AB	B	A	BC	AB	BC
Tukey class, by aquifer 4 (middleEVGL)	A	BC	<i>nd</i>	BC	A	AB	B	C	B	C
Tukey class, by aquifer 5 (lowerEVGL)	BC	BC	<i>nd</i>	AB	AB	A	B	ABC	AB	A
Probability value of Tukey class by aquifer	<0.001	<0.001	0.045	<0.001	<0.001	0.001	<0.001	<0.001	0.001	<0.001
aquifer1,median	233	0.79	7.0	15.5	2.6	1.9	522	4.6	2.4	2.8
aquifer2,median	228	0.27	13.3	17.3	5.4	1.3	618	2.8	2.7	2.7
aquifer3,median	286	0.06	108	17.9	9.4	1.9	603	0.4	2.3	2.8
aquifer4,median	278	0.06	114	8.3	18.6	2.4	294	0.08	0.4	1.7
aquifer5,median	136	0.06	139	23.3	6.9	10.5	219	0.14	0.4	12.7

Groups										
(C) By aquifer designation grouping										
Aquifer designation grouping	Arsenite, filtered (μg-As/L)	Boron, filtered (μg/L)	Selenium, filtered (μg/L)	Gross alpha radioactivity, 30-day count, filtered (pCi/L)	Gross alpha radioactivity, 72-hour count, filtered (pCi/L)	Gross beta radioactivity, 30-day count, filtered (pCi/L)	Gross beta radioactivity, 72-hour count, filtered (pCi/L)	Radium-226, filtered (pCi/L)	Radon-222, unfiltered (pCi/L)	Uranium (natural), filtered (μg/L)
Tukey class, by aquifer 1 (lowerCHCT, upperEVGL)	C	BC	AB	A	A	AB	<i>nd</i>	A	<i>nd</i>	A
Tukey class, by aquifer 2 (lowerCHCT, fullyEVGL)	C	BCD	A	A	A	A	<i>nd</i>	ABC	<i>nd</i>	A
Tukey class, by aquifer 3 (fullyEVGL)	BC	ABCD	BC	A	B	ABC	<i>nd</i>	AB	<i>nd</i>	BC
Tukey class, by aquifer 4 (middleEVGL)	B	BCD	C	B	C	BC	<i>nd</i>	BC	<i>nd</i>	C
Tukey class, by aquifer 5 (lowerEVGL)	A	A	C	B	C	C	<i>nd</i>	C	<i>nd</i>	C ¹
Probability value of Tukey class by aquifer	<0.001	<0.001	<0.001	<0.001	<0.001	0.002	0.364	0.001	0.841	<0.001
aquifer1,median	0.5	56	2.1	6.5	12.2	3.72	3.03	1.61	550	3.92
aquifer2,median	0.5	47	14.1	9.5	12.8	4.75	3.22	0.397	727	7.77
aquifer3,median	0.5	65	0.26	7.45	8.10	3.36	3.25	1.60	720	1.00
aquifer4,median	1.6	38	0.04	1.19	4.36	2.75	3.00	0.598	500	0.06
aquifer5,median	9.3	436	0.04	1.13	1.80	1.35	2.03	0.273	700	0.02

¹Tukey class for uranium by aquifer 5 (lowerEVGL) was updated from “BC” to “C” because of a small sample anomaly.

The minimum, median, and maximum specific conductance and alkalinity were typically greater for wells in the northwest and southwest areas than from wells in the northeast area (app. 4A). The specific conductance and alkalinity ranges in measurements from wells in the southwest and northwest areas were significantly higher than those in the northeast area with a higher mean rank and an assigned "A" Tukey class (table 4A) and where these constituents were significantly less than the other areas assigned the "B" Tukey class. The majority of the wells in the southwest area are completed in the aquifer system considerably down-dip from the wells in the northeast area (figs. 1 and 6). The observed geochemical differences (table 4; app. 4A) are consistent with the results of a previous investigation (Chowdhury and others, 2006) showing that dissolved solids in the groundwater increase, in general, with increasing sample collection depth and proximity to the Gulf of Mexico. Differences in specific conductance and alkalinity by well location indicate that the type and quality of the water withdrawn from the wells in these three areas are different.

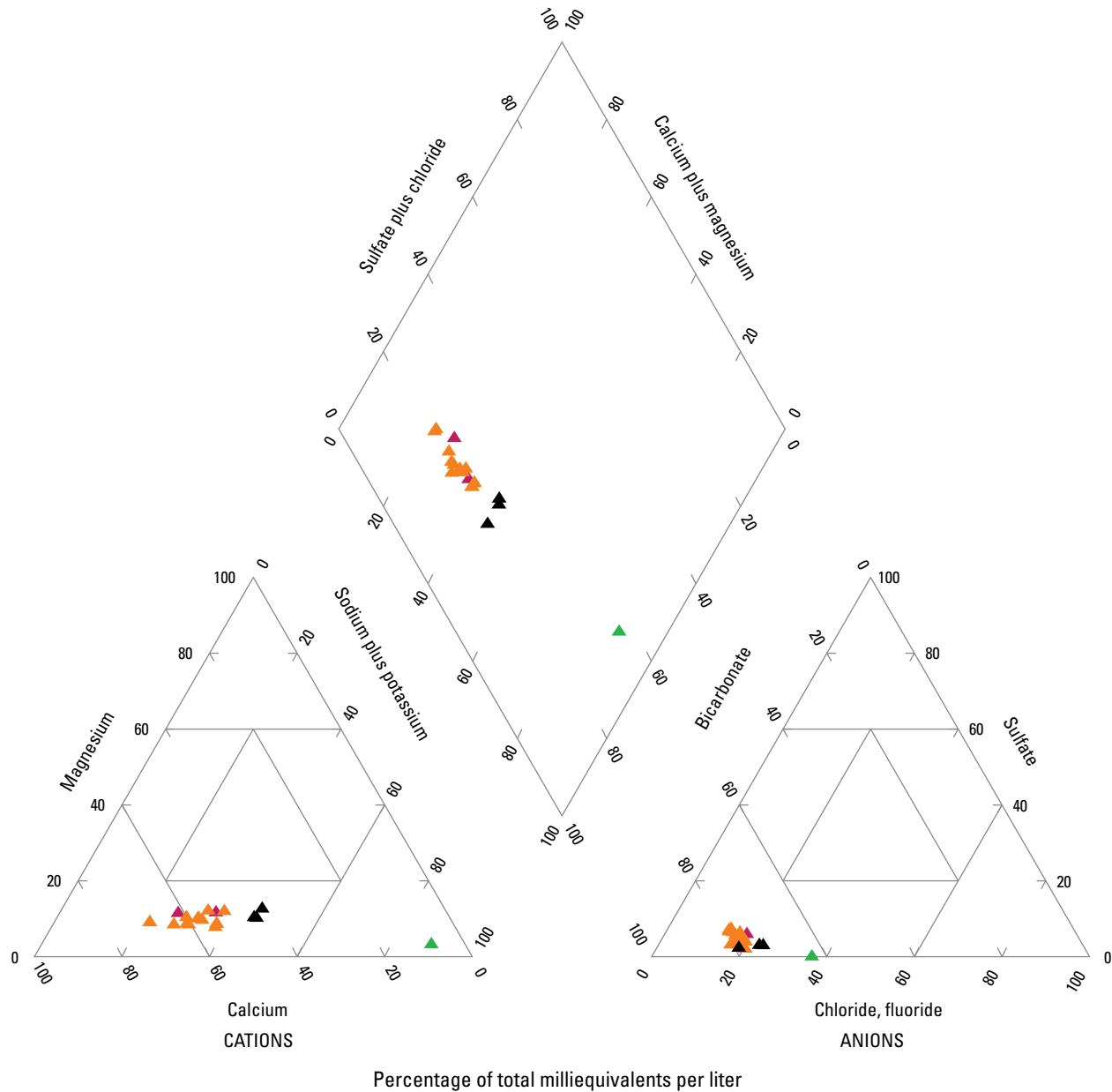
Major-Ion Chemistry and Predominant Cations and Anions

The major ions in the groundwater samples were typically as variable as the physicochemical properties, although the concentrations of some major ions varied more than those of others. The largest ranges for major-ion constituents for the 91 sampled wells were measured for the cations Ca and Na and for the anions HCO_3^- (as inferred from the measured alkalinity) and Cl (table 2). Simplified water types, as represented by the predominant major ions in the water samples, are listed in table 3 for each of the 91 wells. Piper diagrams depict the differences in major-ion chemistry composition among groundwater samples and help define major water types. Piper diagrams were prepared for each of the three sample-collection areas, with samples further grouped by aquifer designation (fig. 8). Calcium was the predominant cation in 56 of the 91 groundwater samples that were collected; among the remaining 35 samples, Na was the predominant cation (table 3). Bicarbonate was the predominant anion in 89 of the 91 groundwater samples, with Cl predominant in the 2 remaining samples (table 3). The predominant cation was Na in the two samples where Cl was the predominant anion. Approximately 62 percent (56 of 91) of the groundwater samples can thus be described as Ca- and

HCO_3^- -dominated water types, 36 percent (33 of 91) as Na- and HCO_3^- -dominated water types, and 2 percent (2 of 91) as Na- and Cl-dominated water types (table 3). The Ca- HCO_3^- type water is consistent with the description of the types of sediment that make up the Chicot and Evangeline aquifers, including sands cemented with calcium carbonate or a matrix of caliche, which is composed mostly of calcium carbonate (Sellards and others, 1932; Hosman, 1996). Water types are consistent with Chowdhury and others (2006), who also found that samples from the Gulf Coast aquifer system are mainly composed of Ca- HCO_3^- and Na- HCO_3^- type waters.

Selected major cations (Na, Ca, K, and Mg) were used to assess minor compositional variations by water type. Compared to the other cations, Na concentration varied the most among the groundwater samples. In samples representing the Ca-predominant water type, Na concentrations ranged from 14.2 to 51.0 mg/L, with a median of 34.8 mg/L (app. 4B). Compared to samples representing the Ca-predominant water type, Na concentrations were appreciably larger in the Na-predominant water type, ranging from 40.9 to 182 mg/L, with a median of 65.6 mg/L (app. 4B). Only small concentrations of K and Mg were measured in either the Na- or Ca-predominant water-type samples, and the concentrations of K and Mg varied little (K ranged from 1.47 to 2.76 mg/L, with a median of 2.17 mg/L; Mg ranged from 1.99 to 12.3 mg/L, with a median of 7.34 mg/L, table 2). For the entire sample set, Na plus K represented from 20 to 95 percent of the total ions of which the percentage of K was minimal (fig. 8). The maximum K and Mg concentrations for the entire sample set were less than the minimum Na concentration (14.2 mg/L; table 2). For all samples, Ca represented from about 5 to about 80 percent of the total cations, and Mg represented less than or equal to 20 percent of the total cations (fig. 8). In the Na-dominated water, Ca concentrations were greater than concentrations of Mg and K. The range of Ca concentrations for the samples in which Na was the predominant cation was relatively large, 8.23 to 65.9 mg/L (app. 4B), and similar to the range in Ca concentrations for the entire sample set (8.23 to 69.9 mg/L) (table 2). In Ca-dominated waters, Ca concentrations ranged from 35.8 to 69.9 mg/L. Differences in the concentration ranges for Na, Ca, Mg, and K in the different water types indicate that the variation in the concentration of Na, not K, has the largest effect on water chemistry among the singly charged (monovalent) cations, and the concentration of Ca, not Mg, has the largest effect among the doubly charged (divalent) cations.

A. Northeast



EXPLANATION

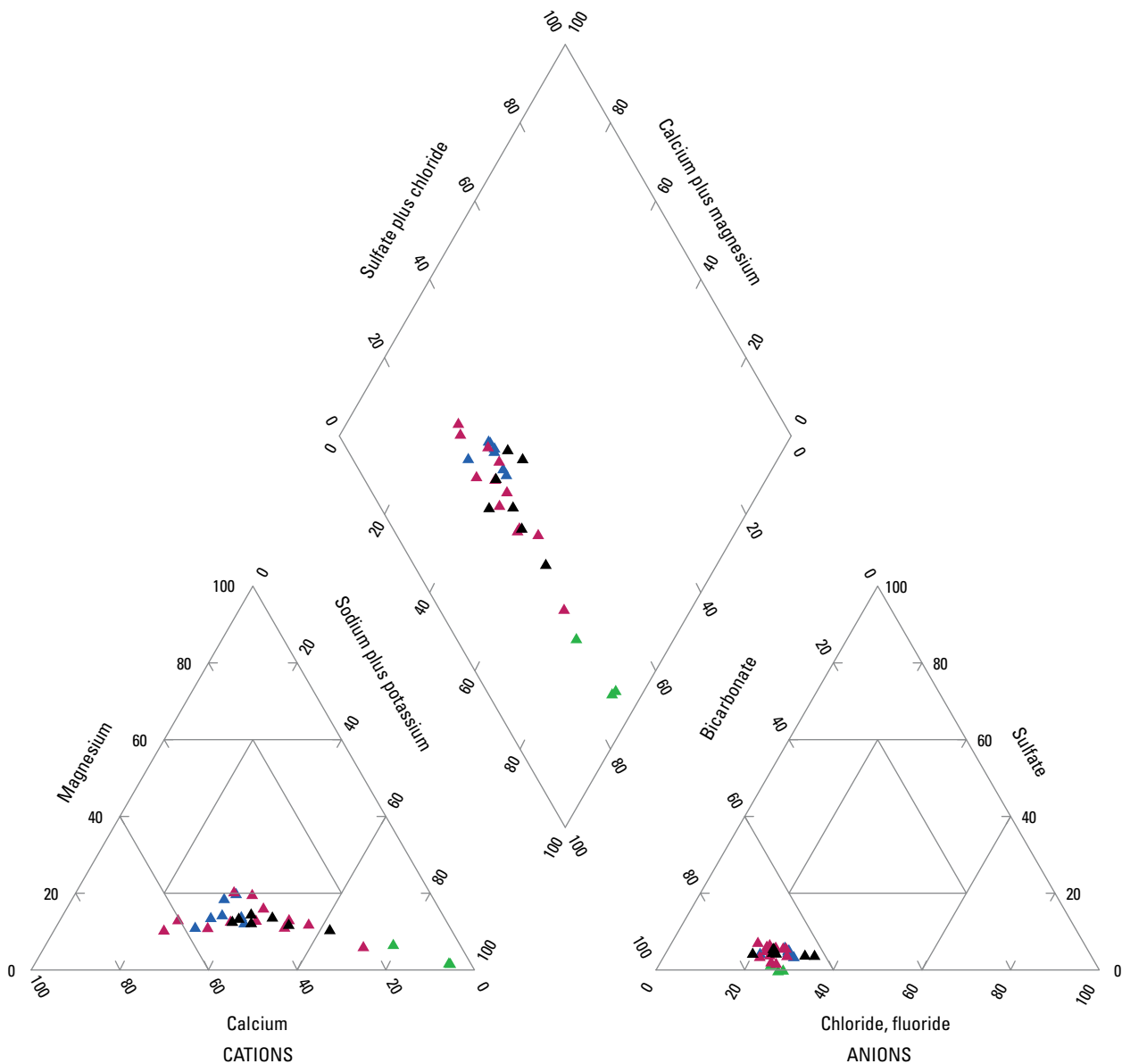
Aquifer designation grouping (table 1)

- ▲ FullyEVGL
- ▲ LowerCHCT, upperEVGL
- ▲ LowerEVGL
- ▲ MiddleEVGL

CHCT, Chicot aquifer
 EVGL, Evangeline aquifer

Figure 8. Water chemistry of the samples collected from municipal supply wells sampled during 2007–11 in the A, northeast; B, northwest; and C, southwest areas of Houston, Texas.

B. Northwest



Percentage of total milliequivalents per liter

EXPLANATION

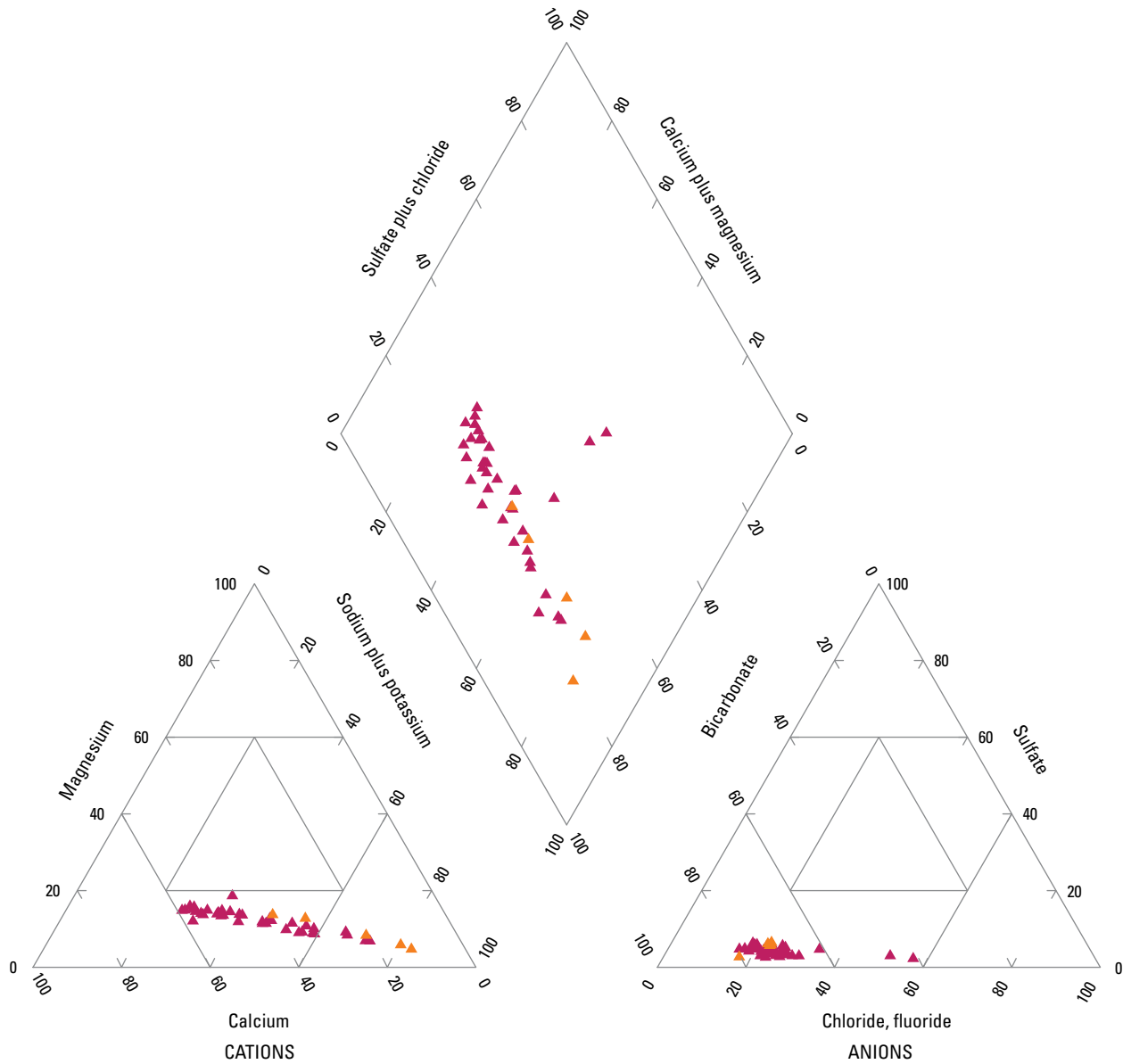
Aquifer designation grouping (table 1)

- ▲ FullyEVGL
- ▲ LowerCHCT, fullyEVGL
- ▲ LowerCHCT, upperEVGL
- ▲ LowerEVGL

CHCT, Chicot aquifer
 EVGL, Evangeline aquifer

Figure 8. Water chemistry of the samples collected from municipal supply wells sampled during 2007–11 in the A, northeast; B, northwest; and C, southwest areas of Houston, Texas.—Continued

C. Southwest



Percentage of total milliequivalents per liter

EXPLANATION

Aquifer designation grouping (table 1)

- ▲ LowerCHCT, upperEVGL
- ▲ MiddleEVGL

CHCT, Chicot aquifer
 EVGL, Evangeline aquifer

Figure 8. Water chemistry of the samples collected from municipal supply wells sampled during 2007–11 in the A, northeast; B, northwest; and C, southwest areas of Houston, Texas.—Continued

Among the anions, HCO_3^- was predominant in all but 2 of the 91 wells sampled, but the relative variability of HCO_3^- concentrations is less than the relative variability of Cl, Na, and Ca concentrations (table 2); the percentage of total milliequivalents per liter for HCO_3^- was between 60 and 80 for most groundwater samples (fig. 8). The range in Cl concentrations measured in the HCO_3^- -dominated samples was substantial, from 15.3 to 85.4 mg/L (app. 4B), and the range in concentration in the Ca-dominated samples was similar, being from 15.3 to 62.6 mg/L (app. 4B). In contrast, the Cl concentrations were greater than 29 mg/L in samples where Na was predominant, with a maximum of 216 mg/L (app. 4B). In samples in which Na was the predominant cation, HCO_3^- was the predominant anion for 33 of the 35 samples, and the relative percentages of Cl were generally between 20 and 40 percent of total milliequivalents per liter (fig. 8). The Cl concentrations in the groundwater samples that were Cl predominant were 142 and 216 mg/L, with greater than 50 percent of total milliequivalents per liter (fig. 8C; app. 4B), substantially higher than in water samples from the other wells.

Sulfate concentrations varied more in the Na-predominant-type waters than in the Ca-predominant-type waters. The range in SO_4 concentrations measured in all 91 groundwater samples was small (table 2), less than 20 percent meq/L (fig. 8), and much less than the range of HCO_3^- and Cl concentrations (table 2). The relative percentages of SO_4 were lowest in samples with the highest percentages of Na in the northeast and northwest areas (figs. 8A, 8B). The occurrence of relatively low SO_4 concentrations with relatively high Na concentrations is a result of the redox process of SO_4 reduction (Chapelle and others, 2009) and is likely related to a longer residence time, which allows for the continued evolution of water chemistry to compositions that differ from the dilute Ca- and HCO_3^- -dominated type intercepted by the shallowest wells that were sampled.

Major-ion concentrations and water types varied by well location, as related to the outcrop areas of the aquifer system, and by assigned aquifer designation grouping. By using the Tukey multiple comparison test to determine if there were differences among the northeast, northwest, and southwest areas, a statistically significant difference between the northeast area ("B" Tukey class, table 4A) and the other areas ("A" Tukey class, table 4A) was detected for the Na concentrations, along with an increase in median concentrations from northeast to southwest for both predominant cations, Na and Ca (app. 4A). The amount of Na increased as a percentage of total milliequivalents per liter in association with an increase in the percentage of Cl in water samples from wells located in the southwest area relative to those from the northeast area (fig. 8A and 8C). Absolute and relative increases for Na were associated with an increase in alkalinity (measured in milligrams per liter as CaCO_3) and in specific conductance, as measured in the water samples collected from wells in all the three areas (app. 4A). In the northeast Houston area, Ca was the predominant cation in 18

of 20 wells sampled (90 percent), whereas in the northwest Houston area, Ca was the predominant cation in 18 of 29 wells sampled (62 percent) (table 3). Oden and Truini (2013) collected samples near the updip extents of the aquifers from wells in Montgomery County, north of Houston, and also found predominantly Ca- HCO_3^- water and described it as relatively dilute with a homogeneous composition. Chowdhury and others (2006) also found that the groundwater in the outcrop areas in the northern part of the system were commonly Ca- HCO_3^- types that evolve into mixed Ca-Na- HCO_3^- -Cl water along regional flow paths and to Na- HCO_3^- water in the discharge areas near the coast. The predominant cation was Na in slightly more than 50 percent (22 of 42) of the groundwater samples collected in the southwest area. With Ca predominant in most samples in the northeast and northwest areas, the ranges in concentrations for Ca were substantial and about the same as those in the southwest area (no statistical difference in concentration ranges among the three areas was found by using the Tukey test, table 4A; actual concentration ranges are presented in app. 4A). Other than the outlying high Cl concentrations, the Cl-concentration range for the remaining samples in the southwest area was otherwise similar to the Cl-concentration range in the northwest area and the general concentration and compositional range for all the samples (fig. 8; table 2; app. 4A). A statistically significant difference in Cl concentration was detected between the northeast area ("C" Tukey class) and the other areas (northwest, "A" Tukey class, and southwest, "B" Tukey class) (table 4A). Three of the four wells assigned to the aquifer designation grouping of "lowerEVGL" were in the northwest area, and the Cl concentrations in wells in the "lowerEVGL" grouping ("A" Tukey class) were statistically significantly higher compared to wells in the other aquifer designation groupings (table 4C). These water-concentration and composition data indicate that there is a source of saltwater to the south or southwest of the study area, and at depth, this source mixes with groundwater derived from recharged surface water. The saltwater mixes in with the groundwater in the southwest area (closest to the Gulf of Mexico) and at depth in the northwest area.

For the northeast and northwest areas, outlying high Na concentrations were measured in a few groundwater samples; for example, each maximum Na concentration was almost three times greater than the maximum Ca concentration (app. 4A). On figures 8A and 8B, the data points representing these two wells plotted in the diamond representing the Na-predominant-type water (Na plus K composed more than 80 percent of the total milliequivalents per liter, of which the percentage of K was minimal and is referred to hereafter as "Na"), and the samples from these were classified with the aquifer designation grouping of "lowerEVGL." The minimum Ca concentration for each area also was in the water from these wells and for the entire dataset (table 2, app. 4A). In these samples, the concentrations of the monovalent Na^+ ions were increasing at the expense of the divalent cations (mostly Ca^{2+} with minor amounts of divalent Mg^{2+}); that is, the divalent

cations were being removed from solution as the concentration of Na increased (a cation-exchange reaction). For the northeast and northwest areas, the samples plotted in the diamond of the piper diagram along a line showing a transition from a Ca-predominant water type to a Na-predominant water type, indicating the reaction progress of ongoing cation exchange (figs. 8A and 8B). This exchange primarily of Ca for Na cations occurs on the surfaces of clay minerals as groundwater percolates through sediments composed largely of clay. This cation-exchange reaction is common on the surfaces of clay minerals in nearshore sediments that have been exposed to saline waters (Appelo, 1994) and results in Na-rich waters in many coastal aquifers (Back, 1966). Cation exchange in nearshore sediments affects the pH of the associated water and the concentrations of HCO_3^- (generally by increasing both), leading to considerable change in overall water chemistry (Appelo, 1994). Chowdhury and others (2006) observed increased mineralization in groundwater along regional flow paths in Harris and Galveston Counties and proposed the increase to be related to cation-exchange reactions. Elevated concentrations of Na and corresponding low concentrations of Ca were found in water samples collected from wells in Montgomery County that were screened in the Jasper aquifer where the well depths were more than 1,000 ft below datum (Oden and Truini, 2013); these wells were updip from the wells sampled in this study. Oden and Truini (2013) postulated that these Na-dominated waters were a result of cation exchange. Cation exchange also is likely the mechanism controlling the chemical evolution of groundwater in the deepest parts of the Evangeline aquifer in Houston.

The minimum Na concentration for the entire dataset was measured in the Ca-dominated water-type sample collected from well LJ-60-63-510 in the northeast area. This sample was collected from the part of the Evangeline aquifer designated as “middleEVGL.” The Ca concentration in this sample was 45.4 mg/L, which was greater than the 75th percentile of all Ca concentrations measured in wells sampled in the northeast area (app. 4A). Well LJ-60-63-510, and other wells with similar construction in the northeast area, is installed near the outcrop of the sediments composing the Evangeline aquifer. In this area near the outcrop, the clay-mineral surfaces are likely to be saturated with exchangeable Ca (and divalent Mg as well), and replacement of divalent cations by cation exchange is not likely. A similar pattern of high concentrations of Ca and Mg cations in sediments near an aquifer outcrop in the mid-Atlantic Coastal Plain has been described by Back (1966).

As a percentage of total ions in milliequivalents per liter, the amount of Ca in the northeast area decreased, and the corresponding amount of Na increased as the aquifer designation grouping of the wells changed from “lowerCHCT, upperEVGL” and “middleEVGL” to “fullyEVGL” and then “lowerEVGL” (fig. 8A). As the open intervals intersected the deeper (lower) parts of the aquifer, the type of water withdrawn by the wells changed from Ca predominant to Na predominant. As the open intervals intersected the deeper parts of the aquifer in the northwest area, Ca as a percentage

of total ions in milliequivalents per liter generally decreased, whereas Na as a percentage of total ions in milliequivalents per liter increased. The amount of Ca in samples collected from wells with an aquifer designation of “lowerCHCT, upperEVGL” varied considerably, with Ca representing from about 25 to 70 percent of the total ions (fig. 8B). Among these samples assigned an aquifer designation of “lowerCHCT, upperEVGL,” the water type of the five samples from wells that intersected only the Chicot aquifer was Ca predominant, whereas the water type of samples collected from wells intersecting only the Evangeline aquifer was primarily Na predominant (low percentage of Ca) (fig. 8B; table 3).

The predominant cation was sodium in most of the water samples collected from wells in the southwest, with the maximum Na concentration nearly twice as large as the maximum Ca concentration (app. 4A). In contrast to the tendency for relatively low Ca concentrations to accompany relatively high Na concentrations in the northeast and northwest areas, relatively high Ca concentrations were often measured in samples collected from wells in the southwest area with some of the highest Na concentrations. As an example, the Na and Ca concentrations measured in the sample collected from well JY-65-29-109 were 134 and 65.9 mg/L, respectively (app. 1), and the Ca concentration of 65.9 mg/L was greater than the 75th percentile of all Ca concentrations measured for the entire dataset (table 2). The aquifer designation grouping for this well was “lowerCHCT, upperEVGL” (table 1), as was the case for many of the wells from the southwest area. The samples collected in the southwest area were generally composed of higher Na concentrations compared to the Na concentrations measured in samples collected in the northeast and northwest areas (fig. 8). The relatively higher Na concentrations in the southwest area are likely derived from multiple sources, including the mixture with NaCl-bearing saltwater. Water becomes more saline in the downdip and in more deeply buried parts of the aquifers near the coast because of the long residence time of the water and continued reaction with the aquifer minerals (Baker, 1979; Chowdhury and others, 2006).

For the southwest area, the majority of the analyses plotted in the diamond of the piper diagram along a line delineating a transition from a Ca-predominant water type to a Na-predominant water type, again indicating that cation exchange was ongoing (fig. 8C). The Na concentrations in two samples in the southwest area were greater than 100 mg/L (converted into milliequivalents per liter, Na was about 80 percent of the total cations) and a corresponding low Ca concentration (Ca was less than 20 percent of the total cations) (fig. 8C), indicating a Na- HCO_3^- water type as a result of the cation-exchange process. These two wells were classified as “middleEVGL” (fig. 8C). The altitude of the open intervals intersected the Evangeline aquifer approximately 1,000 to 1,750 ft below datum (fig. 6); in the northeast and northwest areas, similar altitudes corresponded to wells classified as screened in the “lowerEVGL” (figs. 4–5). This difference

in relative vertical position within the aquifer system is a function of spatial position as the aquifers deepen and thicken towards the Gulf of Mexico and makes it possible to withdraw water of different chemistry from wells of similar construction in different areas.

The importance of the relative increase in the concentrations of Na in groundwater chemistry of the northeast and northwest areas as opposed to the southwest area indicates different geochemical processes controlling water-chemistry evolution, with cation exchange appearing to be the primary process to the north and an additional process of an increasing influx of saltwater from the north to the south. The observations of predominant cation concentrations, alkalinity, and specific conductance in the water from the wells in the three areas would appear to indicate evolution from Ca-HCO₃ type water to Ca-HCO₃ type water with higher concentrations of Na and Cl, and finally Na-HCO₃ type or Na-Cl type.

Redox Categories

Redox processes affect the water quality of groundwater in all aquifer systems (Lovley and Chapelle, 1995; McMahon and Chapelle, 2008) and can mobilize naturally occurring constituents, such as As and radionuclides, present in the aquifer material (Bose and Sharma, 2002; Smedley and Kinniburgh, 2002; Chapman and others, 2013). Redox processes are catalyzed by microorganisms competing for resources that generate the maximum amount of available energy (Lovley and Phillips, 1987); oxidized elemental species such as NO₃⁻, Mn(IV), Fe(III), and SO₄²⁻ are usually consumed by electron transfer from a reduced species available in the sediments at depth. The order of preferential electron acceptor utilization (consumption for net energy gain by microbes) is referred to as the “ecological succession of terminal electron-accepting processes”—O₂ to NO₃⁻ to Mn(IV) to Fe(III) to SO₄²⁻ to CO₂ (McMahon and Chapelle, 2008). The terminal electron acceptors are the ions that become reduced (Lovley and Chapelle, 1995). The redox categories proposed by McMahon and Chapelle (2008) are based on the relative concentrations of these terminal electron acceptors and the end products of the redox processes in the sample.

To further illustrate the variability of water chemistry in the 91 groundwater samples collected in Houston, each sample was assigned to 1 of the 4 of the redox categories proposed by McMahon and Chapelle (2008) (table 3). Of the 91 samples, 42 (about 46 percent) were anoxic, 33 (about 36 percent) were oxic (DO was greater than 0.5 mg/L), 8 (about 9 percent) were mixed, and 8 (about 9 percent) were suboxic (DO was less than 0.5 mg/L, but concentrations of terminal electron acceptors were low, and the dominant redox processes were indeterminate).

Different concentrations of terminal electron acceptors present in the 42 anoxic samples defined the presumed predominant reduction process: Fe(III)/SO₄ (Fe or SO₄ or both) reducing, Fe(III) reducing, Fe(III)-SO₄ (Fe and SO₄) reducing, or CH₄gen (methanogenic) (table 3). Thirty-two of the

anoxic samples met the criteria for the Fe(III)/SO₄-reducing, presumed predominant reduction process characterized by concentrations of Fe greater than 29 μg/L (maximum Fe concentration, 612 μg/L) and concentrations of SO₄ greater than 4 mg/L (maximum SO₄ concentration, 17.2 mg/L) (fig. 9A; table 3). In these samples, reduction of either Fe, SO₄, or both may occur as the dominant electron-accepting process, although the abundance of Fe in most samples indicates that Fe reduction is likely the predominant reduction process. Five anoxic samples (collected from wells LJ-60-63-510, LJ-60-63-508, LJ-60-63-505, LJ-60-63-503, and LJ-60-63-502) met all the criteria for Fe(III) reducing as the presumed predominant reduction process; their concentrations of Fe and SO₄ were greater than redox threshold values of 29 μg/L and 4 mg/L, respectively, and their Fe-to-sulfide mass ratios were greater than 10 (table 3) (Chapelle and others, 2009). Detectable concentrations of sulfide were present in these samples, indicating Fe(III)-reducing conditions and SO₄ reduction but likely dominance of Fe(III) reduction on the basis of the high Fe-to-sulfide ratio (Chapelle and others, 2009). Two samples collected from wells TS-60-63-507 and LJ-60-63-709 were classified as anoxic (mixed) because they met the criteria for the predominant reduction process Fe(III)-SO₄ reducing, with both Fe(III) and SO₄ reduction occurring. The criteria that they met included Fe and SO₄ concentrations greater than threshold values of 29 μg/L and 4 mg/L, respectively, and an Fe-to-sulfide mass ratio between 0.3 and 10 (Chapelle and others, 2009). Usually one of these reduction processes is dominant, with Fe(III) reduction initiated first (Lovley and Phillips, 1987), but depending on the sediment composition, the microbial community, and other factors, the two reactions, Fe(III) and SO₄ reduction, can occasionally proceed simultaneously (Jacobsen, 1994). If these reduction processes occur independently in discrete sediment layers at individual depth intervals, reaction end products can be combined in the well by mixing during production (Chapelle and others, 2009). Three samples (TS-60-62-604, LJ-65-13-224, and LJ-65-13-222) met the criteria for the presumed predominant reduction process of methanogenesis, with moderately low Fe(II) concentrations, typically about 100 μg/L, and relatively low concentrations of SO₄ of about 1 mg/L or less; the low concentrations of SO₄ were less than the amounts specified for inclusion in the SO₄-reduction process (fig. 9A; table 3) (Jurgens, McMahon, and others, 2009). The three potentially methanogenic-anoxic samples did not contain detectable amounts of sulfide even though DO concentrations were less than 0.5 mg/L in these samples. Methanogenesis and SO₄-reducing reduction processes can coexist in the environment (Holmer and Kristensen, 1994), although only the methanogenesis reaction proceeds after the aqueous SO₄ is mostly consumed (reduced sulfidic water) (Kirk and others, 2004). Methanogenesis is presumed to have occurred in at least the three samples with the lowest SO₄ concentrations (less than 0.18 mg/L, 0.81 mg/L, and the estimated value of 0.17 mg/L), although measurements of methane and other soluble organic compounds indicative of methanogenesis

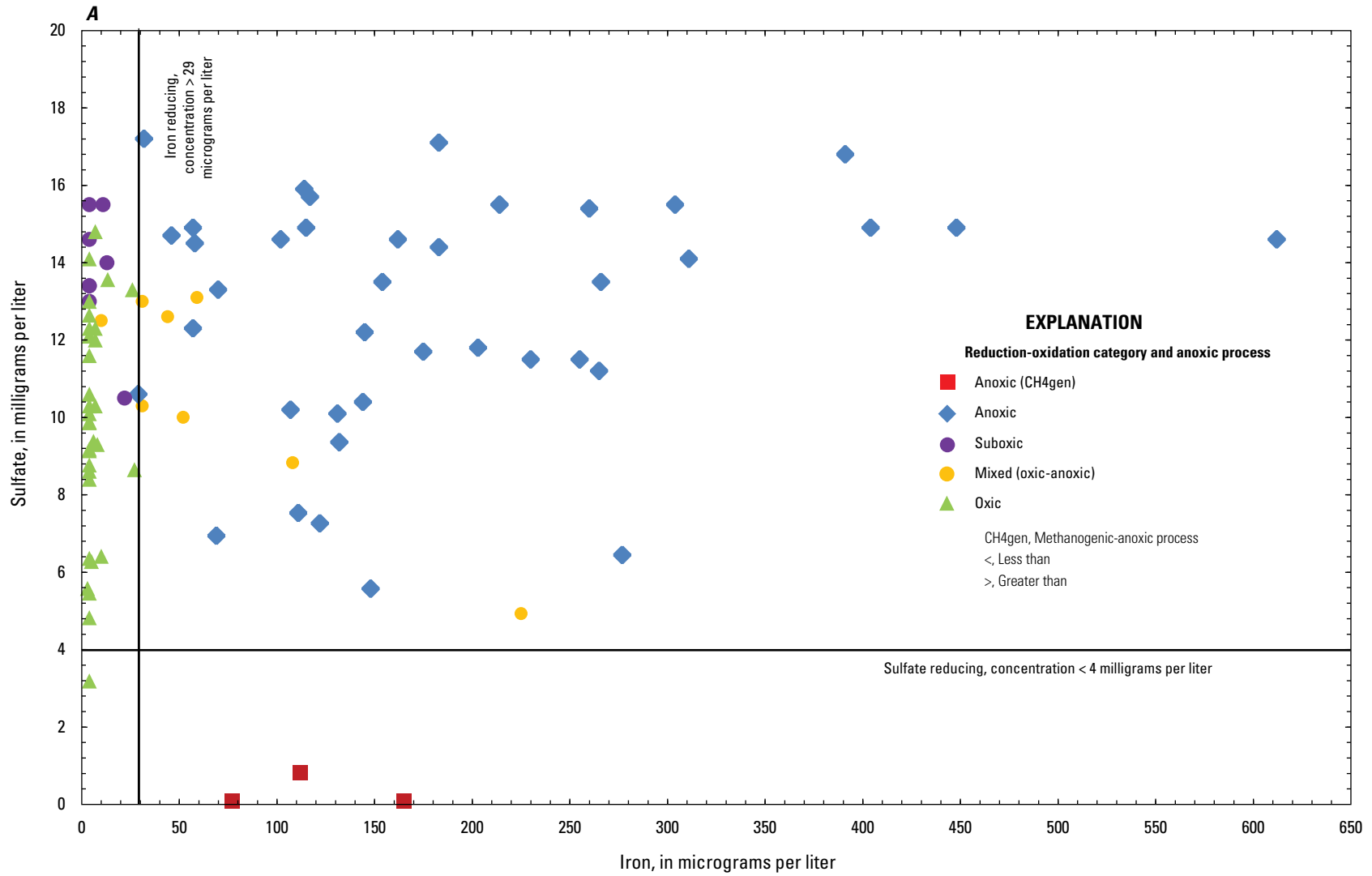


Figure 9. Water samples collected from 91 municipal supply wells in Houston, Texas, during 2007–11. *A*, Sulfate compared to iron concentration; and *B*, Sulfate compared to sodium concentration.

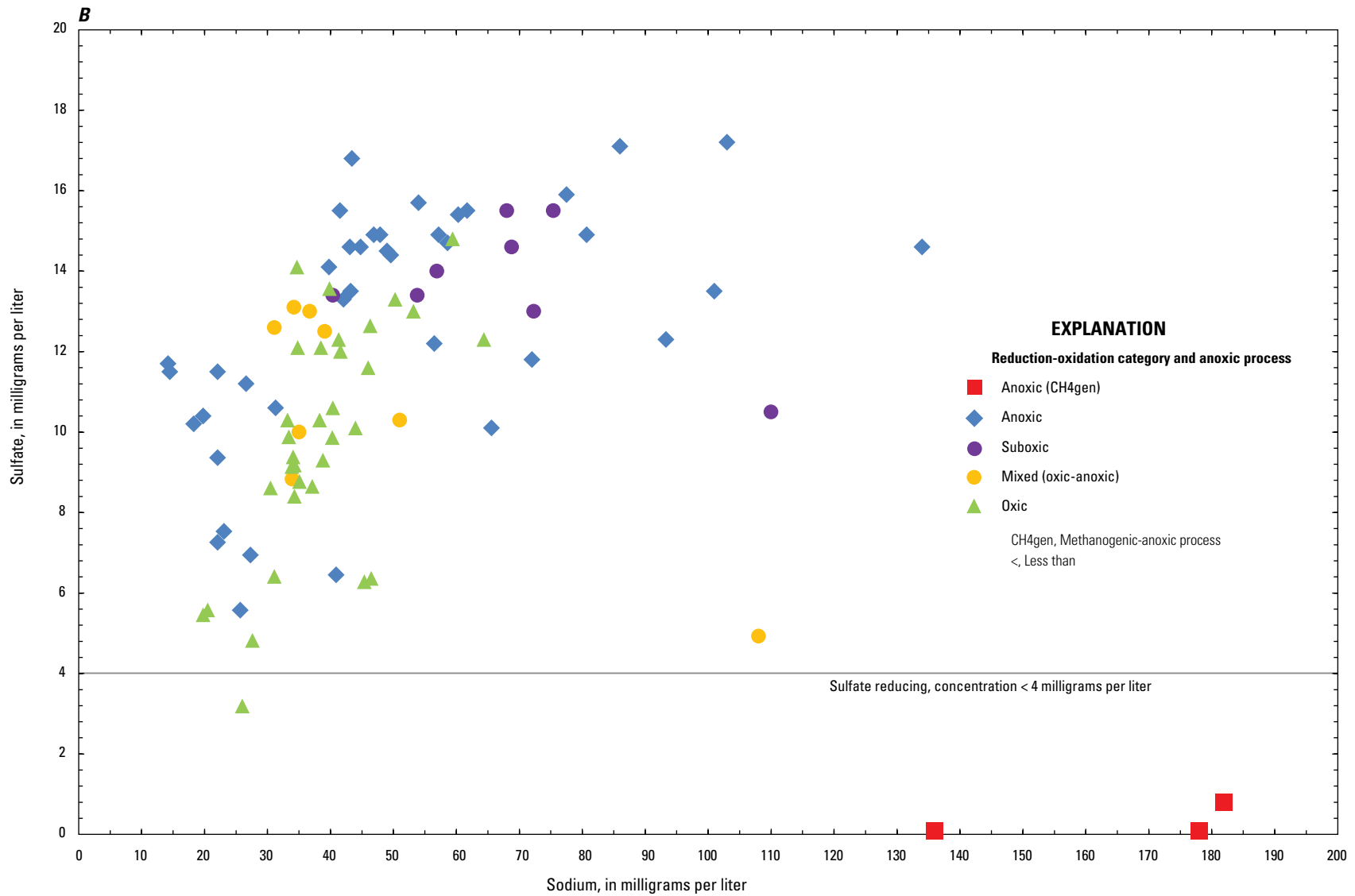


Figure 9. Water samples collected from 91 municipal supply wells in Houston, Texas, during 2007–11. *A*, Sulfate compared to iron concentration; and *B*, Sulfate compared to sodium concentration.—Continued

were unavailable at the time of sampling to verify that methane was actually being produced. The Fe and SO₄ in that methanogenic water was assumed to have been reduced and mostly sequestered as solid-phase Fe sulfides (Slowey and Brown, 2007) or pyrite, a process documented to occur in many sandy aquifer sediments, including those deposited south of Houston (Goldhaber and others, 1978). After the aqueous SO₄ is mostly consumed (reduced), however, some excess Fe (reduced Fe(II) species) remains in solution, and excess Fe remaining in the sediment may also be reduced (Kirk and others, 2004).

In the eight samples classified as suboxic, SO₄ concentrations were greater than 4 mg/L, but Fe, Mn, and DO concentrations were low (less than 29 µg/L, 50 µg/L, and 0.5 mg/L, respectively). These samples are presumably not methanogenic anoxic because each contained more than 4 mg/L of SO₄ (Chapelle and others, 2009), and concentrations of Fe and Mn were low, the opposite of what is typical of methanogenic-anoxic conditions (Kirk and others, 2004).

Eight samples were assigned to the mixed (oxic-anoxic) redox category because the concentrations of DO and Fe did not clearly fit the criteria described by McMahon and Chapelle (2008) for either reducing or oxic redox processes (table 3). In the eight samples classified in the mixed redox category, DO was greater than or equal to 0.5 mg/L, the Fe concentration was greater than 29 µg/L in seven of these samples, and the sulfide concentration was 0.4 mg/L in the eighth sample (table 3). The mixing of Fe-bearing and oxygen-bearing waters, most likely in the well casing during pumping, resulted in well waters that contained DO and Fe in readily detectable amounts, which is an indication of waters with mixed redox chemistry (McMahon and Chapelle, 2008). The mixed redox chemistry may be indicative of highly variable sediment lithology in the variegated deltaic deposits composing the Gulf Coast aquifer system where redox zones are variable but proximal, or it may be indicative of extensive withdrawals that result in the mixing at or near the well borehole of the water types that are present in different parts of the aquifer, or both. Wells classified with a multiple aquifer group are likely to produce a mixture of waters withdrawn in varying proportions from the Chicot and Evangeline aquifers that may not be representative of or unique to either aquifer. Because the Chicot and the underlying Evangeline aquifers are not separated by a distinct or thick confining unit (fig. 2), increasing the production of groundwater by setting well open intervals that partially penetrate both aquifers is commonly done. Water produced from wells with the open intervals intersecting the full extent of the Evangeline aquifer is likely to be a mix of various water compositions from the upper, middle, and lower parts of the aquifer. Through turbulence in the bowls of the turbine pumps or through exposure to air during sampling, it is possible to introduce small amounts of DO to anoxic waters. DO introduced to anoxic waters by pumping or sampling cannot be distinguished from mixing of anoxic groundwater with oxygenated groundwater within the casing, and hence the general term of “mixed redox” is used to characterize such samples. In addition, the samples collected

from wells LJ-65-12-619 and LJ-65-05-814 serve as examples of the difficulty of classifying the redox of the samples. A DO concentration of 1.2 mg/L (only slightly greater than the 0.5-mg/L threshold value) was measured in the sample collected from well LJ-65-12-619, along with an Fe concentration of 10 µg/L, which was less than the Fe threshold of 29 µg/L. A detectable concentration of sulfide (0.40 mg/L) was also measured in the sample collected from well LJ-65-12-619, indicating anoxic conditions with predominant reduction processes of O₂ and SO₄. The mixed classification for the LJ-65-05-814 well (table 3) was applied because an Fe concentration of 31 µg/L was detected in the water, exceeding the criterion limit of 29 µg/L that was imposed for this study, and DO concentration was 1.03 mg/L.

Groundwater-Residence Time

Transient environmental-tracer data were used to bracket or constrain apparent groundwater age (groundwater residence time since recharge). It was assumed that the transient environmental tracer constituent concentration was unaltered by mixing or dispersion from the point of entry at recharge to the measurement point in the open interval of the well. A simple piston-flow transport model (Cook and Böhlke, 1999) of groundwater flow is assumed, which does not represent the complexities of the actual groundwater-flow system, but examination of the effects of mixing and dispersion on tracer concentrations are beyond the scope of this report. Samples analyzed for concentrations of tritium were used to estimate if the groundwater had been recently recharged (post-1940s). Additionally, ¹⁴C data were used to evaluate whether the groundwater might have been recharged more than 1,000 years ago.

Tritium has a 12.32-year half-life and is used as a tracer of young groundwater to determine the time elapsed since recharge (apparent recharge age) of the groundwater. Prior to the initiation of widespread atmospheric testing of nuclear weapons in 1953 (Cook and Böhlke, 1999), the natural tritium concentration in precipitation ranged from 1 to 5 tritium units (TU); because of the relatively short half-life of tritium of 12.32 years, groundwater that does not contain detectable tritium is inferred to have been recharged prior to 1953 (Cook and Böhlke, 1999). Releases of tritium from aboveground testing of thermonuclear devices during the 1950s and early 1960s resulted in a peak of tritium concentration not only in the atmosphere but also in all components of the hydrologic cycle, including groundwater recharged at that time (Michel, 1989). This time period, called the “bomb peak,” is used as a reference point in time to determine relative age of recharge of the groundwater since 1953.

Tritium was detected at a concentration greater than 0.4 pCi/L (equivalent to 0.124 TU) in 1 of 28 samples collected during 2007–8 in Houston (Oden and others, 2010). Because the sampled groundwater contained only small or undetectable amounts of tritium, it is inferred to have infiltrated the subsurface prior to 1953 (Cook and Böhlke, 1999).

With its long half-life of 5,730 years, ^{14}C is useful for dating groundwater thousands to tens of thousands of years old (Wigley and others, 1978). Carbon-14 is produced naturally in the upper atmosphere by the effects of cosmic radiation; as with tritium, additional amounts of ^{14}C were generated from aboveground testing of thermonuclear devices during the 1950s and early 1960s. Carbon-14 is typically reported as percentages of modern carbon (pmc) (Cook and Böhlke, 1999). Carbon in most groundwater flow paths will interact with geological carbonate minerals that do not contain ^{14}C , resulting in decreased percentage of modern ^{14}C carbon; that decrease is not a function of the radioactive decay but of dilution. This dilution of the percentage of modern ^{14}C input from the land surface results in estimated groundwater ages that appear older than the actual groundwater ages. To estimate specific recharge dates or groundwater ages corrected for this dilution, the percentage of modern ^{14}C must be adjusted to account for chemical-reaction mass balance of the added geological carbonate minerals (Wigley and others, 1978; Plummer and Back, 1980) by using geochemical reaction-path modeling, which is beyond the scope of this report. The transient tracers are used in this report for establishing relative residence times among the water samples and not to establish absolute ages or residence times. Without specific or absolute dating, generalized estimates of recharge rates or relative residence times can however be done, with limitations (Oden and Truini, 2013).

During 2008–10, 10 samples were collected and analyzed for ^{14}C . The detected ^{14}C ranged from 0.20 to 30.73 pmc, and ^{14}C was not detectable in 2 of these 10 samples at concentrations less than 0.33 pmc (Oden and others, 2010, 2011). Well LJ-65-13-221, completed in the Chicot aquifer, was the shallowest well sampled for ^{14}C , and the highest percentage of modern carbon (30.73 pmc) was measured in the sample collected from this well. This was also the only sample with a percentage of modern carbon greater than 5.1. Because there were measurable amounts of ^{14}C in the majority of the 10 groundwater samples collected, the “apparent recharge” age of water samples is likely greater than a few thousand years but is less than about 50,000 years, the age limit beyond when ^{14}C is considered no longer detectable because of radioactive decay (Cook and Böhlke, 1999).

The radioactive tracers tritium (not detected) and ^{14}C (generally detected in concentrations considerably less than in modern recharge) both independently indicate that residence time for water is long in the Gulf Coast aquifer system, on the order of hundreds to thousands of years. These tracer-concentration results were obtained from a subset of 10 samples from the wells sampled in this study and are consistent with the results from wells with comparable depths (600 to 800 ft bls) sampled in Montgomery County, north of Houston (Oden and Truini, 2013). Those wells were screened in the Evangeline aquifer, and the apparent groundwater ages were estimated from concentrations of ^{14}C and helium-4 present in the groundwater samples and were

corrected for presumed dilution with geological sources of carbon by using a geochemical reaction-path model as recommended by Wigley and others (1978). The corrected apparent groundwater ages for those wells ranged from 2,000 to 27,000 years (Oden and Truini, 2013). Residence times for groundwater estimated from transient environmental-tracer concentrations are dependent upon assumption of values for several hydrogeologic variables and thus have considerable inherent uncertainties (Wigley and others, 1978), but at the most general level, the initial estimates of recharge ages of many hundreds to thousands of years are reasonable for the deep production wells sampled in this study.

Coincidence of Redox Categories, Predominant Cation and Anion Water Types, and Aquifer Designations

Water-quality types and redox categories appear to be stratified by depth in the aquifer and do not occur randomly. The co-occurrence in water types and redox categories is related to depth and residence time as the water chemistry evolves. Exact depths of zones of redox stratification and chemical facies vary spatially according to distance along the groundwater flow paths from the point of recharge at the land surface in outcrop areas and by the residence time on the flow paths. The variation in thickness of the strata forming the aquifer units also affects the length and orientation of the flow paths and chemical-reaction progress. The assignment of possible depth horizons or presumed relative residence times to various redox categories and water types is problematic. The transition from water table to confined conditions with increasing depth in the Gulf Coast aquifer system is gradual (Kasmarek and Robinson, 2004), and the hydrological complexity is considerable, making it difficult to infer residence time at any given point. Residence-time estimates of hundreds of years for water-table conditions to thousands of years for confined conditions can be generalized (Oden and Truini, 2013). The overall hydrological complexity of the aquifer system is such that concentrations of transient tracers as age-dating tools are needed to provide more direct estimates of relative water residence times at the sampled points in the aquifer system, which was beyond the scope of this study. There is likely a local effect on residence time of the sediment texture, as advection may proceed at a much slower rate in organic-carbon- and clay-rich, fine-grained sediments than in organic-carbon-poor sand layers. When there is an abundance of reactive solid phases (reactive minerals and other amorphous solid phases) in the sediment composition of the aquifer (such as dolomite, calcite, clay minerals, feldspar minerals, amorphous metal oxyhydroxides, organic carbon, and perhaps sulfide minerals), the chemical composition of groundwater can be altered along flow paths. These reactive solids can undergo or foster redox reactions, and undergo congruent and incongruent mineral

dissolution reactions, and cation-exchange reactions, altering the groundwater chemical composition (Plummer and Back, 1980). Oden and Truini (2013) identified clayey, fine-grained layers in abundance in the Gulf Coast aquifer system near Houston, and these fine-grained layers likely contain reactive solid phases, especially clay minerals, in abundance. Other reactive solid phases in the sediment composition of the Gulf Coast aquifer system may include carbonate minerals such as calcite and dolomite, feldspar minerals, amorphous metal oxyhydroxides, organic carbon, sulfide minerals, and perhaps trace minerals bearing uranium or other trace elements (Eargle and others, 1975; Goldhaber and others, 1978; Cook, 1980; Chowdhury and others, 2006). The fine-grained sediment layers identified by Oden and Truini (2013) might also be a source of elevated concentrations of reactive solutes contained within the pore water (Szabo and others, 2006). There is likely a local effect of the sediment texture with regard to geochemistry as the reduction and mineralization reactions may proceed at a greater rate in fine-grained organic carbon-rich sediments than in organic-carbon-poor sand layers.

Percolation along flow paths has led to simultaneous geochemical evolution of the major-ion composition and the redox characteristics of the waters. It is presumed that the combination of the low recharge rates, heterogeneous flow paths, long residence times, and the abundance of clay layers are major factors allowing the reduction and cation-exchange reactions to proceed enough in the Gulf Coast aquifer system to affect the redox status and the chemical composition of the water. Presumably, the estimated long residence time (ranging from a few to many thousands of years [Oden and Truini, 2013]) provides the time for specific microbial communities to consume DO (McMahon and Chapelle, 2008), then oxidize Mn and Fe species (by electron transfer resulting in reduction), and then SO_4 , until sulfidic and methanogenic-anoxic waters were generated. Not enough sediment-composition data and hydrological information are available to determine specifically if sediment composition or residence time is the dominant factor in determining the amount of reaction progress for the reduction and cation-exchange reactions in the various parts of the aquifer system.

A similar sequence of vertical gradients in water chemistry and redox status was identified in a previous study of the southern High Plains aquifer in north-central Texas. Near the water table, the water was oxygenated, but as the water percolated into the aquifer, it exhibited variable rates of DO consumption that varied on the basis of differences in local aquifer composition and the types of microorganisms present. The residence time (age since recharge) of the water increased with depth and was long enough to allow for consumption of the DO resulting in anoxic conditions at depth (McMahon and others, 2004).

The oxic waters coincided in general (29 of 33 samples) with Ca- HCO_3 -type major-ion chemistry (table 3), with comparatively low Na concentrations (fig. 9B); 17 of these

29 samples were collected from wells in the southwest area (table 3), with open intervals that intersected both the Chicot and Evangeline aquifers (table 1), and 1 of the samples (LJ-65-20-520) was collected from a well that was screened entirely in the Chicot aquifer (table 1). The chemical composition of the groundwater withdrawn from wells completed or partially completed in the Chicot aquifer is likely different compared to the chemical composition of groundwater withdrawn from wells with open intervals intersecting only the Evangeline aquifer. Because DO, the first in the succession of terminal electron acceptors through the redox process, is still present in relatively large concentrations in these samples, it is likely that water in these wells has either not resided long enough for the DO to be consumed, or the sediment material is devoid of available reductants (most important of which is organic carbon). Similarly, with regard to the Ca dominance, it is likely that either the residence time was not sufficiently long for the cation-exchange process to replace Ca ions with Na ions or the sediment material is devoid of clay minerals, thereby limiting the capacity for the cation-exchange process to replace Ca ions with Na ions.

The samples classified as reducing (anoxic or suboxic) primarily coincided with Na-predominant groundwater (fig. 9B) in the northwest and southwest areas (table 3). With the presumed increased residence time along flow paths, results of increasing reaction progress can be noted for reduction and cation-exchange reactions. The DO is typically consumed, creating reducing conditions, along with the process of cation exchange, resulting in a Na-predominant water type. In the northwest and southwest areas, a majority (16 of 28) of the wells with anoxic water intersected the upper part of the Evangeline aquifer or included the lower part of the Chicot (all designated as “lowerCHCT, upperEVGL”); the remainder of the wells intersected the upper, middle, and lower parts (designated “fullyEVGL”) or the middle part (designated “middle EVGL”) of the Evangeline aquifer. The methanogenic-anoxic waters coincided with Na- HCO_3 -type major-ion chemistry (fig. 9B; table 3). The water samples classified as methanogenic anoxic were collected from the wells with the deepest open intervals and were classified with the “lowerEVGL” aquifer designation in the northeast (1 well) or northwest (2 wells) areas (figs. 4 and 5). Furthermore, specific conductance and the concentrations of alkalinity, Na, and Cl were highest in the water samples collected from the wells screened at or near the base of the Evangeline aquifer (“A” Tukey class, table 4C). The wells classified as “lowerEVGL” with their open intervals screened to depths relatively near the base of the Evangeline aquifer are likely withdrawing water of a chemically distinct composition compared to that of water intercepted by wells open to other parts of the aquifer. Chowdhury and others (2006) also found concentrations of HCO_3 , Na, and Cl that increased along flow paths and increased ratios of Na to Cl from the shallower to deeper aquifers that were likely caused by progressive cation exchange (replacement of Ca by Na).

The anoxic waters in the northeast area were primarily Ca dominated (table 5), with Na concentrations generally less than 41 mg/L (figs. 9B and 10; app. 4A) withdrawn from wells with open intervals intersecting the middle part of the Evangeline aquifer (fig. 4). Most (18 of 20) of the water samples collected from wells in the northeast area were Ca dominated regardless of redox status or aquifer designation (fig. 8A; table 5). The pattern of Ca-dominated water in the northeast area most likely was observed because the wells from which these samples were collected are closest to the recharge zones for the aquifers (located the farthest north, up dip from the wells in the northwest and southwest areas) (fig. 1). Specific conductance and concentrations of alkalinity, Na, and Cl were all significantly lower in the water samples collected from the wells in the northeast area than in water samples collected from the northwest and southwest areas. On the basis of the Tukey test results that were used to compare the concentrations of water-quality constituents in the northeast, northwest, and southwest areas, the lowest mean ranks for alkalinity and Na also were in the northeast

Table 5. Number of samples are indicated for predominant cation and anion water type, reduction-oxidation (redox) category and anoxic process, and aquifer designation grouping for all 91 samples and for each sampled area (northeast, northwest, and southwest) collected from wells in Houston, Texas, 2007–11.

[Ca, calcium; HCO₃, bicarbonate; Na, sodium; Cl, chloride; CH₄gen, methanogenic-anoxic process; CHCT, Chicot aquifer; EVGL, Evangeline aquifer; the category with highest number of samples for predominant water type, redox category and aquifer designation grouping are highlighted in yellow for all samples and for each area; grey shading indicates no samples]

Category (number of samples)	All samples (91)	Northeast (20)	Northwest (29)	Southwest (42)
Predominant cation and anion water type				
Ca, HCO ₃	56	18	18	20
Na, HCO ₃	33	2	11	20
Na, Cl	2			2
Redox category and anoxic process				
anoxic	39	13	14	12
anoxic (CH ₄ gen)	3	1	2	
mixed (oxic-anoxic)	8	1	6	1
oxic	33	5	7	21
suboxic	8			8
Aquifer designation grouping				
lowerCHCT, upperEVGL	51	2	12	37
lowerCHCT, fullyEVGL	7		7	
fullyEVGL	10	3	7	
middleEVGL	19	14		5
lowerEVGL	4	1	3	

area samples (mean ranks for alkalinity and Na measured in samples from the northeast area were assigned to the “B” Tukey class, and the mean ranks for Cl were assigned to the “C” Tukey class, table 4A). The type of water chemistry in the northeast area is consistent with abundant flushing by dilute waters (Plummer and Back, 1980; Appelo, 1994) and with the fact that the Evangeline aquifer crops out in the northeast part of the study area. The concentrations of Na, HCO₃, and Cl increased along flow paths from the shallower aquifer (“lowerCHCT, upperEVGL” aquifer designation grouping) to the deeper aquifer (base of the Evangeline aquifer), where progressive cation exchange (replacement of Ca by Na) was ongoing as the water penetrated into the subsurface.

The differences in aquifer sediment thickness, depending on sampling area, help to explain how sediment composition and texture differs among the areas for wells in the “lowerCHCT, upperEVGL” aquifer designation grouping and the resulting spatial difference in water composition from wells with this aquifer designation grouping. The eight samples classified as suboxic were all collected from wells completed in the southwest area (tables 3 and 5), primarily from the “lowerCHCT, upperEVGL” aquifer designation grouping (table 1). Low DO concentrations (less than 0.5 mg/L) were measured in the water from these wells, but the redox process was not categorizable by the chemical composition. The water type was defined as Na-HCO₃ type for 7 of these 8 samples (fig. 10; table 3). In the northwest area, waters collected from the wells with open intervals spanning part of the lower Chicot aquifer and part of the upper Evangeline aquifer (resulting in the “lowerCHCT, upperEVGL” aquifer designation grouping) were often anoxic (table 5). The Chicot and Evangeline aquifers are thicker in the southwest area than in the northeast and northwest areas, and only the coarser grained Chicot aquifer sediments crop out in the southwest. The areal difference in water composition implies that sediment composition and texture in the southwest may be different from the composition and texture of the sediments in these same aquifers to the northeast and northwest. Wells in the southwest area in the “lowerCHCT, upperEVGL” aquifer designation grouping intercept waters from a relatively thick layer of Chicot aquifer sediments, whereas the wells screened in the Chicot aquifer in the northeast and northwest areas intercept waters from much thinner layers of Chicot aquifer sediments overlying relatively thick layers of Evangeline aquifer sediment. The mixing of waters from various zones in the “lowerCHCT” and “upperEVGL” aquifer designation groupings in the southwest area may therefore result in water composition different from the northeast and northwest areas. Hydrological flow paths arriving at the open intervals of wells in the southwest area also may have different geometry than those at the open intervals of wells in the northeast and the northwest because of the difference in aquifer outcrop among the areas and possible difference in the sediment composition and texture; the residence time along the flow paths also may be affected accordingly.

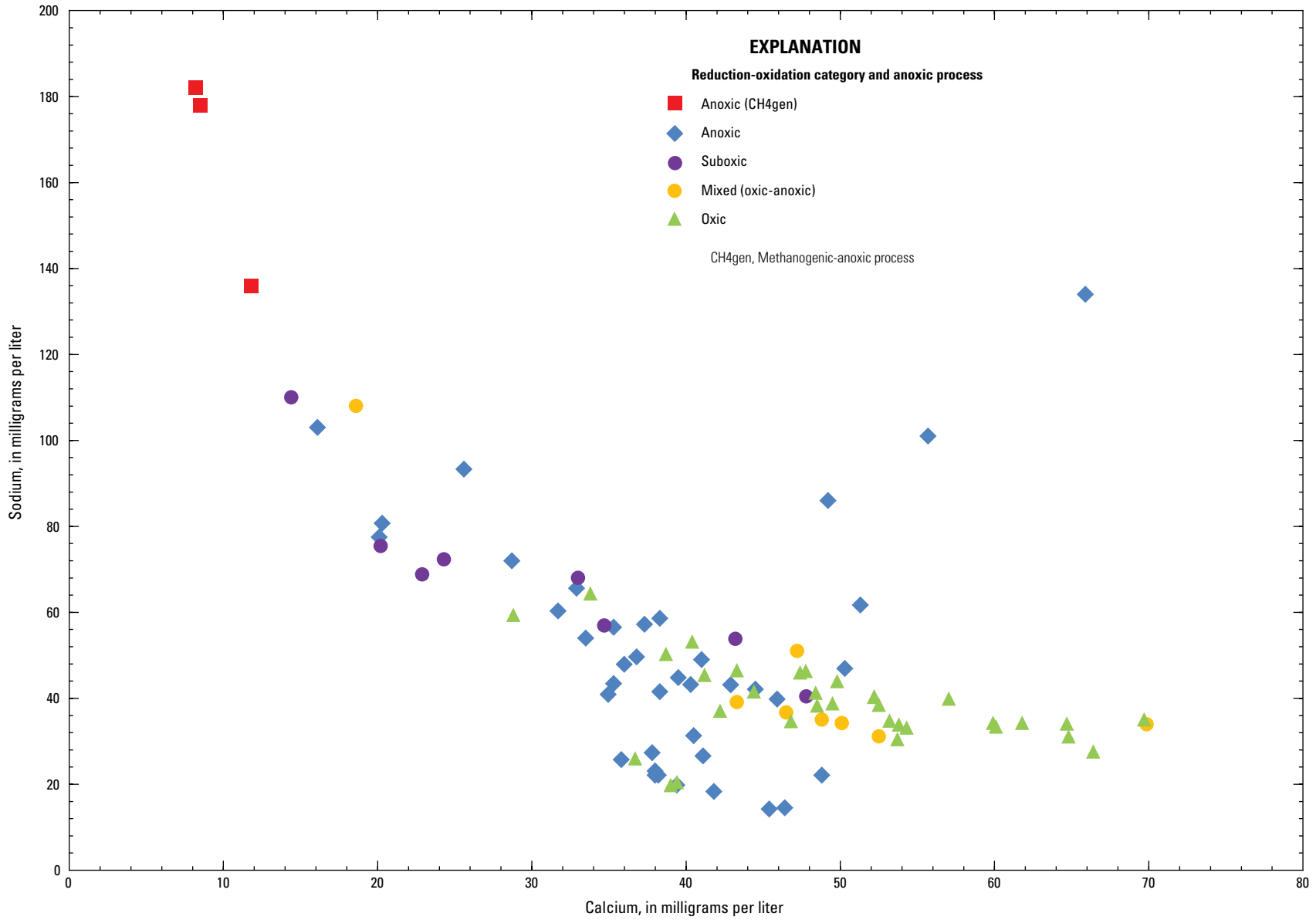


Figure 10. Sodium concentration compared to calcium concentration (with reduction-oxidation categories and anoxic process indicated) for the water samples collected from 91 municipal supply wells in Houston, Texas, 2007–11.

The eight samples classified with a mixed redox category were primarily Ca-HCO₃ predominant, with comparatively low Na concentrations (fig. 10), and were primarily (6 of 8) collected from wells in the northwest area (table 5). The aquifer designations for these eight wells are the ones expected to be most associated with the potential of mixing waters from multiple sources and include the multiple aquifer designation “lowerCHCT, upperEVGL” and the designation “fullyEVGL” for wells intersecting essentially the full extent (upper, middle, and lower parts) of the Evangeline aquifer (fig. 5). Each part of the aquifer is used for water supply in the northwest area, where the aquifer is thinner than in the southwest, possibly making the mixed water types more common in the northwest area. The mixing may complicate geochemical interpretations.

Arsenic Occurrence

The concentrations of filtered As (also referred to as “inorganic As” or the “total unspiciated As”) for the source waters sampled from the 91 wells ranged from 0.58 to 23.5 µg/L (table 2), with relatively low median and 75th percentile concentrations (2.7 and 3.6 µg/L, respectively) (table 2). Among trace elements, As is one of the most frequently detected (6.8 percent of samples nationally from domestic wells; DeSimone, 2009) naturally occurring trace elements that exceed drinking-water standards in the United States.

Arsenic concentrations measured in water samples from wells in the “lowerEVGL” aquifer designation grouping were significantly higher than arsenic concentrations measured in samples from wells in the rest of the aquifer designation groupings (fig. 11A; “A” Tukey class, table 4C). For these wells, the tops of the open intervals were within approximately

600 ft (fig. 11A) of the top of the Burkeville confining unit, the formation underlying the Evangeline aquifer. The maximum As concentration (23.5 µg/L) was measured in the sample collected from well LJ-65-12-328 with deep open intervals, and the second highest As concentration (15.3 µg/L) was measured in the sample from another deep well, TS-60-62-604. Most of the deep wells open primarily to the lower part of the Evangeline aquifer and have similar water-quality characteristics, with highly reducing waters (methanogenic anoxic with low or undetectable concentrations of DO, but high concentrations of Na and As; figs. 9B and 12A). Of the remaining samples (other than those that are methanogenic anoxic), As concentrations were nearly the same regardless of redox status or aquifer designation (figs. 11A, 12A, and 13B, C; table 4B, C). There were a few As concentrations greater than or equal to 5 µg/L (maximum 5.2 µg/L) that were measured in samples collected from wells screened in the “lowerCHCT, upperEVGL” grouping and in a sample collected from a well screened in the “middleEVGL” grouping (4.9 µg/L) (figs. 11A and 13C; app. 4C).

There were only minor differences in the median concentrations or IQRs of As concentrations among the northeast, northwest, and southwest Houston areas (table 4A; app. 4A), but there was a large difference among the high As concentrations among the three areas (fig. 13A). The highest As concentrations were measured in groundwater in the northeast and the northwest areas (app. 4A). The range in As concentrations, 0.86 to 23.5 µg/L, was largest in water samples from the 29 wells in the northwest Houston area (fig. 13A), with a median of 2.9 µg/L (app. 4A). For the 20 wells sampled in the northeast Houston area (fig. 1), the range in As concentration, 0.58 to 15.3 µg/L, was second largest among the water samples (fig. 13A) and with the greatest proportion of anoxic samples (app. 4A, table 3).

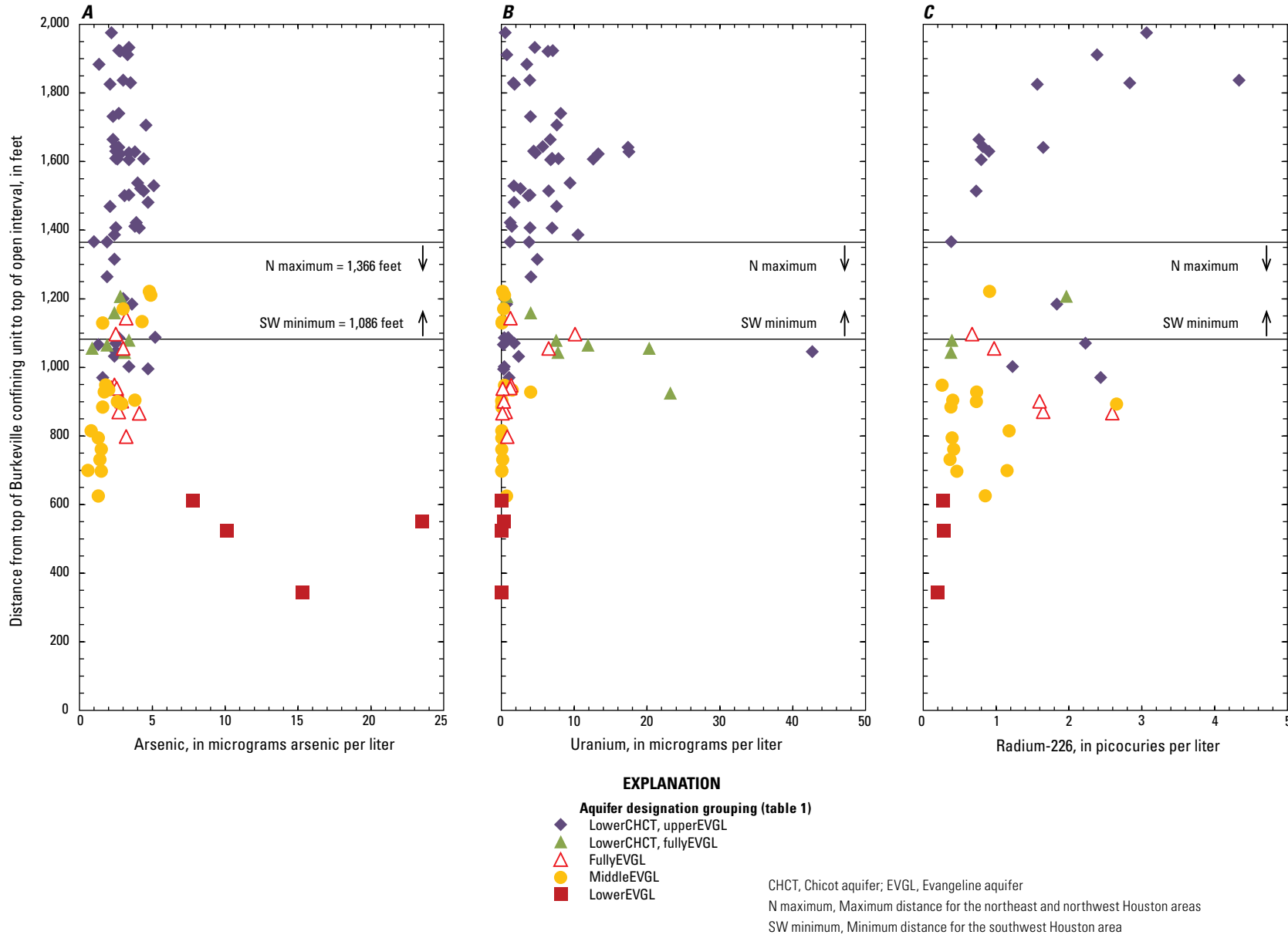


Figure 11. Distance from top of the Burkeville confining unit to top of the well open interval and *A*, filtered arsenic concentration (91 samples); *B*, filtered uranium concentration (91 samples); and *C*, filtered radium-226 concentration (41 samples). Samples were collected from municipal supply wells in Houston, Texas, during 2007–11 and grouped by aquifer designation.

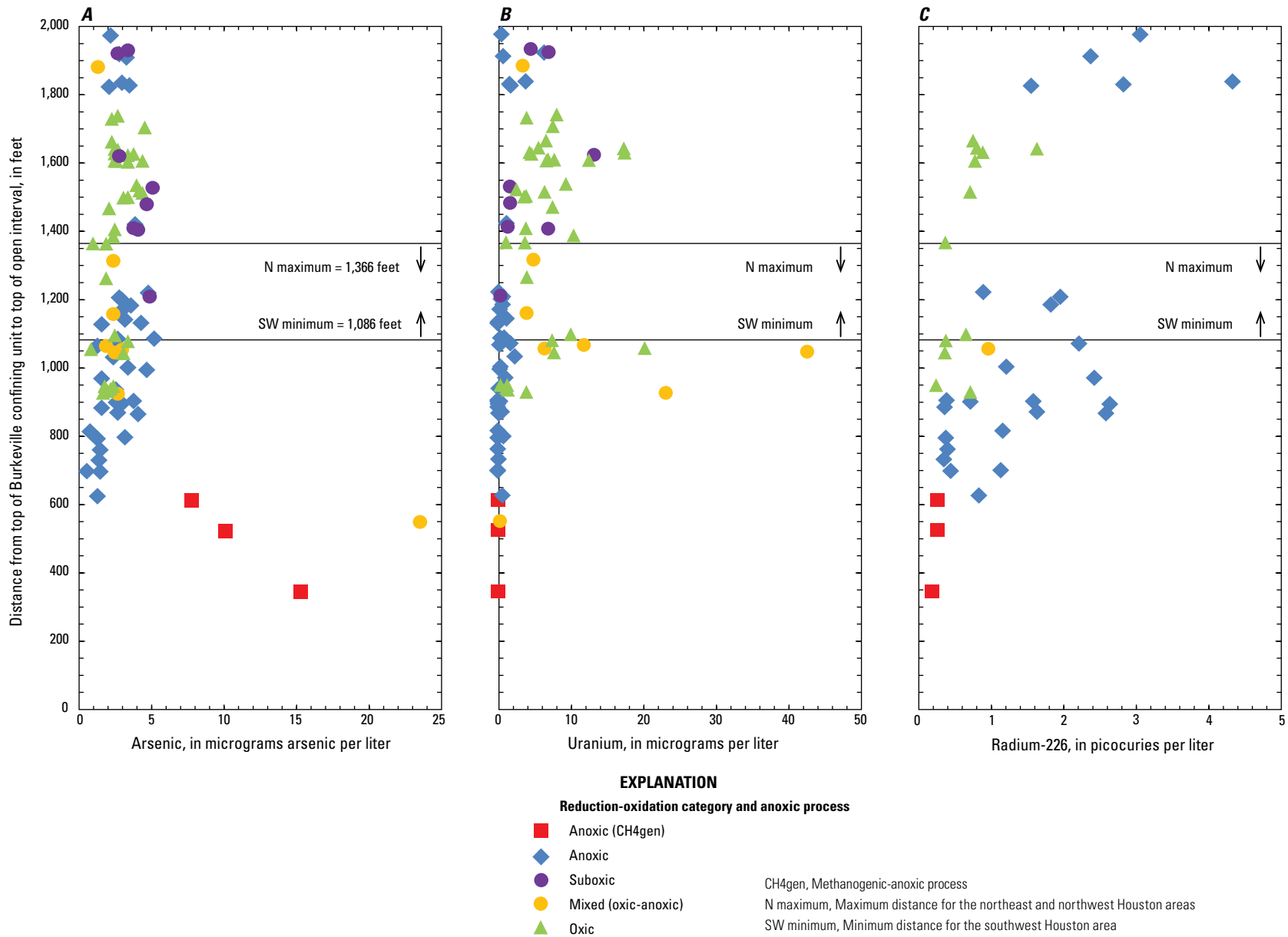


Figure 12. Distance from top of the Burkeville confining unit to top of the well open interval and *A*, filtered arsenic concentration (91 samples); *B*, filtered uranium concentration (91 samples); and *C*, filtered radium-226 concentration (41 samples). Samples were collected from municipal supply wells in Houston, Texas, during 2007–11 and grouped by reduction-oxidation category and anoxic process.

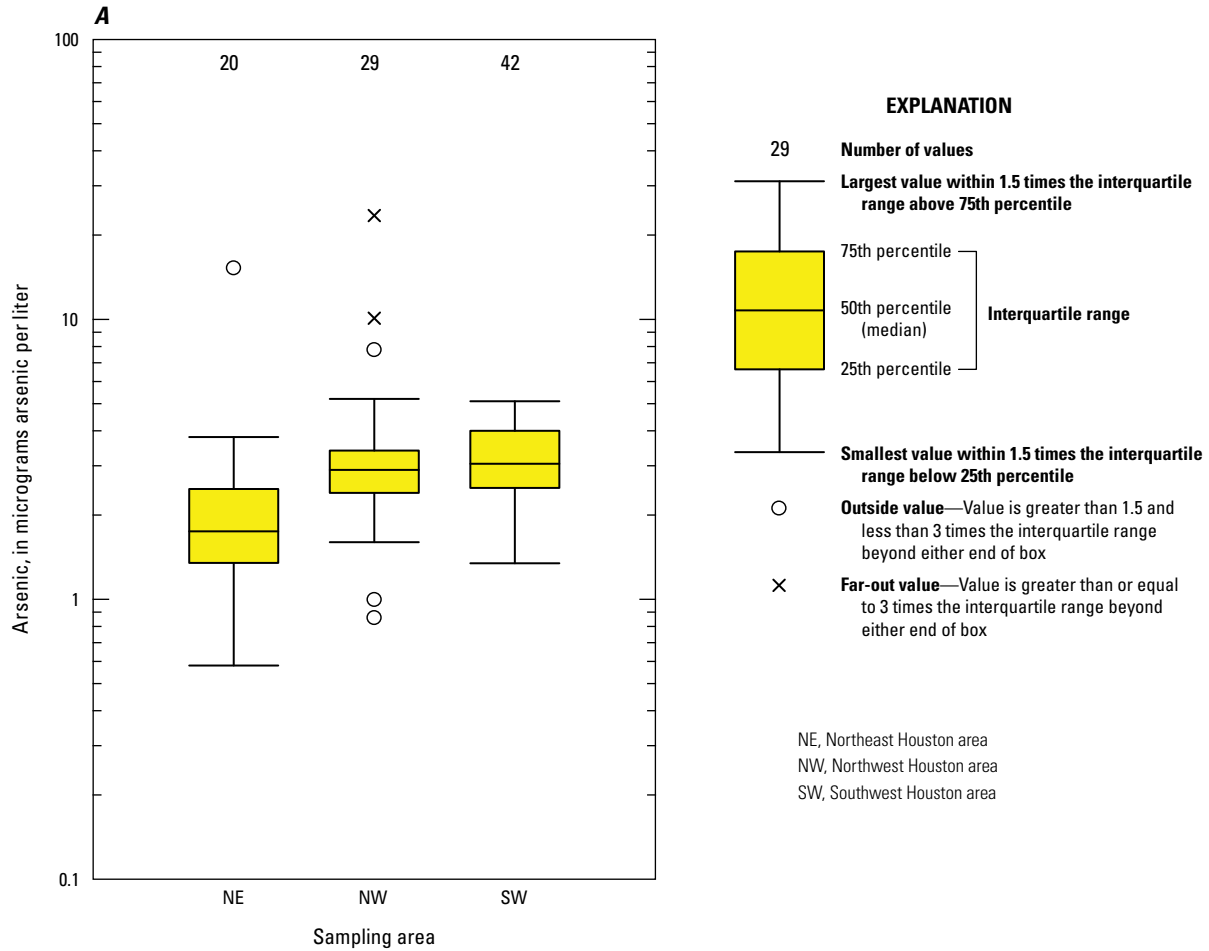


Figure 13. Concentrations of *A*, filtered arsenic grouped by location (91 samples); *B*, filtered arsenic grouped by reduction-oxidation (redox) category and anoxic process (91 samples); *C*, filtered arsenic grouped by aquifer designation (91 samples); *D*, filtered arsenite grouped by redox category and anoxic process (31 samples); and *E*, filtered arsenate grouped by redox category and anoxic process (31 samples) collected from municipal supply wells in Houston, Texas, 2007–11.

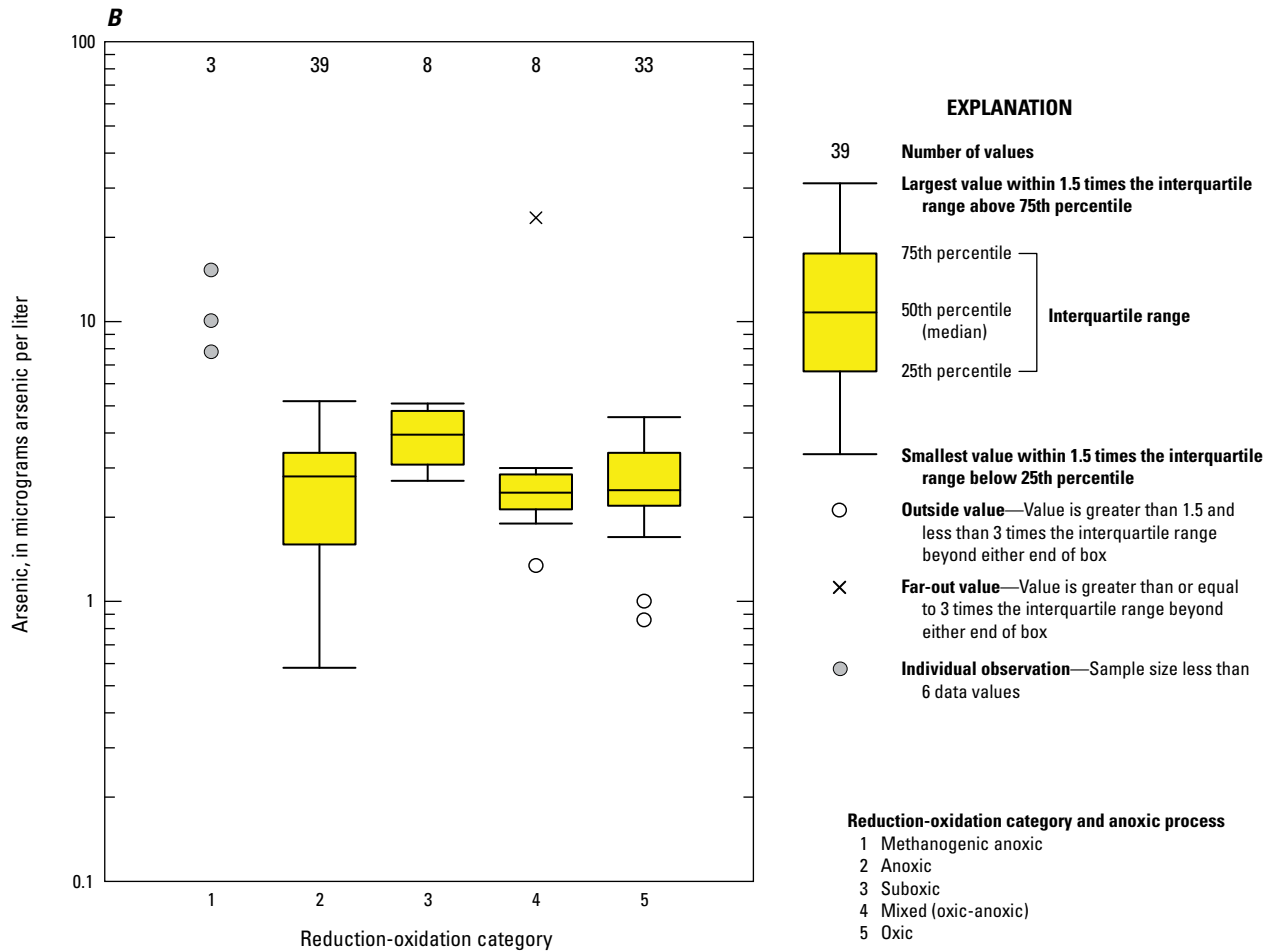


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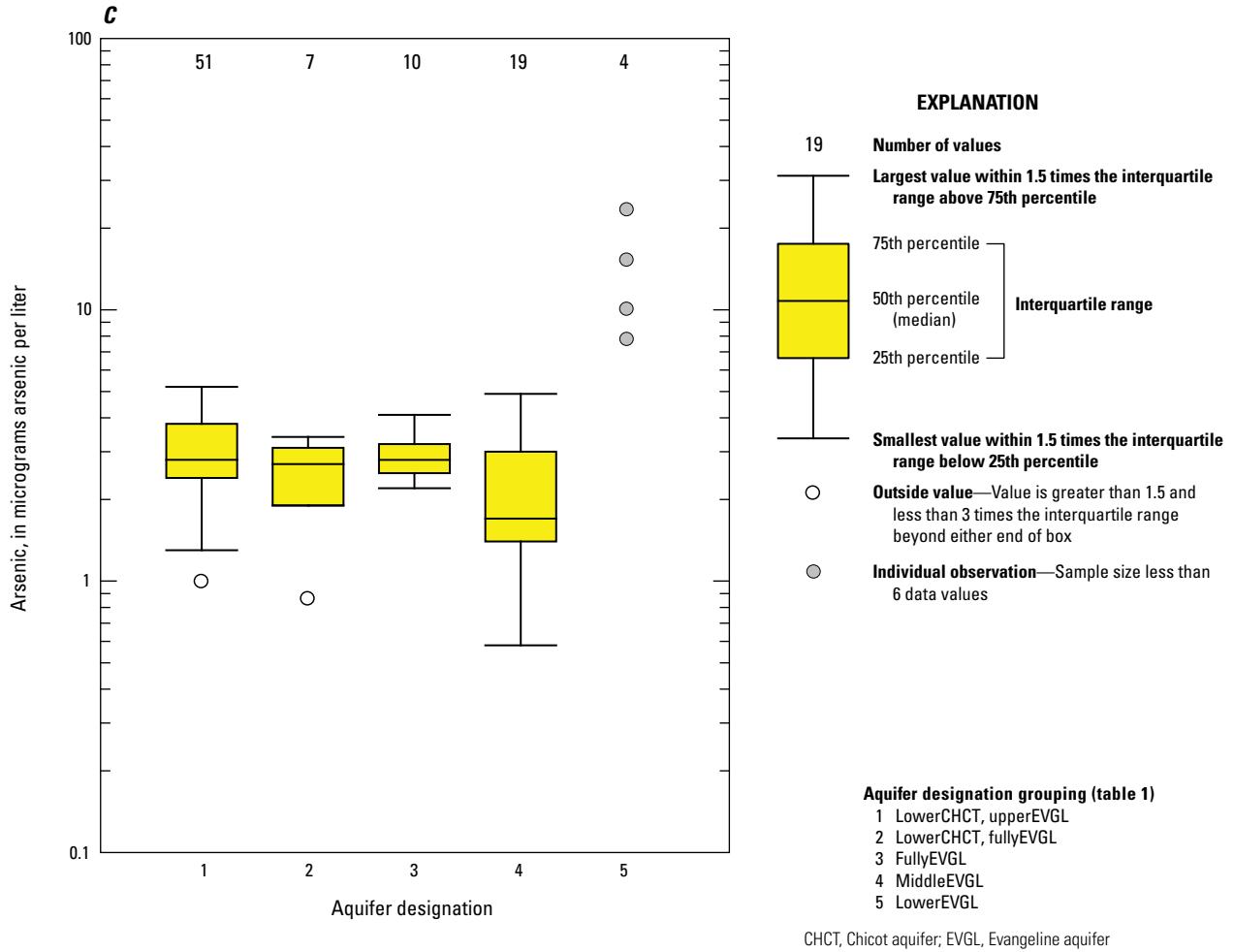


Figure 13. Concentrations of *A*, filtered arsenic grouped by location (91 samples); *B*, filtered arsenic grouped by reduction-oxidation (redox) category and anoxic process (91 samples); *C*, filtered arsenic grouped by aquifer designation (91 samples); *D*, filtered arsenite grouped by redox category and anoxic process (31 samples); and *E*, filtered arsenate grouped by redox category and anoxic process (31 samples) collected from municipal supply wells in Houston, Texas, 2007–11.—Continued

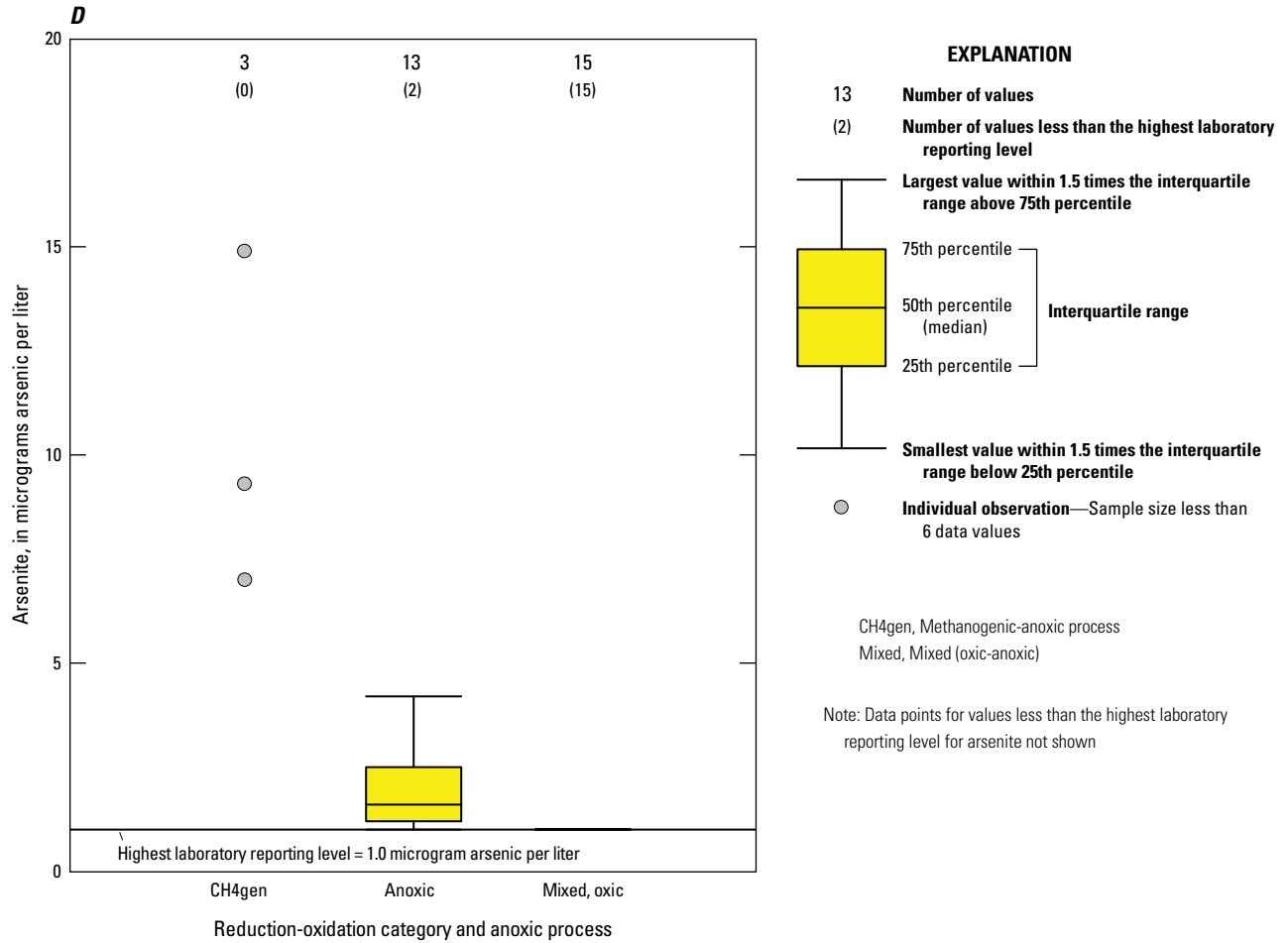


Figure 13. Concentrations of *A*, filtered arsenic grouped by location (91 samples); *B*, filtered arsenic grouped by reduction-oxidation (redox) category and anoxic process (91 samples); *C*, filtered arsenic grouped by aquifer designation (91 samples); *D*, filtered arsenite grouped by redox category and anoxic process (31 samples); and *E*, filtered arsenate grouped by redox category and anoxic process (31 samples) collected from municipal supply wells in Houston, Texas, 2007–11.—Continued

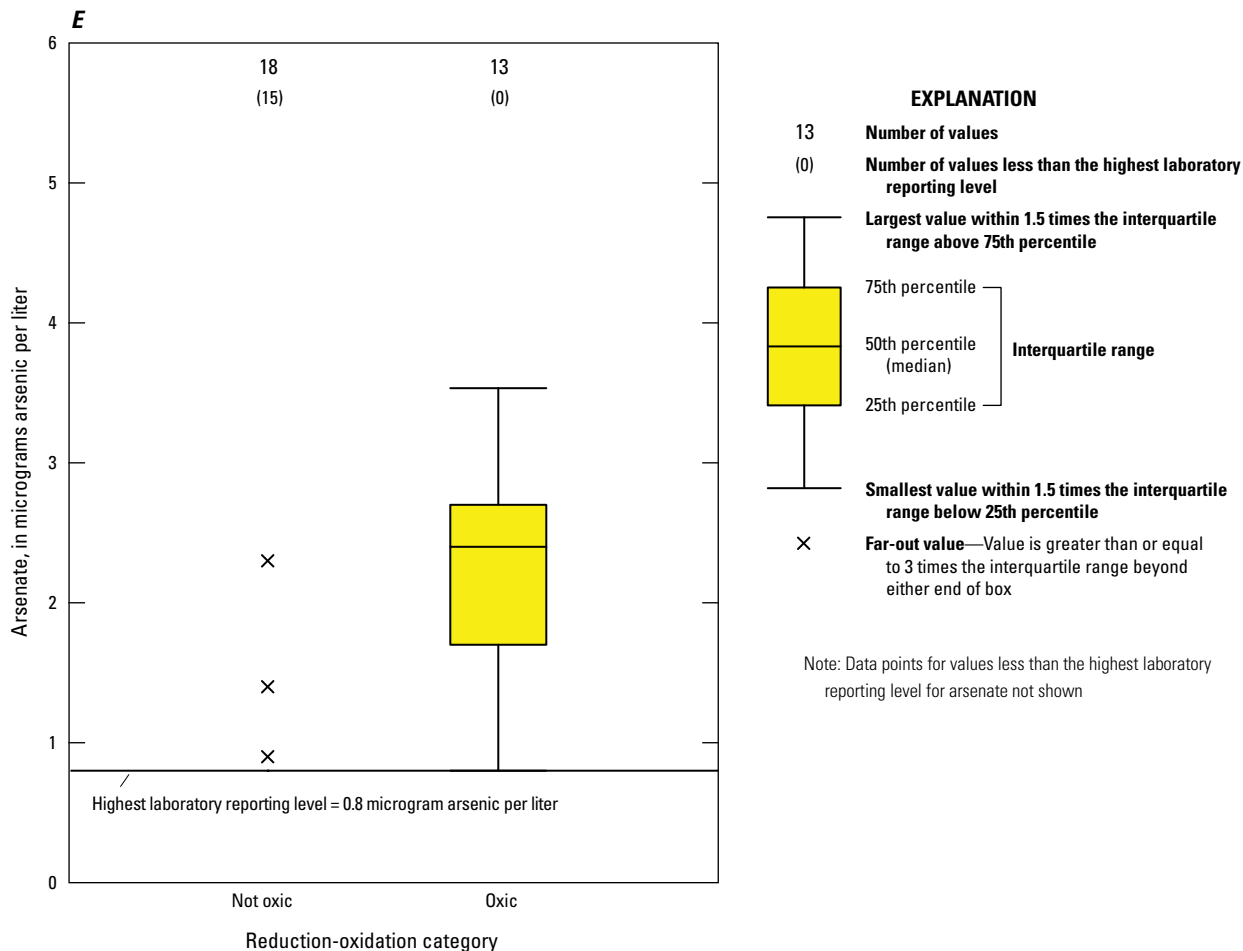


Figure 13. Concentrations of *A*, filtered arsenic grouped by location (91 samples); *B*, filtered arsenic grouped by reduction-oxidation (redox) category and anoxic process (91 samples); *C*, filtered arsenic grouped by aquifer designation (91 samples); *D*, filtered arsenite grouped by redox category and anoxic process (31 samples); and *E*, filtered arsenate grouped by redox category and anoxic process (31 samples) collected from municipal supply wells in Houston, Texas, 2007–11.—Continued

Arsenic Speciation

Speciation of As is of considerable interest in defining the geochemical factors affecting the mobilization of the As (Cherry and others, 1979). The water samples collected in Houston during 2007–11 represent a variety of redox conditions, but in the absence of As species data, it is uncertain as to whether all the As is present as a single species, as dominantly As(III) or As(V) on the basis of whether the water is anoxic or oxic, or as nearly equally divided between As(III) and As(V) species. If the water sample is a mixture of anoxic and oxic waters, nearly equal amounts of both species are possible. The existence of different redox conditions has implications for the solubility and mobility of total (unspeciated) As in the Gulf Coast aquifer system. It is presumed that at the point of recharge, As occurs as the oxidized As(V) species (Reedy and others, 2007), but fate along the flow path, including speciation and other chemical transformation, remains poorly understood.

The As-speciation analyses were completed for a subset of 31 samples to further describe As occurrence in the aquifer system. In all but five samples with detections above the LRL of these As species, either the reduced As(III) or the oxidized As(V) species composed all the As present. The As(III) was the most prevalent species of As in water from 14 of the 31 wells sampled, with the As(III) concentrations ranging from less than 0.4 to 14.9 micrograms As per liter ($\mu\text{g-As/L}$) (fig. 14; tables 2 and 3), with an estimated value of 0.3 $\mu\text{g-As/L}$ measured in one sample. The As(V) concentrations greater than or equal to 0.8 $\mu\text{g/L}$ (the highest LRL used during the study) were in the water from 15 of the 31 sampled wells. The range in concentrations for the As(V) was less than 0.3 to 3.5 $\mu\text{g-As/L}$ (table 2). The As(III) concentration exceeded 4 $\mu\text{g/L}$ in the groundwater from the Gulf Coast aquifer system in Houston in 4 of the 14 samples in which As(III) was dominant, whereas concentrations of As(V) did not exceed 3.5 $\mu\text{g/L}$ in any of 14 samples in which As(V) was dominant (though the level of total As was measured at a concentration of 4 $\mu\text{g/L}$ in 2 of these samples). The 4- $\mu\text{g/L}$ concentration level for total As is a reasonable threshold, or “cut point,” in determining the difference in occurrence of the As species. As a preliminary indication, concentrations of total As greater

than 4 $\mu\text{g/L}$ may be presumed to contain primarily As(III) in the study area. Because As(III) is perhaps slightly more toxic on ingestion (Hughes and others, 2011) and is somewhat more soluble than As(V) (Dixit and Hering, 2003), indicators for its occurrence are important to identify.

The occurrence of As species was controlled by redox of the groundwater. The bar graph in figure 14 shows the As species in each sample generally arranged in order by the ORP (highest potential to lowest potential from left to right). Detectable (greater than 1.0 $\mu\text{g-As/L}$) concentrations of As(III) were associated with waters with low ORP, less than -100 mV, and an anoxic redox category where DO was not detected or was present in concentrations less than 0.5 mg/L (fig. 13D). By using the Spearman rank correlation coefficient (r), it was determined that the concentrations of As(III) correlated negatively with DO ($r=-0.703$) (table 6), indicating a substantial correlation with anoxic waters (fig. 14). Detectable (greater than 0.8 $\mu\text{g-As/L}$) concentrations of As(V) were associated primarily with oxic water (fig. 13E), where DO was readily measurable in concentrations greater than 0.5 mg/L and redox potential was high (fig. 14). The concentrations of As(V) correlated positively with DO ($r=0.770$) (table 6), indicating a substantial correlation of the more oxidized form of As with oxic waters (fig. 14), but the maximum value for As(V) was only 3.5 $\mu\text{g-As/L}$ (table 2).

Radionuclide Occurrence

The decay of the naturally occurring, long-lived radionuclides U-238 and Th-232 (fig. 3), which are trace elements found in rocks, soils, and waters, produces other intermediate radioactive elements (progeny) (Faure, 1977; Durrance, 1986), all of which have individually distinct chemistries, resulting in detectable concentrations of these elements and radioactivity in waters over a wide range of geochemical conditions. The most common radionuclides in groundwater are Ra-226, Ra-228, Rn-222, U-238, and U-234 (Durrance, 1986; Wanty and others, 1992). Detailed descriptions of types of radioactive decay are provided by Oden and others (2010).

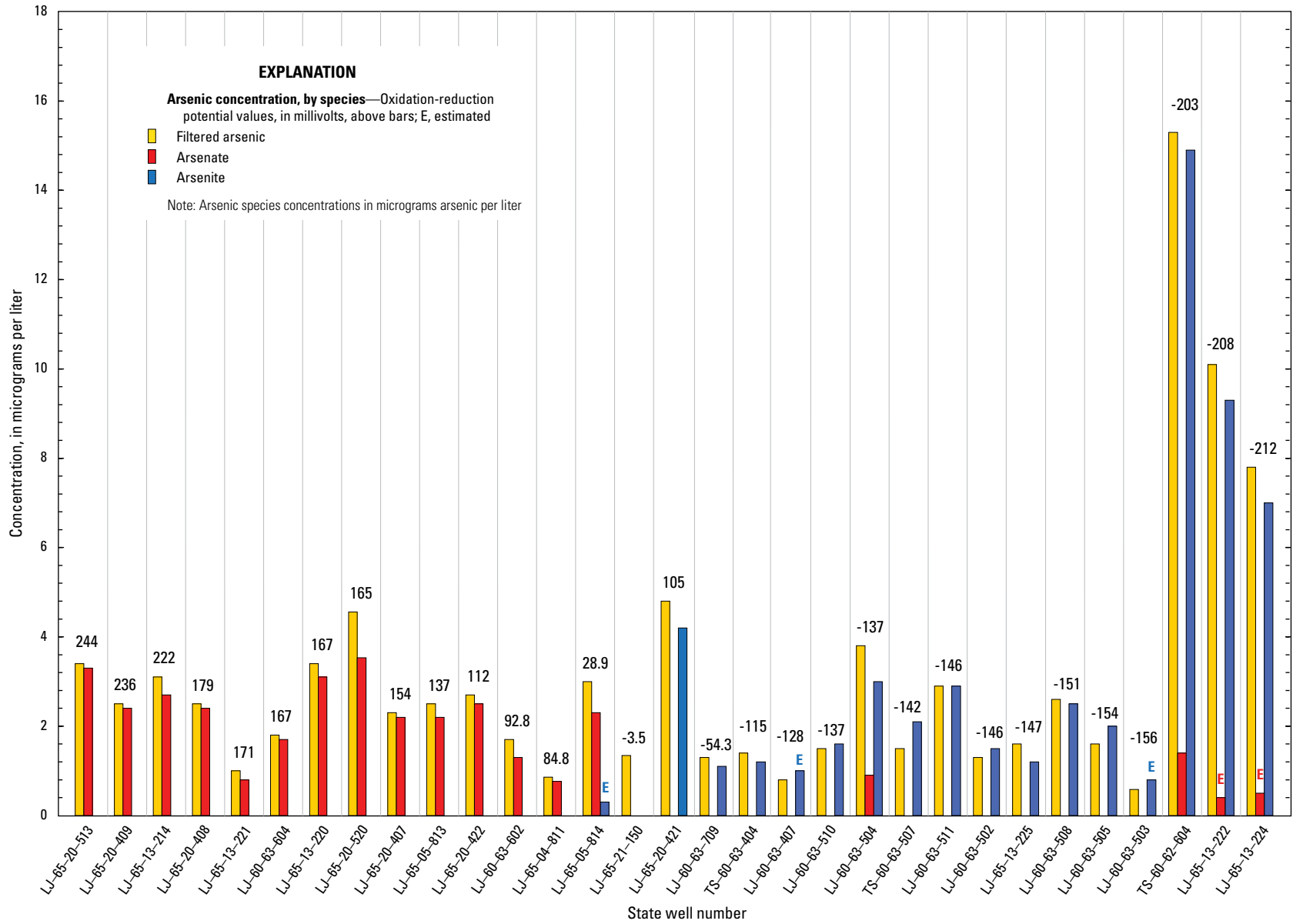


Figure 14. Filtered arsenic concentrations with arsenic species concentrations, generally ordered from the most oxidic to the most reducing samples (with oxidation-reduction potential measurements indicated), collected during 2007–11 from 31 municipal supply wells located in Houston, Texas.

Table 6. Spearman rank correlation coefficients among selected physicochemical properties and concentrations of arsenic and selected trace elements, major ions, and selected radionuclides for water samples collected from 91 municipal supply wells in Houston, Texas, 2007–11.

[All coefficients shown are significant at the 95-percent confidence level; DO, dissolved oxygen concentration; SC, specific conductance; --, the correlation coefficient is not significant; +, plus; -, minus; *, 30-day count]

Constituent	Constituent							
	Arsenic	Arsenic(III)	Arsenic(V)	Radium-226	Uranium	DO	pH	Sodium
Arsenic	1	+0.370	+0.418	--	--	--	+0.323	+0.672
Arsenic(III)	+0.370	1	-0.605	--	-0.743	-0.703	+0.706	--
Arsenic(V)	+0.418	-0.605	1	--	+0.759	+0.770	-0.521	+0.359
Radium-226	--	--	--	1	--	-0.319	-0.326	--
Uranium	--	-0.743	+0.759	--	1	+0.665	-0.628	--
alpha-activity*	--	-0.672	+0.540	+0.634	+0.662	+0.241	-0.416	--
DO	--	-0.703	+0.770	-0.319	+0.665	1	-0.516	-0.303
pH	+0.323	+0.706	-0.521	-0.326	-0.628	-0.516	1	+0.317
SC	+0.365	--	--	--	+0.216	--	-0.244	+0.595
Sodium	+0.672	--	+0.359	--	--	-0.303	+0.317	1
Calcium	-0.455	-0.720	+0.493	--	+0.568	+0.536	-0.876	-0.502
Magnesium	--	-0.605	+0.548	+0.487	+0.638	+0.399	-0.717	--
Alkalinity	+0.443	--	--	--	--	--	--	+0.591
Chloride	+0.205	--	--	--	+0.290	+0.271	-0.351	+0.385
Sulfate	+0.296	--	--	+0.681	--	-0.417	--	+0.460
Fluoride	+0.717	--	--	--	--	-0.329	+0.363	+0.909
Potassium	-0.257	--	--	--	-0.200	-0.255	--	--
Manganese	--	+0.596	-0.785	--	-0.676	-0.825	+0.385	--
Iron	--	+0.678	-0.761	+0.418	-0.634	-0.786	+0.324	--
Molybdenum	+0.310	+0.637	-0.375	--	-0.557	-0.677	+0.614	+0.588
Chromium	--	-0.773	+0.794	--	+0.741	+0.890	-0.605	-0.284
Selenium	--	-0.774	+0.815	--	+0.866	+0.768	-0.503	--
Vanadium	--	-0.669	+0.742	--	+0.787	+0.704	-0.496	--
Boron	+0.649	--	--	--	--	-0.297	+0.291	+0.910
Strontium	--	-0.544	+0.556	+0.565	+0.363	--	-0.341	--

Constituent	Constituent								
	Calcium	Chloride	Alkalinity	Sulfate	Iron	Molybdenum	Selenium	Vanadium	Boron
Arsenic	-0.455	+0.205	+0.443	+0.296	--	+0.310	--	--	+0.649
Arsenic(III)	-0.720	--	--	--	+0.678	+0.637	-0.744	-0.669	--
Arsenic(V)	+0.493	--	--	--	-0.761	-0.375	+0.815	+0.742	--
Radium-226	--	--	--	+0.681	+0.418	--	--	--	--
Uranium	+0.567	+0.290	--	--	-0.634	-0.556	+0.866	+0.787	--
alpha-activity*	+0.345	+0.384	+0.298	+0.326	--	-0.291	+0.465	+0.366	--
DO	+0.536	+0.271	--	-0.417	-0.786	-0.677	+0.768	+0.705	-0.297
pH	-0.876	-0.351	--	--	+0.324	+0.614	-0.503	-0.496	+0.294
SC	--	+0.835	+0.704	--	--	--	--	--	+0.522
Sodium	-0.502	+0.385	+0.591	+0.460	--	+0.588	--	--	+0.910
Calcium	1	+0.344	--	--	-0.286	-0.662	+0.459	+0.399	-0.496
Magnesium	+0.649	+0.517	+0.200	+0.226	--	-0.527	+0.473	+0.383	--
Alkalinity	--	+0.512	1	--	--	--	--	--	+0.573
Chloride	+0.344	1	+0.512	--	--	--	--	--	+0.294
Sulfate	--	--	--	1	+0.278	+0.302	--	--	+0.361
Fluoride	-0.529	+0.272	+0.586	+0.481	--	+0.566	--	--	+0.890
Potassium	--	--	-0.344	--	+0.311	--	-0.265	-0.379	+0.226
Manganese	-0.309	-0.293	-0.217	+0.276	+0.832	+0.495	-0.762	-0.794	--
Iron	-0.286	--	--	+0.278	1	+0.475	-0.744	-0.778	--
Molybdenum	-0.662	--	--	+0.302	+0.475	1	-0.604	-0.513	+0.573
Chromium	+0.568	--	--	-0.280	-0.833	-0.704	+0.805	+0.818	-0.266
Selenium	+0.459	--	--	--	-0.744	-0.604	1	+0.828	--
Vanadium	+0.399	--	--	--	-0.778	-0.513	+0.828	1	--
Boron	-0.496	+0.295	+0.573	+0.361	--	+0.573	--	--	1
Strontium	+0.244	+0.436	--	+0.362	--	-0.729	+0.208	--	--

Uranium

Uranium was detected in about 88 percent (80 of 91) of the samples collected. The range in U concentrations was from less than 0.02 to 42.7 $\mu\text{g/L}$, with a median value of 1.69 $\mu\text{g/L}$ and a 75th-percentile value of 6.48 $\mu\text{g/L}$ (table 2). The maximum U concentration of 42.7 $\mu\text{g/L}$ was measured in the source-water sample from well LJ-65-04-729 (aquifer designation grouping of “lowerCHCT, upperEVGL”) (table 2). Significantly higher U concentrations were associated with the aquifer designation groupings of “lowerCHCT, upperEVGL” and “lowerCHCT, fullyEVGL” than the other aquifer designation groupings (fig. 11B; “A” Tukey class, table 4C). The 75th-percentile concentration of 6.48 $\mu\text{g/L}$ indicates that most of the U concentrations from source-water samples were moderate to low. The highest U concentrations were in waters categorized as oxic, mixed, and suboxic redox conditions (figs. 12B, 15A; table 4B). Samples with the highest U concentrations (10 concentrations were greater than 10 $\mu\text{g/L}$) were primarily from the oxic and mixed redox conditions (figs. 12B, 15A) with relatively large DO concentrations. Those 10 water samples were all from wells located in the northwest and southwest areas, with six of the wells having open intervals intersecting the shallower aquifers composing the “lowerCHCT, upperEVGL” aquifer designation grouping (fig. 11B). Three wells were in the “lowerCHCT, fullyEVGL” aquifer designation grouping, and one well was “fullyEVGL.” The altitudes of the tops of the open intervals for the wells were screened either in the Chicot aquifer or relatively close to the base of the Chicot aquifer and greater than 920 ft from the top of the underlying Burkeville confining unit (fig. 11B). In the subset of wells where ORP was measured, the ORP was significantly greater among samples from the “lowerCHCT, upperEVGL” and “lowerCHCT, fullyEVGL” aquifer designation groupings than the other groups (“A” Tukey class, table 4C).

The median U concentration for the southwest area of 4.20 $\mu\text{g/L}$ was higher than concentrations for samples collected in the other two areas and was significantly higher than that for the northeast area (app. 4A); the U concentrations for the northeast area were assigned to the “B” Tukey class (table 4A). Oxic water occurred mostly in wells in the southwest area (21 of 42 samples were classified as oxic; table 3), and U occurrence was most frequent in those oxic waters (figs. 12B and 15A). The smallest range in U concentrations (less than 0.04 to 4.92 $\mu\text{g/L}$, with a median of 0.10 $\mu\text{g/L}$) was measured in the northeast area, where only 5 of 20 water samples were classified as oxic (table 3; app. 4A).

Uranium is present in mineable amounts in roll-front-type U deposits in sediments of Eocene, Miocene, and Pliocene ages along or near the Texas Gulf Coast in southern Texas (Eargle and others, 1975; Goldhaber and others, 1978; Baker, 1979; Hall, 2009), which coincides with the Catahoula confining system and Jasper and Evangeline aquifers of the Gulf Coast aquifer system. Because U is present in the aquifer material, U is commonly present in groundwater; U

can be soluble, depending on the geochemical conditions. Uranium was detected in all of the 33 samples classified in the oxic redox category, ranging in concentration from 0.38 to 20.3 $\mu\text{g/L}$, with a median concentration of 6.48 $\mu\text{g/L}$ (figs. 12B and 15A; app. 4D). The median in U concentrations in oxic samples was equivalent to the 75th-percentile value for the entire dataset. Only the oxic U (VI) species are soluble, whereas the reduced U (IV) species are essentially insoluble (Langmuir, 1978). The occurrence of U was directly associated with the oxic geochemical conditions optimal for its solubility.

Of the 42 groundwater samples classified as anoxic, U was detected at a concentration greater than or equal to 0.04 $\mu\text{g/L}$ (the highest LRL) in 31 of 42 samples (74 percent). The range in detected U concentrations was small, from 0.04 $\mu\text{g/L}$ to 6.4 $\mu\text{g/L}$ (figs. 12B and 15A; table 4B; app. 4D), which is about equal to the median U concentration for the oxic samples or the 75th percentile for all of the samples (table 2). The 11 anoxic samples with U concentrations less than the LRL were from wells that were assigned an aquifer designation of “middleEVGL” or “lowerEVGL” (fig. 11B), for which U concentrations were significantly less than the other aquifer designation groupings (“C” Tukey class, table 4C). The wells that produced water with U concentrations less than the LRL were screened with tops of their open intervals far below the base of the Chicot aquifer to intersect the part of the aquifer near the base of the Evangeline aquifer. The 31 anoxic samples with detectable concentrations of U primarily were from wells assigned to the aquifer designation groupings “lowerCHCT, upperEVGL” or “fullyEVGL,” so the altitudes of the tops of the open intervals for these wells were screened in the Chicot aquifer or were relatively close to the base of the Chicot aquifer (figs. 11B and 12B). The wells from which the 31 anoxic samples were collected may be drawing water from different redox zones (oxic, suboxic, or anoxic); for example, an oxic source of water that may be DO and U bearing may be flowing into these wells from open intervals in or relatively close to the base of the Chicot aquifer, along with additional deeper sources of water flowing into the well that may be suboxic or anoxic. During mixing within the borehole, the DO may be diluted or consumed (depleted), resulting in the anoxic classification for these water samples, but detectable concentrations of U may remain despite dilution. Even with dilution, detection of small amounts (as little as 0.03 $\mu\text{g/L}$ [Oden and others, 2011]) of U was still possible with the inductively coupled plasma-mass spectrometry analytical method; in comparison to the low detection level that was used for U analysis in this study, the Clark-cell electrode, amperometric, and spectrophotometric methods used for measuring DO concentration (U.S. Geological Survey, variously dated) are not very sensitive, with detection levels on the order of about 0.10 mg/L.

The range of U concentrations in the eight samples assigned to the mixed redox category was from 0.32 to 42.7 $\mu\text{g/L}$, with a median concentration of 5.70 $\mu\text{g/L}$. The range in U concentrations in the eight samples classified

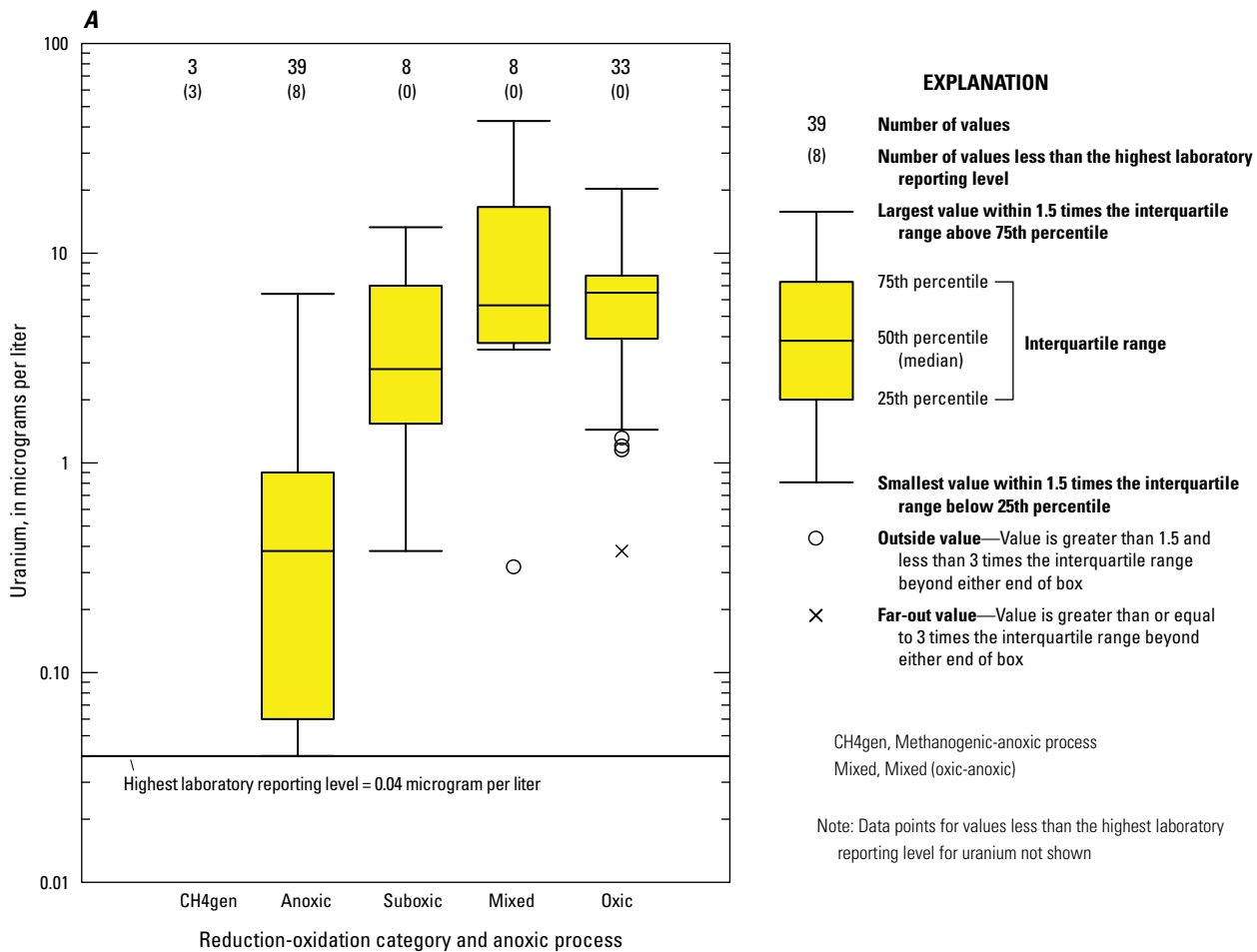


Figure 15. Concentrations of *A*, filtered uranium; and *B*, filtered radium-226 grouped by reduction-oxidation categories and anoxic process collected during 2007–11 from municipal supply wells in Houston, Texas.

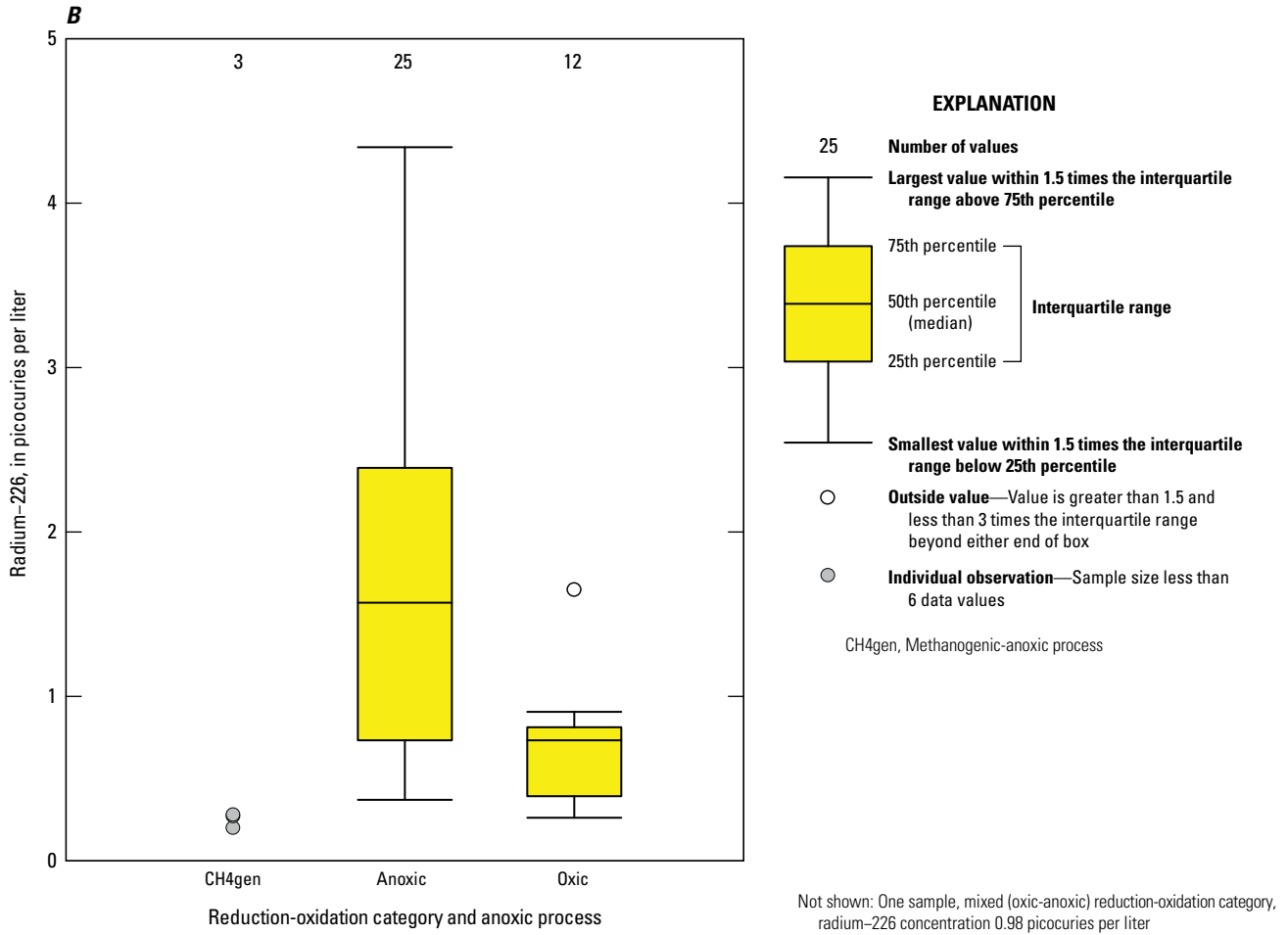


Figure 15. Concentrations of A, filtered uranium; and B, filtered radium-226 grouped by reduction-oxidation categories and anoxic process collected during 2007–11 from municipal supply wells in Houston, Texas.—Continued

with the suboxic category was from 0.38 to 13.3 $\mu\text{g/L}$, with a median concentration of 3.14 $\mu\text{g/L}$ (fig. 15A; app. 4D). These concentrations are mostly between those typical of the oxic and anoxic samples. These samples were collected from partially and fully penetrating wells, and most of the open intervals for these wells were designated “lowerCHCT, upperEVGL,” “lowerCHCT, fullyEVGL” or “fullyEVGL.” These aquifer designation groupings are conducive to producing water of mixed redox conditions as previously described. During mixing, the DO, Fe, and Mn may be diluted or partially consumed but not to such a degree that their concentrations decrease to values that are less than measurable thresholds (LRLs). It is unlikely that these results are an artifact of sample collection but rather represent true mixtures of waters with various redox characteristics in the well bore during pumping. These mixed redox wells withdraw varying amounts of water from multiple redox zones of varying geochemical conditions that may or may not be favorable for U solubility, resulting in this wide range of detectable U concentrations. The sample with the maximum U concentration of 42.7 $\mu\text{g/L}$ (from well LJ-65-04-729) was classified among the wells in the mixed redox category because the DO concentration of the water was 1.0 mg/L, with relatively high concentrations of Mn and Fe.

Radium

Radium-226 concentrations were greater than the associated sample-specific critical level (ssL_c) in all 41 groundwater samples analyzed for Ra-226 (table 2). For each measurement of a radionuclide constituent, the laboratory computes an ssL_c , which is the minimum quantity of radionuclide detectable by the counting instrument during the analysis of the sample that is statistically different from the instrument background or analytical blank. If the measured concentration is greater than the ssL_c , it is considered a detected value (McCurdy and others, 2008). The Ra-226 concentrations measured in the samples ranged from 0.204 to 4.34 pCi/L, with a median concentration of 0.853 pCi/L (table 2). The third quartile of the Ra-226 measurements was 1.65 pCi/L (table 2). Of the 41 samples collected, Ra-226 concentrations were greater than 1.0 pCi/L in 17 samples and greater than 0.9 pCi/L in 20 samples (fig. 16). These concentration distributions are similar, although slightly less than those collected from Gulf Coast aquifers to the north and east of Houston during a large-scale national sampling program (Szabo and others, 2012). The maximum Ra-226 concentration was measured in the water sample from well LJ-65-29-108, which was anoxic. The samples from all but one of the wells producing waters with detectable Ra-226 greater than 1 pCi/L were characterized as anoxic (figs. 12C and 16). Eighty-two percent of the 28 samples with Ra-228 concentrations were greater than the ssL_c (Oden and others, 2010). The Ra-228 concentrations measured in the samples ranged from R-0.18 to 1.10 pCi/L, with a median of 0.47 (the “R” preceding the first value refers to a nondetected result less

than the ssL_c , and when reported as a negative value, the result is less than long-term background radiation reported routinely by the instrument; table 2). The Ra-228 concentration was greater than 1 pCi/L in 2 of the 28 water samples. The maximum Ra-228 concentration was measured in the water sample from well LJ-65-20-409 (Oden and others, 2010). The summed concentrations of Ra-226 plus Ra-228 (combined Ra) ranged from 0.246 to 3.23 pCi/L (from well LJ-60-63-511), with a median concentration of 1.16 pCi/L for the subset of 28 wells for which they were both determined (Oden and others, 2010), indicating that most of the source-water sample Ra concentrations were moderate to low. The maximum concentrations of radium-226 and combined radium (sum of radium-226 plus radium-228) were 4.34 pCi/L and 3.23 pCi/L, respectively.

The minimum Ra-226 concentration (0.204 pCi/L), as well as the minimum Ra-226 plus Ra-228 concentration (0.246 pCi/L), was measured in the sample collected from well TS-60-62-604. Among all of the wells sampled, the second deepest top of open interval (altitude, 1,073 ft below datum) was measured in well TS-60-62-604, and the open interval of this well was within 344 ft of the base of the Evangeline aquifer (table 1). The sample collected from well TS-60-62-604 was anoxic (methanogenic) (table 3) with one of the highest concentrations of Na (136 mg/L) measured in the study area (fig. 16A). Many of the other deep wells open primarily to the lower part of the Evangeline aquifer with similar water-quality characteristics (highly reducing, low concentrations of DO and U but high concentrations of As and Na) also produced water with among the lowest Ra-226 concentrations (figs. 11C, 12C, 15B, and 16). The Na concentrations in these wells were likely high because of ion-exchange process, as evidenced by the corresponding low Ca concentrations (fig. 10). In the southwest area, high Na concentrations (greater than 100 mg/L) were likely from saline sources, and the associated Ra-226 concentrations were more variable but consistently higher than in the northeast and northwest areas (fig. 16C). Two samples were identified as containing a Na-Cl water type, as indicated by the oval area on figure 16. Ra-226 has been found to increase with increasing salinity in brines from the Gulf Coast deposits (Kraemer and Reid, 1984).

The Ra-226 isotope, rather than the Ra-228 isotope, was predominant in groundwater in Houston. In five samples, the concentration of Ra-226 was greater than 2.5 pCi/L (figs. 11C and 12C). The Ra-226 concentration was greater than 2 pCi/L only in anoxic water samples (fig. 15B), and significantly higher Ra-226 concentrations were associated with the anoxic redox category rather than the other categories (“A” Tukey class, table 4B). Where the Ra-226 isotope typically is dominant in sand aquifers, U enrichment has occurred post deposition, usually in association with organic-carbon-rich layers of strata and variable redox conditions (Turner-Peterson, 1980; Szabo and Zapeczka, 1991; Szabo and others, 2012; Chapman and others, 2013), termed “roll-front-type U deposits” (Eargle and others, 1975). The reported U

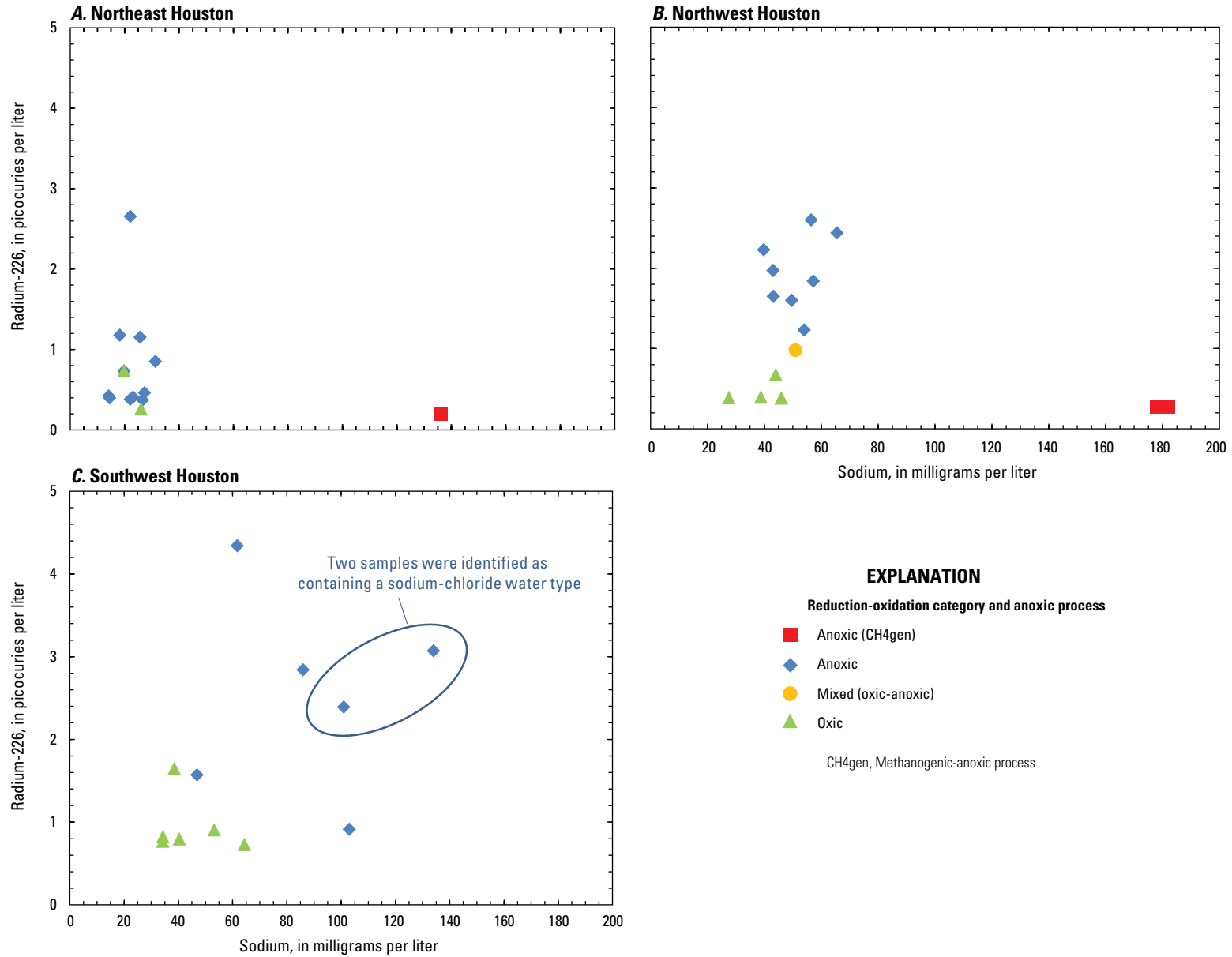


Figure 16. Correspondence of the lowest radium concentrations with those of elevated sodium grouped by reduction-oxidation category and anoxic process for the water samples from 41 municipal supply wells in *A*, northeast, *B*, northwest, and *C*, southwest areas, Houston, Texas, 2007–11.

enrichment in the sediment relative to Th enrichment at some locations in the Gulf Coast aquifer system sediments in Texas is consistent with the noted predominance of Ra-226 relative to Ra-228 in the waters derived from the aquifer system; this pattern in Ra isotope ratios is consistent with the pattern noted for several U-rich aquifer systems in the United States in which a Ra-226 isotope was determined to be dominant (Szabo and others, 2012; Chapman and others, 2013).

Gross Alpha and Gross Beta

For gross alpha-particle activities measured within 72 hours of sample collection, gross alpha-particle activities were greater than their associated ssL_c and greater than 1 pCi/L in 89 of 91 samples. Of these 89 samples, gross alpha-particle activities also were greater than 5 pCi/L in 74 samples, greater than 20 pCi/L in 6 samples, and greater than 30 pCi/L in 2 samples (Oden and others, 2010, 2011; app. 1). Gross alpha-particle activities ranged from R-1.1 to 39.7 pCi/L, with a median of 10.3 pCi/L (table 2). When activities were remeasured in 30 days, 79 of the samples collected were greater than their associated ssL_c (Oden and others, 2010, 2011; app. 2). Of the 79 samples, gross alpha-particle activities were greater than 5 pCi/L in 48 samples and 4 were greater than 20 pCi/L. The gross alpha-particle activities in the samples ranged from R-0.94 to 25.5 pCi/L, with a median of 5.60 pCi/L (table 2). For more than half the samples (52 of 91 samples), the differences between gross alpha-particle activities determined at the two different time intervals for counting were small, typically 2 to 4 pCi/L or less. Gross alpha-particle activities measured in 22 samples were within the uncertainty ranges defined by the associated 1-sigma combined standard uncertainty (CSU), representing all components of the measurement error; that is, they could not be distinguished from one another within the precision of the measurement. The CSU is a calculated measure of uncertainty of the laboratory analysis, specifically the sum of the laboratory and counting uncertainty. By definition, the true radionuclide concentration plus or minus the 1-sigma CSU has a 68-percent probability (on the basis of 1 standard deviation of the radioactivity count) that it is within range of the reported measured value (McCurdy and others, 2008).

The median gross alpha-particle activity (30 days after sample collection) for the northwest area of 7.20 pCi/L was significantly higher (“A” Tukey class, table 4A) than that of the northeast area and similar to the median for the southwest area of 6.60 pCi/L (app. 4A); the pattern was similar for the measurements made 72 hours after sample collection, indicating no difference in short-lived radionuclide concentrations between the two areas (northwest and southwest). The samples with the highest gross alpha-particle activity were mostly from wells with open intervals intersecting the shallower parts of the aquifers, designated

“lowerCHCT, upperEVGL” and “lowerCHCT, fullyEVGL,” or wells open only to the upper, middle, and lower parts of the Evangeline aquifer, designated “fullyEVGL” (table 4C); the range of activities was significantly higher for these aquifer designation groupings (“A” Tukey class, table 4C) than for the other aquifer designation groupings. The highest U concentrations were similarly from the northwest and southwest areas and mostly from the same samples; these mostly U-rich samples were oxic or mixed redox (figs. 12B and 17). The lowest range in gross alpha-particle activity was measured in the northeast area, where the lowest U concentrations were measured (“B” Tukey class, table 4A), with U concentrations less than 0.04 $\mu\text{g/L}$ measured in about half the samples (app. 4A), along with low Ra concentrations (“B” Tukey class, table 4A).

The maximum gross alpha-particle activities measured 30 days after sample collection, 21.7 and 25.5 pCi/L (fig. 17; Oden and others, 2011), were from the samples from wells LJ-65-04-723 and LJ-65-04-729, respectively, that were the highest and second highest U concentration of any of the sampled wells of 42.7 and 23.2 $\mu\text{g/L}$, and were also the two highest activities measured 72 hours after sample collection. Both wells were located in the northwest area. The gross alpha-particle activity from the two measurements for these samples and for the other similar samples with minimal change over the 30-day holding period must be from one or more long-lived isotopes that do not change notably in activity in the 30-day period, such as isotopes of U or Ra-226.

Estimated U activities were calculated and subtracted from the gross alpha-particle activities to assess if U is the predominant source of the alpha activity. Estimated U activities were calculated by using the activity value of 0.68 pCi/L provided by each 1 $\mu\text{g/L}$ of U mass (on the basis of the assumption that the U-234 and U-238 isotopes are present in equal activities, also known as natural U, as defined by Osmond and Cowart, 1976). The estimated activity of “natural” U is representative for most bedrock but is conservative for U activities in groundwater, with typical values being on the order of 0.75 pCi/L per 1 $\mu\text{g/L}$ of U (Osmond and Cowart, 1976) or, in some cases, considerably higher (Wong and others, 1999; Arndt, 2010). Resolution of this discrepancy likely requires additional monitoring and detailed isotopic U analysis (Arndt, 2010). Most of the highest U concentrations were in the 10 samples with the highest gross alpha-particle and beta-particle activity measured 30 days after sample collection, with U concentrations greater than 10 $\mu\text{g/L}$ measured in 5 of the 10 samples (fig. 17). For eight samples with relatively high concentrations of Ra-226, U did not seem to be the dominant source for gross alpha-particle activities greater than 10 pCi/L, as indicated by the oval area on figure 17. The segregation of Ra from U is a function of the redox condition.

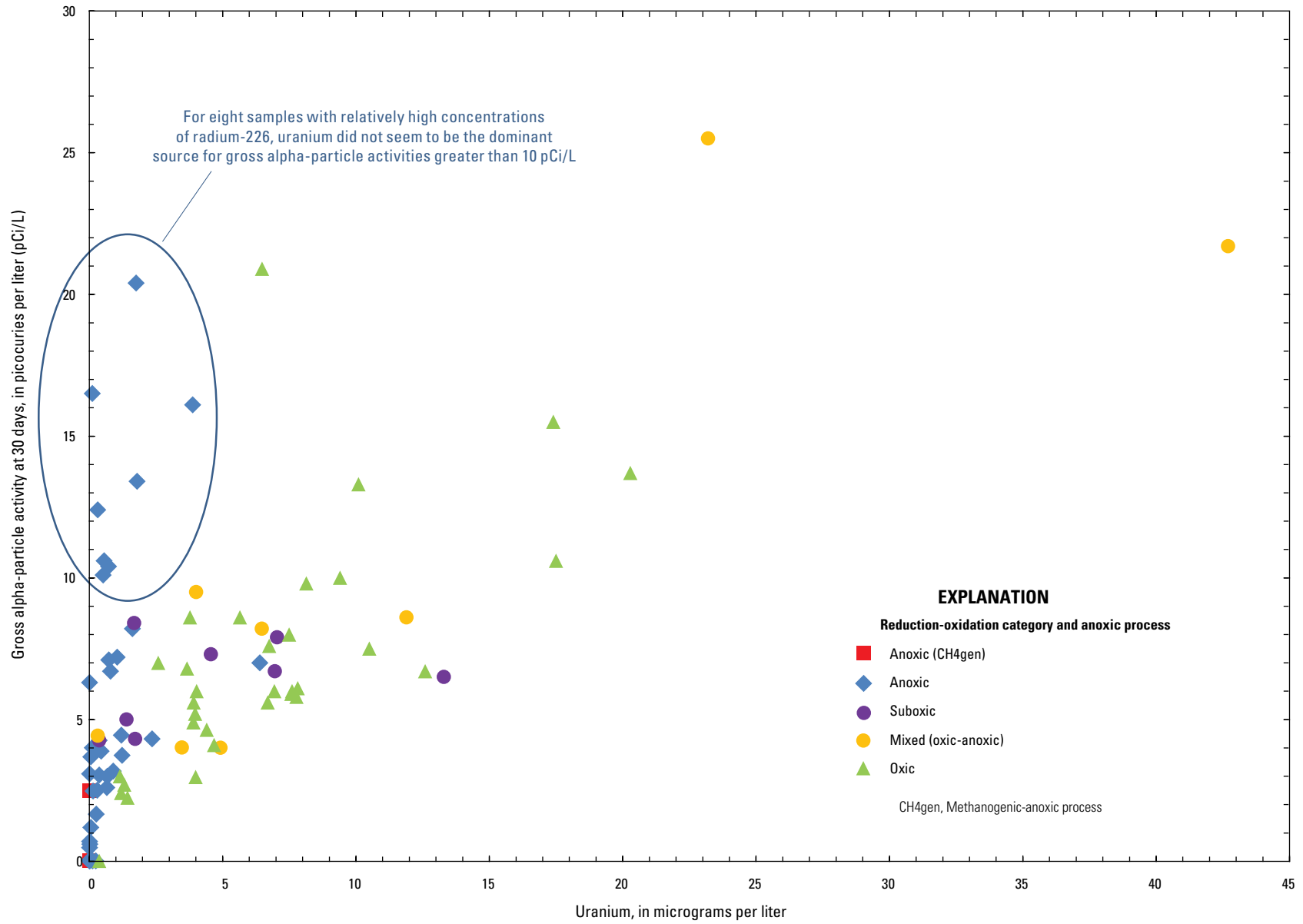


Figure 17. Gross alpha-particle activity as a function of uranium concentration, with reduction-oxidation category and anoxic process indicated for the water samples from 91 municipal supply wells in Houston, Texas, 2007–11.

For the gross beta-particle activities measured in the samples at 72 hours, all of the gross beta-particle activities were greater than the ssL_c (Oden and others, 2010, 2011; app. 2), and the range was from 1.48 to 6.60 pCi/L, with a median activity of 3.07 pCi/L (table 2). Gross beta-particle activities at 30 days were greater than the associated ssL_c in 87 of the 91 samples collected (Oden and others, 2010, 2011; app. 2). The range in activities measured at 30 days was from R-1.04 to 14.4 pCi/L, with a median of 3.48 pCi/L (table 2).

A substantial part of the gross beta-particle activity measurements in many of these 91 samples could be attributed to beta emissions from K-40, which is a weak beta emitter found naturally in the environment (Welch and others, 1995). The maximum gross beta-particle activity measured at 72 hours of 6.60 pCi/L and a K concentration of 2.67 mg/L (a concentration greater than the 75th percentile, table 2) were measured in the sample from well LJ-60-63-602, and a beta activity of about 2.2 pCi/L could be calculated to originate from the K-40 isotope in this sample. Gross beta-particle activity was less than the ssL_c for the sample from TS-60-62-604 when measured at 30 days; a K concentration of 1.82 mg/L (less than the 25 percentile, table 2) and no detectable concentrations of Ra-228 or U also were measured in the sample from this well, hence the absence of detectable beta-particle activity. The maximum concentration of gross beta-particle activity measured after 30 days at 14.4 pCi/L was from the sample from well LJ-65-04-729 that had the highest U concentration (42.7 $\mu\text{g/L}$) and the highest gross alpha-particle activity after 30 days.

Radon

A total of 31 samples collected in 2007–8 and 2010 were analyzed for Rn-222. All of the measured Rn-222 concentrations were greater than the associated sample-specific minimum detectable concentration ($ssMDC$) for samples measured in 2007 and greater than the ssL_c for samples measured in 2008 and 2010 (Oden and others, 2010, 2011). The range in Rn-222 concentrations for all of the samples was from 161 to 2,380 pCi/L, with a median of 570 pCi/L (table 2). The concentrations of Rn-222 were equal to or greater than 830 pCi/L (75th percentile) in 8 of the 31 water samples collected, and Rn-222 concentrations were greater than 1,000 pCi/L in 6 samples. The presence of detectable Rn-222 in all of the samples, as well as the presence of this radionuclide in elevated concentrations (greater than 1,000 pCi/L) in many samples, is an indication that Ra-226 (and presumably U) is present in abundance in the surrounding aquifer material (Senior, 1998). The 75th percentile concentrations of Rn-222 were mostly measured in wells screened in the Evangeline aquifer with open intervals intersecting the upper, middle, or all three parts of the aquifer. One well with an elevated Rn concentration also intersected a part of the Chicot aquifer. The aquifer matrix of the Evangeline aquifer is silty in some places (Chowdhury

and Turco, 2006). In a detailed study of Rn-222 occurrence in a coastal plain sand aquifer in New Jersey, Szabo and others (1997) showed that concentrations of Rn-222 were much higher in water from silts containing modest amounts of radionuclides than from water in homogeneous sand with minimal radioactivity; thus, silty zones intersected by the open intervals of wells are plausible sources of elevated Rn-222 concentrations in the wells sampled in Houston. Six of the eight wells with the highest Rn concentrations produced anoxic water. This result implies that perhaps somewhat uraniferous, silty strata may be in the upper or middle parts of the Evangeline aquifer where groundwater has had sufficient residence time for most of the DO to be consumed. The sediment materials composing the Evangeline aquifer are finer grained texture (relatively more silt and clay) compared to those composing the Chicot aquifer (Baker, 1979).

The highest Ra-226 concentration (4.34 pCi/L) was measured in the sample collected from well LJ-65-29-108; the highest Rn-222 concentration (2,380 pCi/L) was also measured in the sample collected from this well. An aquifer designation grouping of “lowerCHCT, upperEVGL” (fig. 11C; table 1) was assigned to well LJ-65-29-108. The lowest Rn-222 concentration (161 pCi/L, table 2) was measured in a sample collected from a well screened in the Chicot aquifer (LJ-65-13-221); the water sample from this well was categorized as oxic. In addition to the low Rn-222 concentration, a low U concentration also was measured in the sample from well LJ-65-13-221, indicating that this well was likely screened in a part of the aquifer composed of sediments containing little U. Low Rn-222 concentrations also were measured in samples from some wells screened in the “middleEVGL” aquifer designation grouping, indicating that locally variable factors besides the U concentration of the sediment may exert control on the Rn-222 concentration (Wanty and others, 1992).

Relations Among Trace Elements, Radionuclides, and Geochemistry

The ranges of the concentrations for total As, As species, selected trace elements, and selected radionuclides vary considerably laterally and with depth in the Gulf Coast aquifer system underlying the study area. The majority of these trace-element constituents are likely involved in redox reactions and other geochemical reactions. To understand the spatial and vertical extent of the occurrence of these trace-element constituents, the optimal geochemistry for their solubility in water was determined. Statistical analyses were used to determine relations of As, trace elements, and radionuclides from water from the 91 sampled municipal supply wells with concentrations of cations, anions, and redox species; with general water-quality properties; and with distributions of water types and redox categories. Redox categories and water-chemistry types that co-occurred with the distributions

of As, trace elements, and radionuclides were evaluated to determine if the associated predominant chemical reactions may control the distributions of the As, trace elements, and radionuclides.

Predominant Relations Among Trace Elements, Radionuclides, Water Types, and Redox Categories

The principal components as determined by PCAs indicated three components (listed in order of explanatory power), which characterized the predominant geochemical relations in the Gulf Coast aquifer system: (1) redox conditions, (2) water types, and (3) degree of mineralization (tables 7–9). These three components are ranked by the amount of the variability that each explains and describe the constituents commonly occurring in association with or in exclusion from one of the different redox categories (methanogenic anoxic, oxic, or Fe-reducing anoxic) and most correlated constituent of concern (As, U, As species, Ra-226, or gross measures of radioactivity). Together the first three components explain 70 to 80 percent of the variability in the water-quality data (depending upon the subset used); for example, for the entire 91-sample dataset, these first three components describe 71 percent of the variability. The PCA was computed for the entire 91-sample set and each subdatabase, grouped by well location, samples with Ra-226 data, and samples with As-speciation data. The first two principal components for all PCAs had appreciable loadings for concentrations of As and U. For Ra-226, an appreciable loading was noted for component 3 among the subset of samples with Ra-226 data, and the additional constituents loading to this component 3 can be described as relating to Fe-reducing, anoxic conditions. These same constituents loading to component 3 for the subset of samples with Ra-226 data define component 3 for the entire 91-sample dataset, indicating that the loading (preferential occurrence) of Ra-226 is related to the occurrence of the Fe-reducing, anoxic conditions. Nonredox constituents may be associated with changes in redox constituents because the progress of the controlling chemical reactions may have an indirect association with the progress of the redox reactions. The reaction associations defined by the associations among the chemical constituents were hypothetically linked to geological and hydrological factors by aquifer mineralogy, depth of penetration along flow paths, reaction rates, and residence times.

When considering the entire 91-sample dataset, the first three components explained about 71 percent of the variability (table 7). The three components corresponded to three dominant geochemical conditions (defined by the controlling redox and chemical reactions and corresponding classes of constituents). The concentrations of As, U, and Fe loaded substantially to these three components. Constituents that were not analyzed in every sample are excluded from the analysis,

an inherent limitation of PCA (Helsel and Hirsch, 2002); the analytes not analyzed in every sample, and therefore excluded from this PCA, were Ra-226 concentration, Rn-222 concentration, As species, and field-measured ORP. The three principal components can be described as component 1, association of end members of redox and water-chemical evolutionary processes (Ca compared to Na dominated; oxic compared to strongly anoxic, perhaps methanogenic); component 2, association of constituents affected by (associated with) oxidizing redox category and mineralization (increasing Na, HCO_3 , Cl, Br, F, and specific conductance); and component 3, association of constituents affected by anoxic (Fe-reducing) redox category and Fe-oxide dissolution.

Component 1 accounted for 35.6 percent of the variability (presented in table 7 as proportion of variance explained) in the water-quality data and is directly associated with, most importantly, the trace element As, and in addition, with the properties of temperature (surrogate for depth), pH (increases with increasing ion exchange), and the major ion Na (the concentration of Na increases with the progressive replacement of Ca by Na as part of the cation-exchange reaction process) (table 7). In addition, component 1 is associated with the minor halide F and the oxyanions B and Mo (both are elements difficult to remove from water and are typically associated with clays). Component 1 also is inversely (loading in opposite direction) associated with oxic conditions (defined by loading of DO), the major ion Ca, the major constituent silica, U, and the trace elements Cr, Se, and V. The strong association of Na with component 1 is not matched by the strength of association of Cl, indicating that saline water is not critical to the occurrence of the Na. The cation-exchange process affects only the concentrations of Na and Ca. Factors and processes associated with enriching the waters in Cl are not directly associated with the cation-exchange process. Arsenic was directly associated with Fe (typically associated with anoxic water), and the occurrence of As was substantially correlated to anoxic waters (of SO_4 -reducing and methanogenic conditions). Arsenic also was coupled or associated with ion exchange (Na rich, Ca poor). These loadings of constituents associated with As for component 1 are inverse (loading in opposite direction) to those constituents associated with U, which is associated with oxic waters rich in Ca. The most substantial differences in water quality in the study area were that Na and As concentrations increased with increasing depth (water temperature), pH, and ion exchange, whereas in the absence of ion exchange, Ca concentration is associated with oxic water that contains U and other oxyanion trace elements.

Component 2, which explained 23.8 percent of the variation in the water-quality data, is associated with oxidizing conditions and increasing amounts of mineralization, as indicated by the substantial loadings of DO, U, and specific conductance (table 7). Increasing mineralization also is indicated by the associated loadings of the anions HCO_3 and Cl, the cation Na, and the divalent cations Mg and Sr. Divalent cations may increase in oxic waters with general mineral

Table 7. The three principal components that explain about 71 percent of the variability of the water-quality data correlated to arsenic, alpha activity, uranium, and beta activity, in the 91 samples of water collected from the Gulf Coast aquifer system in Houston, Texas, 2007–11.

[^, constituent discussed in text; --, component loading less than plus or minus (\pm) 0.100; hr, hour; proportion of variance explained multiplied by 100 equals percentage of the variability; constituents in **bold** are constituents of concern for study]

Principal components	All wells (91)		
	Component 1	Component 2	Component 3
Eigenvalue	10.7	7.14	3.49
Proportion of variance explained	0.356	0.238	0.116
Predominant geochemical environments	End members of redox and water chemical evolutionary processes (calcium versus sodium; oxic versus anoxic)	Oxidizing, mineralized	Iron reducing

Constituent	Component loadings		
Arsenic	0.164 [^]	-0.201 [^]	--
Alpha activity (30-day hold time)¹	-0.127	-0.214 [^]	0.206
Alpha activity (72-hr hold time)¹	-0.204	-0.160	0.170
Uranium	-0.221 [^]	-0.203 [^]	--
Beta activity (30-day hold time)¹	-0.168	--	0.124
Beta activity (72-hr hold time)¹	-0.129	--	0.180
Dissolved oxygen	-0.211 [^]	-0.138 [^]	-0.235 [^]
Manganese	0.142	0.221 [^]	0.224 [^]
Iron	0.173 [^]	0.127	0.323 [^]
Sulfate	-0.119	--	0.312 [^]
pH	0.248 [^]	--	-0.140
Specific conductance	--	-0.313 [^]	0.123
Temperature	0.243 [^]	--	--
Calcium	-0.261 [^]	--	0.158
Magnesium	-0.188	-0.175 [^]	0.256 [^]
Potassium	--	0.135	0.288 [^]
Sodium	0.212 [^]	-0.252	--
Bicarbonate	0.113	-0.282 [^]	--
Bromide	--	-0.311 [^]	--
Chloride	--	-0.288 [^]	0.164
Fluoride	0.234 [^]	-0.205 [^]	--
Silica	-0.267 [^]	--	--
Chromium	-0.219 [^]	-0.138	-0.244
Barium	--	0.148	0.164
Boron	0.238 [^]	-0.207	--
Lithium	0.106	-0.277 [^]	0.189
Molybdenum	0.249 [^]	--	--
Selenium	-0.210 [^]	-0.166 [^]	-0.149
Strontium	-0.109	-0.175 [^]	0.330 [^]
Vanadium	-0.209 [^]	-0.161 [^]	-0.229

¹Gross measures of radioactivity.

dissolution and in waters with an increase in salinity (Na and Cl) in the absence of cation exchange. A suite of soluble oxyanions U, As, Se, and V load together onto this component (with associated elevated gross alpha-particle activity likely originating from the U). In contrast to their inverse association with respect to component 1, the U and As both correspond along with DO to component 2, indicating that these trace elements mutually increase in oxic waters with increasing mineralization. Manganese had an inverse association (loading in opposite direction) with these constituents with respect to component 2; Mn is least soluble in oxic waters.

Component 3 explained 11.6 percent of the variation in the water-quality data and characterized the Fe reducing, anoxic redox condition (table 7). Component 3 is directly associated with elevated concentrations of Fe and Mn that are inversely associated with concentrations of DO. These inverse-loading relations represent the geochemical processes of the reductive dissolution of the oxides of Fe and Mn that result in the mobilization of Fe and Mn and, in turn, the associated trace elements. Direct association with concentrations of SO_4 (indicating absence of SO_4 reduction) also are noted in association with this component; once initiated, SO_4 reduction results in sulfidization of the sediment and removes Fe and sulfide from solution to the solid phase (Burton and others, 2011). The direct association with the divalent cations Mg and Sr is again indicative of the general absence of cation exchange in the Fe-reducing, anoxic waters. The direct association of the concentrations of K with component 3 perhaps indicates association with clay-mineral-rich sediments.

The occurrence of As in groundwater in Houston relates to multiple geochemical water types and redox categories (table 7). Knowledge of As chemistry and distributions of the individual As species is needed to understand the As occurrence. The PCA was computed for the 31 samples with As-speciation data. Three components explained about 80 percent of the variability of the dataset (table 8A) and corresponded to the same geochemical environments and redox categories with which the concentrations of As, U, and Fe were substantially associated for the entire 91-sample dataset (table 7). Component 1 is directly associated with the concentration of As, but more importantly, there was an appreciable loading of the As(III) species onto component 1. In addition, the same properties and constituents were associated with component 1 as noted for the entire 91-well dataset. Component 1 indicates that the primary occurrences of elevated As concentrations are controlled by the occurrences of As(III) in strongly anoxic (SO_4 -reducing and methanogenic, DO poor) waters that also have substantial ion exchange (Na rich, Ca poor). The strong correspondence of these constituents with the minor halide F, the oxyanions B and Mo, the increase in pH, and the weak correspondence with Fe indicates that the Na and As concentrations are related by

the reduction of As to As(III) in strongly anoxic (SO_4 reducing and methanogenic) waters and the associated increasing effect of cation exchange with depth. Uranium is associated with oxic waters rich in Ca (and to a lesser extent Mg) and is not present in waters that have the reduced As(III) species.

The U and As, along with DO, correspond to component 2, but in this case, the As is present as the oxidized As(V) species (table 8A). The concentrations of As(V), along with DO, U, and other soluble oxyanion constituents (Se, V, and others to a lesser extent), that were associated with oxic waters relate most strongly to component 2. The concentrations of total As and the As(V) species, however, had a strong inverse association with the concentrations of Fe and Mn, just as did the concentrations of U. It is important to note that, although considered separately, components 1 and 2 explained 43 and 32 percent, respectively, of the overall data variability; considered together, components 1 and 2 explained about 75 percent of the data variability (table 8A). Both components, which represent multiple geochemical water types and redox categories, are needed to fully explain the variability of total As concentrations because one or the other of the components are strongly related to one or the other of the As species. The different inorganic As species are all soluble, but solubilities for the different As species were optimal in different geochemical conditions, resulting in differing loading intensities for the individual species, stronger for select conditions than that for total As concentrations. Component 3 explained only 6 percent of the overall data variability, with appreciable loadings of K, Mo, and gross-beta activity (table 8A).

With respect to Ra-226 occurrence, the 41 samples with available (measured) Ra-226 concentration data were evaluated by using PCA. Three components that correspond to the same geochemical environments described for the three components for the 91-sample set explained about 77 percent of the variability of the 41-sample dataset (table 8B). The first two components corresponded to geochemical classes of constituents to which As and U corresponded, respectively, as previously described for the 91-sample dataset and for the 31-sample subset with As species data, and these two components are not discussed further. For component 3, representing Fe-reducing, anoxic conditions, Ra-226 and Fe had appreciable loadings, indicating a high association among their concentrations, followed by loading of Mn. Component 3 also had an association with DO, U, and other oxyanions soluble in oxidized water (such as Cr, Se, and V) that was inverse with respect to Ra-226, Fe, and Mn. The amorphous hydroxide phases of Fe and Mn are insoluble in oxic water and strongly sorb Ra (Ames, McGarrah, and others, 1983). Both radionuclides (Ra and U) are derived from sedimentary strata, but the geochemistry with respect to the solubility of Fe and Mn in anoxic waters is the dominant factor accounting for the Ra and U occurrence.

Table 8. The three principal components that explain about 80 percent of the variability of the water-quality data measured in selected municipal supply wells in Houston Texas during 2007–11. *A*, Samples collected from 31 municipal supply wells and analyzed for various water-quality data including arsenic species; and *B*, Samples collected from 41 municipal supply wells and analyzed for various water-quality data including radium.

[^, constituent discussed in text; #, not included in some of the principal components analysis because results were missing from some samples; NA, no result because analysis was not completed for each sample; --, component loading less than plus or minus (\pm) 0.100; hr, hour; proportion of variance explained multiplied by 100 equals percentage of the variability; constituents in **bold** are constituents of concern for study]

Principal components	(A) 31 wells with arsenic species results			(B) 41 wells with radium-226 results		
	Component 1	Component 2	Component 3	Component 1	Component 2	Component 3
Eigenvalue	13.8	10.1	2.01	11.1	7.86	4.92
Proportion of variance explained	0.432	0.317	0.063	0.358	0.254	0.159
Predominant geochemical environment	Reducing (methanogenic with low sulfate), sodium rich (ion exchange), high pH, mineralized, boron	Oxic, mineralized, chloride-rich	Beta activity	Reducing (methanogenic with low sulfate), sodium rich (ion exchange), high pH, mineralized, boron	Oxic, mineralized, chloride-rich	Iron reducing
Most correlated constituents of concern	Arsenite	Arsenate, uranium	Beta activity	Arsenic	Uranium with alpha activity	Radium-226

Constituent	Component loadings			Component loadings		
	Component 1	Component 2	Component 3	Component 1	Component 2	Component 3
Arsenic	0.183 [^]	0.166 [^]	--	0.235 [^]	0.125	--
Arsenite#	0.254 [^]	--	--	NA	NA	NA
Arsenate#	-0.126	0.204 [^]	0.139	NA	NA	NA
Alpha activity (30-day hold time)¹	-0.142	0.175 [^]	0.183	--	0.256 [^]	-0.164
Alpha activity (72-hr hold time)¹	-0.206	0.124	--	-0.150	0.223	-0.171
Uranium	-0.181 [^]	0.215 [^]	--	-0.141	0.285 [^]	--
Beta activity (30-day hold time)¹	-0.152	--	--	-0.150	--	--
Beta activity (72-hr hold time)¹	-0.133	--	0.432 [^]	-0.169	--	--
Radium-226#	NA	NA	NA	--	0.114	-0.358 [^]
Dissolved oxygen	-0.158 [^]	0.196 [^]	--	-0.131 [^]	0.183 [^]	0.292 [^]
Manganese	--	-0.256 [^]	--	--	-0.229 [^]	-0.276 [^]
Iron	0.152 [^]	-0.200 [^]	--	0.113	-0.132	-0.349 [^]
Sulfate	-0.203 [^]	--	--	-0.184	--	-0.272
pH	0.238 [^]	--	0.168	0.215 [^]	-0.146	0.128
Specific conductance	0.111	0.273 [^]	--	0.165 [^]	0.258 [^]	--
Temperature	0.227 [^]	--	0.190	0.259 [^]	--	--
Calcium	-0.256 [^]	--	-0.144	-0.259 [^]	--	-0.127
Magnesium	-0.199 [^]	0.162	--	-0.134	0.266	-0.174
Potassium	--	-0.122	0.575 [^]	-0.102	--	-0.185
Sodium	0.188 [^]	0.215 [^]	--	0.242 [^]	0.193	--
Bicarbonate	0.138	0.241 [^]	-0.130	0.199 [^]	0.219 [^]	--
Bromide	--	0.275 [^]	--	0.174	0.265	--
Chloride	--	0.285 [^]	--	0.136	0.261 [^]	-0.108
Fluoride	0.227 [^]	0.152	--	0.277 [^]	0.100	--
Silica	-0.238	--	-0.134	-0.265	--	--
Chromium	-0.165	0.182	-0.189	-0.143	0.175	0.290 [^]
Barium	-0.167	-0.170	0.255	-0.188	--	-0.157
Boron	0.228 [^]	0.161	--	0.273 [^]	0.113	--
Lithium	--	0.256 [^]	0.142	0.159	0.251	-0.162
Molybdenum	0.217 [^]	--	0.282 [^]	0.221 [^]	--	-0.107
Selenium	-0.167	0.212 [^]	--	-0.132	0.212	0.231 [^]
Strontium	-0.156	0.177	0.206	--	0.252	-0.195 [^]
Vanadium	-0.176	0.209 [^]	--	-0.139	0.207	0.260 [^]

¹Gross measures of radioactivity.

With respect to spatial differences in U, As, and gross measures of radioactivity occurrence, the PCA was used to further examine the data obtained from all of the samples, grouping the analytical results by area (table 9). As in the other PCAs, concentrations of As species or Ra-226 were not analyzed for in all the water samples and therefore were not included in the PCA. For the northeast and northwest areas, three components that correspond to the same redox categories and geochemical environments to which As and U corresponded for the entire 91-sample set (table 7) explained about 75 percent of the variability of the individual areal datasets (table 9). The most important set of associated constituents represented by component 1, which included the constituent of concern, As, and temperature, pH, and Na, is most prominent in the northeast area and to a nearly similar extent in the northwest area (table 9). For the southwest area, the results of the PCA were somewhat different from those of the northeast and northwest areas. In the southwest Houston area, samples were primarily oxic, even at considerable depth, except for samples from wells completed only in the Evangeline aquifer, which were Fe-reducing, anoxic or suboxic. The transition to relatively more oxygenated samples in the southwest area compared to the northeast and northwest areas is evident in the PCA, as indicated by the substantial loading of DO onto component 1 in the southwest compared to the weak to no association in the northwest and northeast areas, respectively. The same was true for U and the associated oxyanions (Cr, Se, and V) soluble in oxic water (table 9). Another difference between the areas was the strong association of As in the groundwater with strongly anoxic geochemical conditions in the northeast and northwest areas—an association not present in the southwest area. The association of As with anoxic geochemical conditions and cation-exchange reactions was predominant in principal component 1 of the PCA for the northeast and northwest areas with substantial loadings of As, Na, and HCO_3^- . The As was associated with and related to the occurrence of U and V only as component 3 in the southwest area (presumably with oxic water, indicating that associations with As were not nearly as important in describing variation in the water quality in the southwest area as in the northeast and northwest areas). In this southwest area, the loading of As onto components 2 and 3 was not associated with jointly elevated loadings of Na and HCO_3^- or with any of the reduced species that were associated with the methanogenic-anoxic redox category. Many of the

Na- and Cl-rich samples in the southwest area are Fe-reducing anoxic (Fe and Mn rich), with similarly high loadings among these constituents for components 1 and 2, but these samples are not methanogenic anoxic as those in the northeast and northwest areas (methanogenic-anoxic conditions were not evident in any of the samples collected in the southwest area). The high concentrations of Na in the southwest area mostly are indicative of saltwater sources, possibly from seawater from the Gulf of Mexico that was trapped in clay layers over geologic time as a result of sea-level transgressions and regressions (Sellards and others, 1932), with minor contributions to the Na concentration possible from cation-exchange reactions. The Na- HCO_3^- dominated samples with high pH also were not collected in the southwest area because cation-exchange reactions likely have not progressed as nearly to completion (completion is indicated by the replacement of Ca by Na) compared to cation-exchange reactions in the samples collected in the northeast and northwest areas.

Relations of Arsenic and Redox Categories

Arsenic was detected at about the same frequency as U, but unlike U, detection of total As was equally frequent in oxic and anoxic redox conditions, although the concentrations for total As were higher in the anoxic waters where DO was absent compared to waters with oxic redox conditions. The concentrations of total As correlated about equally with the concentrations of the more reduced, inorganic As(III) species and the more oxic, inorganic As(V) species, with Spearman rank correlation coefficients (r) of 0.370 and 0.418, respectively (table 6). The concentrations of As(III) correlated negatively with DO ($r = -0.703$) (table 6), indicating higher solubility and concentrations in the more anoxic (reducing) waters than in the oxic waters (fig. 13D). The concentrations of As(V) correlated positively with DO ($r = 0.770$), indicating that oxic conditions were necessary for As(V) to increase to the point of becoming the predominant form of As in groundwater (fig. 13E; table 6). The correlation between concentrations of As(V) and oxic conditions indicates that the As concentration is strongly affected by the solubility of As in waters with different chemistry. Unlike many other trace elements, As can be highly mobile in both oxic (As[V]) and reduced (As[III]) waters, depending on the As species (Dixit and Hering, 2003; Thomas, 2007).

Table 9. The three principal components that explain about 75 percent of the variability of the water-quality data correlated to arsenic, uranium, and gross measures of radioactivity in the 91 samples of water from Gulf Coast aquifer system in Houston, Texas, 2007–11, grouped by geographic area.

[NA, not applicable; ^, constituent discussed in text; --, component loading less than plus or minus (\pm) 0.100; hr, hour; proportion of variance explained multiplied by 100 equals percentage of the variability; constituents in **bold** are constituents of concern for study]

Principal components	20 wells in northeast Houston			29 wells in northwest Houston			42 wells in southwest Houston		
	Component 1	Component 2	Component 3	Component 1	Component 2	Component 3	Component 1	Component 2	Component 3
Eigenvalue	13.2	8.25	3.77	16.4	5.63	2.74	12.9	6.27	3.16
Proportion of variance explained	0.427	0.266	0.122	0.528	0.182	0.089	0.416	0.202	0.102
Predominant geochemical environment	Reducing, sodium rich (ion exchange), boron, mineralized, screen proximal to Burkeville	Oxic, soluble oxyanions	Oxic, potassium rich	Reducing, sodium rich (ion exchange), high pH, boron, mineralized, screen proximal to Burkeville	Oxic, soluble oxyanions, mineralized	Oxic, potassium rich	Oxic, soluble oxyanions	Mineralized (calcium, chloride rich) iron reducing, potassium rich, aquifer thickness	Soluble oxyanions, aquifer thickness
Most correlated constituents of concern	Arsenic	Uranium	Beta activity	Arsenic	NA	Uranium with alpha and beta activity	Uranium	Beta activity	Uranium, with alpha and beta activities, arsenic
Constituent	Component loadings			Component loadings			Component loadings		
Arsenic	0.231 [^]	--	--	0.183 [^]	--	-0.213	--	-0.136 [^]	-0.233 [^]
Alpha activity (30-day hold time)¹	--	0.161	--	-0.168	--	-0.234 [^]	--	0.108	-0.441 [^]
Alpha activity (72-hr hold time)¹	-0.216	0.120	--	-0.197	--	-0.147	-0.159	0.130	-0.326
Uranium	--	0.297 [^]	--	-0.183	--	-0.206 [^]	-0.234 [^]	--	-0.258 [^]
Beta activity (30-day hold time)¹	-0.235	--	--	-0.135	--	-0.215 [^]	--	--	-0.276 [^]
Beta activity (72-hr hold time)¹	-0.111	--	0.283 [^]	-0.134	--	-0.306 [^]	--	0.230 [^]	-0.128
Distance from top of open interval to top of Burkeville confining unit	-0.217 [^]	0.116	--	-0.199 [^]	--	0.268 [^]	--	0.190 [^]	-0.324 [^]
Dissolved oxygen	--	0.268 [^]	0.266 [^]	-0.157	-0.279 [^]	-0.107	-0.241 [^]	--	--
Manganese	--	-0.280 [^]	-0.192 [^]	0.102	0.312 [^]	0.132	0.200 [^]	0.179 [^]	--
Iron	--	-0.246 [^]	-0.310 [^]	0.117	0.314 [^]	--	0.172 [^]	0.227 [^]	0.103
Sulfate	-0.238 [^]	--	-0.202	-0.166 [^]	0.279 [^]	--	0.209 [^]	--	-0.166
pH	0.178 [^]	-0.110	0.278	0.233 [^]	--	--	0.204 [^]	-0.203	--

Table 9. The three principal components that explain about 75 percent of the variability of the water-quality data correlated to arsenic, uranium, and gross measures of radioactivity in the 91 samples of water from Gulf Coast aquifer system in Houston, Texas, 2007–11, grouped by geographic area.—Continued

[NA, not applicable; ^, constituent discussed in text; --, component loading less than plus or minus (\pm) 0.100; hr, hour; proportion of variance explained multiplied by 100 equals percentage of the variability; constituents in **bold** are constituents of concern for study]

Principal components	20 wells in northeast Houston			29 wells in northwest Houston			42 wells in southwest Houston		
	Component 1	Component 2	Component 3	Component 1	Component 2	Component 3	Component 1	Component 2	Component 3
Specific conductance	0.218 [^]	0.165 [^]	-0.174 [^]	0.207 [^]	-0.213 [^]	--	--	0.348 [^]	--
Temperature	0.205 [^]	-0.127	--	0.197 [^]	--	--	0.217 [^]	--	--
Calcium	-0.261 [^]	--	-0.113	-0.242 [^]	--	--	-0.208 [^]	0.238 [^]	--
Magnesium	--	0.173	-0.389	-0.204	0.143	--	-0.194	0.255	--
Potassium	-0.158	--	0.334 [^]	--	0.237	-0.434 [^]	--	0.274 [^]	--
Sodium	0.233 [^]	0.168	--	0.239 [^]	--	--	0.246 [^]	--	-0.137
Bicarbonate	0.151 [^]	0.231 [^]	-0.168	0.199 [^]	-0.158 [^]	--	--	--	-0.154
Bromide	0.240 [^]	0.144	--	0.172 [^]	-0.166	-0.259	--	0.269	0.173
Chloride	0.226 [^]	0.179 [^]	--	0.147 [^]	-0.281 [^]	-0.142	--	0.366 [^]	--
Fluoride	0.265 [^]	--	--	0.235 [^]	--	-0.113	0.242 [^]	--	-0.197
Silica	-0.212 [^]	0.110	--	-0.224 [^]	--	--	-0.250 [^]	--	--
Chromium	--	0.267 [^]	0.248	-0.156	-0.300	--	-0.255 [^]	--	--
Barium	-0.189	0.106	--	-0.141	--	-0.231	--	0.303	0.104
Boron	0.259 [^]	0.105	--	0.234 [^]	-0.111	--	0.237 [^]	--	-0.156
Lithium	0.108	0.279 [^]	-0.185	0.163	0.175	-0.211	0.213 [^]	--	--
Molybdenum	0.238 [^]	--	--	0.196 [^]	--	-0.229	0.243 [^]	--	-0.167
Selenium	--	0.287 [^]	--	-0.144	-0.209 [^]	-0.255 [^]	-0.229 [^]	-0.118	-0.132
Strontium	--	0.199	-0.341	-0.125	0.285	-0.212	-0.107	0.206	0.257
Vanadium	--	0.324 [^]	--	-0.151	-0.292	-0.127	-0.212 [^]	-0.133	-0.216 [^]

¹Gross measures of radioactivity.

The refinement of the redox classification (Chapelle and others, 2009) clarified the distribution of the As(III) with respect to the redox conditions in the Gulf Coast aquifer system, including those among the various presumed predominant reduction processes of anoxic conditions encountered. The difference in distribution for the As species by redox category was significant (95 percent confidence level among Tukey classes; table 4B). The refined redox classification showed that As(III) was present in moderate concentrations in Fe-reducing, anoxic water samples and, at the highest concentrations, occurred in SO₄-reducing, anoxic; methanogenic-anoxic; or both water samples (table 3). The As(III) species was predominant where water was sufficiently reducing such that DO was not detected or was detected in concentrations less than 0.5 mg/L (fig. 13D), Fe was in solution, and pH was relatively high as indicated by strong correlation with As(III) ($r=0.706$) (table 6). Arsenite was predominant throughout all the deepest groundwater collected from near the base of the Evangeline aquifer to the northeast and northwest areas. Sorbed As(III) may be released by multiple mechanisms: (1) by reductive dissolution of Fe hydroxides removing preferential sorption sites for the As(III) (Dixit and Hering, 2003; Stollenwerk, 2003); (2) by the preferential uptake of Fe(II) on any available sorption surface (Silvester and others, 2005); (3) by competitive sorption with hydroxides or other multivalence anions (Appelo and others, 2002; Dixit and Hering, 2003); or (4) by dissimilatory reduction of As sorbed to the Fe hydroxides (Zobrist and others, 2000; Kocar and others, 2006). The highest concentrations of As (as As[III]), however, did not correspond to the highest concentrations of Fe as might be expected on the basis of many studies that have shown reduction and dissolution of Fe and As in similar redox conditions (Cherry and others, 1979; Bose and Sharma, 2002; O'Day and others, 2004), and many factors can affect the respective concentrations of these elements (Kocar and others, 2006). Instead, the highest concentrations of As (as As[III]) corresponded to the methanogenic-anoxic waters (fig. 12A) with moderately low Fe(II) concentrations (typically about 100 µg/L) (fig. 9A), the lowest concentrations of SO₄ (less than 4 mg/L), the highest concentrations of Na (greater than 120 mg/L) (fig. 9B), and the highest values of pH, as indicated by the oval area on figure 18.

Another factor allowing for the high concentrations of As(III) in the methanogenic-anoxic, Na-rich waters might have been the low concentration of SO₄ available for reduction to sulfide, thereby limiting the amount of sulfide formed by SO₄ reduction. The SO₄ concentrations in these Na-rich water samples were substantially less than the 4-mg/L threshold and below which Chapelle and others (2009) described SO₄ reduction (or methanogenesis) to be the presumed predominant reduction process (fig. 9B). Even the most mineralized samples, however, contained only relatively moderate amounts of SO₄ (about 20 mg/L), and SO₄ was not dominant in any sample (fig. 8). It is important to note that the samples with the highest concentrations of Fe,

however, were not the most reducing; the samples with the lowest concentrations of SO₄ were presumed SO₄ reducing, methanogenic anoxic, or both (Holmer and Kristensen, 1994), and thus were the most reducing when considering the succession of terminal electron-accepting processes described by Lovley and Chapelle (1995). In the samples with the lowest concentrations of SO₄ and the highest concentrations of As(III), Fe might have been sequestered from solution by the sulfide formed from the reduction of SO₄ (O'Day and others, 2004), and this reaction might have sequestered some As (Moore and others, 1988; Kirk and others, 2004). The minimal concentrations of sulfide indicated the formation of Fe-sulfide minerals might have been sulfur limited (less sulfur than Fe available for reaction, thereby ending Fe-sulfide formation when the available sulfide in solution was consumed). It was presumed on the basis of the low concentrations of Fe and sulfide in these waters that both the Fe and the sulfide had been removed by sulfide precipitation with Fe (Slowey and Brown, 2007). Because the Gulf Coast aquifer system was low in sulfur, and the sulfide was readily depleted from the aqueous phase by the presumably more abundant Fe, the As(III) that might have otherwise coprecipitated with Fe sulfide was not limited in concentration in solution by this reaction once the sulfide was exhausted. In sulfur-poor systems, binding of As by amorphous Fe sulfide to the sediment is less likely (Burton and others, 2011) than in sulfur-rich conditions where sedimentary pyrite is formed and binds As more strongly than does amorphous Fe sulfide (Kocar and others, 2010). The As and the Fe might have had a considerable source in solid phases in the clay layers; there might not have been a comparable source for sulfur once the sulfur species in the water were converted mostly to sulfide, and the sulfide in the water was consumed by the more abundant Fe. Any As in the sediment was reduced to As(III), was not sorbed readily at the mildly alkaline pH, and was released to solution along with any additional Fe available for reduction in the sediment (Kirk and others, 2004).

A further reason the As(III) might not have sorbed or coprecipitated readily from moderately sulfidic alkaline waters was the formation of strongly soluble aqueous As(III)-thiol species (Burton and others, 2011). Aqueous geochemical and isotopic evidence of SO₄ and sediment solid-phase materials (Goldhaber and others, 1978) needs to be examined to determine the role of sulfide as the cause of relatively low Fe concentrations (30–50 µg/L) in solution in some of the anoxic samples. Another possibility is that some As in the Fe-rich, anoxic waters might be sequestered by reduced-Fe-species- or mixed-Fe-species-bearing minerals, such as green rust and magnetite (Jönsson and Sherman, 2008); formation of these minerals and amorphous solids is possible in anoxic waters dominated by Fe species without abundant sulfide (Burton and others, 2011). The As also can be more readily released, however, with slight changes in the water chemistry more attributable to amorphous solids, such as green rust (Jönsson and Sherman, 2008), than to the presence of Fe-sulfide minerals, such as pyrite.

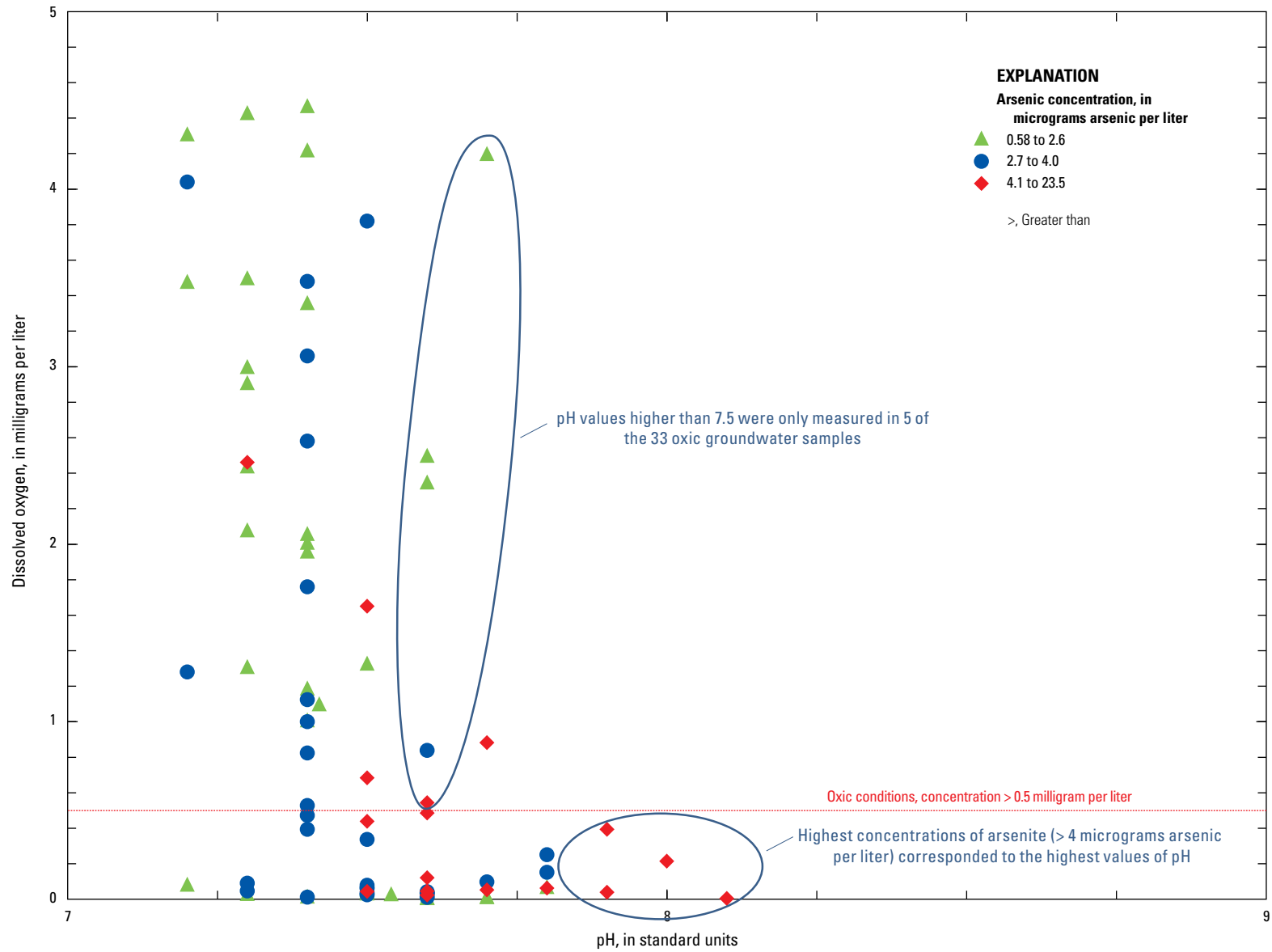


Figure 18. Dissolved oxygen indicating reducing or oxidizing conditions and pH with arsenic concentration indicated for the water samples from 91 municipal supply wells in Houston, Texas, 2007–11.

The hypothesis that the mixing of different water types accounts for the presence of both species of inorganic As in water from a few of the wells is supported by the composition of water chemistry of the sample obtained from well LJ-65-05-814. The dominant As species in this sample was As(V) at a concentration of 2.3 $\mu\text{g-As/L}$, but a small amount of As(III) also was detected at an estimated concentration of 0.3 $\mu\text{g-As/L}$. Water from this well was classified as being in the mixed redox category, sharing oxic and anoxic characteristics (namely concentrations of DO greater than 0.5 mg/L and concentrations of Fe greater than 29 $\mu\text{g/L}$). Samples characteristic of anoxic waters were obtained from three additional wells (TS-60-62-604, LJ-65-13-222, and LJ-65-13-224); moderate to high concentrations of As(III), along with detectable concentrations of As(V), were measured in the samples from these three additional wells, although the As(V) concentration was low in water from two of these wells (estimated at 0.4 and 0.5 $\mu\text{g-As/L}$ in the samples from wells LJ-65-13-222 and LJ-65-13-224, respectively). The As(V) accounted for 10 percent or less of the inorganic As in each of those two samples, with As(III) accounting for the remaining 90 percent or more (table 3). The simultaneous presence of both As species appears to be an indicator of the existence of mixed redox waters being withdrawn at some of the wells in Houston, generally consistent with other indicators. For purposes of defining mixed redox chemistry, measurement of the concentrations of Fe, Mn, and DO is more readily done than analyzing As species. Most samples from wells that contained As(III) concentrations greater than 1 $\mu\text{g-As/L}$ were classified geochemically as anoxic (Fe-reducing, SO_4 -reducing, methanogenic) groundwater. One well for which As(V) was present in a notable amount (21 percent of total As) when As(III) was dominant was well LJ-60-63-504, but even water from this well was classified as anoxic (Fe(III)/ SO_4 reducing; table 3). A few wells with detectable As(III) concentrations produced waters classified as mixed redox. Samples from many or most of the municipal supply wells represented waters entering the well at different depths and were mixed by the pumping, resulting in the mixed redox conditions.

Of the 18 samples with total As concentrations equal to or greater than 4 $\mu\text{g/L}$, As speciation was determined in only 5; for the remaining 13 samples, 4 were oxic, 4 were suboxic, 1 was mixed redox, and 4 were anoxic. The distribution of different water types among the 13 samples implied that concentrations of As(III) greater than 4 $\mu\text{g/L}$ were possible, most likely among the anoxic samples. Concentrations of As(V) exceeded 4 $\mu\text{g/L}$ in oxic (or mixed redox) samples throughout many parts of the western United States (Robertson, 1989; Welch and others, 2000) and in parts of western Texas (Reedy and others, 2007), although similar results have not been obtained among the oxic samples analyzed to date (2011) in the Texas Gulf Coast aquifer system.

Relations of Arsenic, pH, and Predominant Cation Water Types

In addition to the redox condition of the groundwater, pH plays a critical role in controlling As concentrations (Stollenwerk, 2003). The concentrations of As exceeded 4 $\mu\text{g/L}$ primarily in anoxic samples as determined from As concentrations relative to DO (less than or greater than 0.5 mg/L approximately indicating reducing or oxidizing conditions, respectively) and pH for the 91 sampled municipal supply wells in Houston (fig. 18). Some of the highest pH values were measured in the anoxic samples with total As concentrations greater than 4 $\mu\text{g/L}$; a majority of the pH values were greater than 7.5 (fig. 18). The total As concentrations were positively correlated with an increase in pH ($r=0.323$) and were strongly correlated ($r=0.672$) with Na concentrations (fig. 18; table 6). The effect of pH on total As concentration was related directly to the solubility of the inorganic As species with respect to pH, consistent with the results detailing the adsorption properties of As species presented by Stollenwerk (2003).

The pH and redox conditions of groundwater are key factors affecting the solubility and mobility of As(III) and As(V) species (Smedley and Kinniburgh, 2002; Dixit and Hering, 2003; Stollenwerk, 2003). The pH measured in groundwater samples collected from the 91 municipal supply wells in Houston was indicative of slightly alkaline (pH ranging from 7.2 to 8.1) water (table 2). When the pH is near neutral (about 7.0 to 7.5), As(III) is not sorbed readily, and its solubility increases as pH rises above 7.5 (Dixit and Hering, 2003). The concentrations of As(III) correlated positively and strongly with pH ($r=0.706$) (table 6), indicating higher solubility when the pH is greater than 7.5 compared to when the pH is less than 7.5. The pH for the anoxic (Fe reducing, SO_4 reducing, and methanogenic) waters measured in a range from 7.5 to 8.1, except for six samples. The As concentrations were greater than 4 $\mu\text{g/L}$ in all samples with pH values greater than or equal to 7.9 (fig. 18). Only the As(III) species was detected at a concentration greater than 4 $\mu\text{g/L}$ (fig. 14). The results of this water-quality assessment indicate that in the Texas Gulf Coast aquifer system, anoxic redox conditions with a pH greater than about 7.5 are most likely when the groundwater samples contain total As concentrations greater than 4 $\mu\text{g/L}$ (fig. 18), and As(III) species is predominant among these high-As samples (fig. 14).

In addition to representing oxic conditions, the groundwater samples with higher As(V) concentrations were near neutral to slightly alkaline (pH ranging from 7.2 to 7.7) (fig. 18). The desorption of As(V) from aquifer materials tends to peak when pH exceeds 7.5 (Welch and others, 2000), and pH values higher than 7.5 were only measured in 5 of 33 oxic groundwater samples collected from the Gulf Coast aquifer system in Houston, as indicated by the oval area on figure 18. Only one sample was collected in which the total As

concentration was greater than 4 µg/L with a pH less than 7.5, and the DO concentration was greater than 1.0 mg/L—well above the 0.5 mg/L DO concentration defining the oxic redox category.

Many regions throughout the Western United States contain groundwater with high total As concentrations in oxic and alkaline conditions (Robertson, 1989; Welch and others, 2000), where As(V) is determined to be, or presumed to be, the predominant As species. With respect to As concentrations and speciation, DO, and pH, the Texas Gulf Coast aquifer system seems somewhat comparable to glacial aquifers in the upper Midwestern United States, where total As concentrations are highest in anoxic geochemical conditions and the As(III) species is predominant; this combination is typically found when pH is equal to or greater than about 7.3 or 7.4 (Stollenwerk, 2003; Thomas, 2007). The residence times of the groundwater are sufficient, even in the relatively thin glacial aquifers found in the upper Midwestern United States, to allow for enough DO and redox species consumption and water-sediment interaction to make such anoxic conditions possible, likely because the organic carbon content of some of the clayey sediments is relatively high, allowing for rapid consumption of the DO within about 50 to 100 years (Thomas, 2007). Oxic and alkaline conditions were predominant near the water table in the Texas Gulf Coast aquifer system, and the oxic conditions persisted in much of the Chicot aquifer, especially in the southwest Houston area. The As(V) species was predominant when measured and likely predominant when it was not measured in the oxic waters. The As distribution in the unsaturated zone near the water table in many surficial sediments in Texas, as in the Central and Western United States, is controlled by the oxidized As(V) species (Robertson, 1989; Welch and others, 2000). The As(V) species present in oxic groundwater conditions cannot be reduced until after all the DO is consumed (Zobrist and others, 2000; Kirk and others, 2004). The consumption of DO is slow and variable in near-surface aquifers in Texas (McMahon and others, 2004), with the rates likely varying on the basis of the sediment composition. The variable rates of DO degradation along individual flow paths affect the depths at which anoxic conditions develop and vary across Houston, as evident from the data collected during this study.

The occurrence of detectable total As and the dominant As species in the Texas Gulf Coast aquifer system also was related to water type and depth. Because the presumed methanogenic-anoxic conditions and moderately alkaline pH conditions present at the greatest sampling depths near the base of the Evangeline aquifer were favorable for As(III) mobility, the highest concentrations of As were measured in the Evangeline aquifer where the As(III) was predominant. Because the reducing waters near the base of the Evangeline aquifer appear to have long residence times, there is more contact time for release of As to occur in those reducing conditions than in the shallower oxic conditions. Furthermore, As sorption to aquifer material was minimized by the elevated pH conditions, which likely helps the As remain in solution

after it is released from a sediment source. For the wells from which waters were methanogenic anoxic, concentrations of As, Na, and B were among the highest of all the samples (“A” Tukey class, table 4B), even if the samples were from the northeast area (where concentrations of As, Na, B, U, and gross alpha-particle activity were all significantly lower [“B” Tukey class, table 4A] than in the water from the wells in the other two areas).

Some examples of methanogenic-anoxic water samples with high concentrations of As follow. The highest As(III) concentration was measured in the water sample collected from well TS-60-62-604 (14.9 µg/L) where the water type was Na-HCO₃ and the Na-to-Cl ratio was among the highest measured. Well LJ-65-13-222 also produced water with a high As concentration (10.1 µg/L), the highest pH of 8.1 (fig. 18), and a high Na concentration of 178 mg/L (fig. 9B). The As(III) was predominant in reducing and alkaline conditions where Na concentration was high (Na was either one of the highest concentration cations or was the predominant cation), and the Na-to-Cl ratio was much higher than 1.0, typical of the alkaline Na-HCO₃-type water. The loading of As(III) on component 1 and the associated constituents from the PCA (table 8A) coincided with these examples of methanogenic-anoxic water samples; thus, among the major constituents, Na concentrations were correlated with total As concentrations ($r=0.672$), and total As inversely correlated with Ca concentrations ($r=-0.455$) (table 6). This correlation of total As with Na concentration is consistent with the presence of cation exchange and methanogenic-anoxic redox conditions in which As(III) solubility was optimal. This correlation is not readily explained without knowledge of the conditions that are optimal for the solubility of As(III).

For groundwater with relatively high As(V) concentrations (3 to 4 µg/L) (fig. 13E), Ca generally was the predominant cation, with Na concentrations not exceeding about 50 mg/L (fig. 10). The correlation of As(V) concentrations with concentrations of the divalent cations Ca ($r=0.493$) and Mg ($r=0.548$) was substantially stronger than correlation among the concentrations of As(V) and concentrations of Na ($r=0.359$) (table 6), indicating a general increase in total As concentration (as As[V]) and the dissolution of Ca, Mg, and to a lesser extent Na in oxic conditions with increased water-rock interactions. The inverse correlation of As(III) concentrations with concentrations of Ca ($r=-0.720$) was substantially stronger than the correlation between the concentrations of total As and Ca (table 6) because it was the concentration of As(III) that was the highest when the cation-exchange reaction process had progressed the most, culminating in Ca-poor, Na-rich water. The difference in redox conditions of the Ca-dominated and Na-dominated waters and the presence of oxic compared to anoxic conditions were critical in determining As occurrence in the groundwater in the area (figs. 9B, 10, 12A). The highest concentration of As(III) and the highest concentrations of Na coincided, although the correlation in concentrations was not significant, likely because of slight differences in reaction progress where

each well was located and perhaps the amounts of mixing during the well pumping.

Relations Between Selected Trace Elements and Arsenic

Statistically significant correlations were found between the concentrations of selected trace elements and As, but the correlations were different for each As species (table 6). The groups of correlated trace elements and the respective As species were generally characteristic of oxic and anoxic water chemistry, respectively (table 4). Oxic and anoxic alkaline water chemical types are the optimal conditions for the mobility of the As(V) and As(III) species, respectively, and for the trace elements with which they are associated (table 8A).

The highest concentrations of the trace elements B and Mo corresponded with the highest concentrations of As (mostly as As(III) for the samples it was analyzed) (fig. 19; table 8A) and also with the highest concentrations of Na, indicated by the common positive loading on component 1 of the PCA (table 8A). Some of the highest concentrations of B and Mo (about the 90th percentile of their respective concentration ranges; table 2) were associated with the high Na and high As(III) concentrations that occurred preferentially in methanogenic-anoxic waters (grouped as the "A" Tukey class with respect to each of these constituents, table 4B). The concentrations of Mo were positively correlated with concentrations of As(III) (fig. 19; $r = 0.637$, table 6); concentrations of B and Mo were positively correlated with concentrations of total As ($r = 0.649$ and $r = 0.310$, respectively; table 6). The trace elements B and Mo were measured in detectable concentrations in nearly all of the filtered groundwater samples. The corresponding occurrence of elevated concentrations of As(III), B, and Mo likely arises from the fact that these trace elements are generally not readily removed from solution from many similar water types. These water types especially included alkaline waters from which adsorption of these constituents is limited (Goldberg and others, 1996) and strongly reducing waters associated with sediments from which sorptive Mn hydroxides have dissolved (Berrang and Grill, 1974). Concentrations of As(III) and Mo were both positively correlated with concentrations of Mn ($r = 0.596$ and $r = 0.495$, respectively; table 6). The grouping of the trace elements As, B, and Mo have been documented to be associated with elevated levels in Na- and Cl-rich pore waters extracted from deep organic-carbon-rich clay beds (Szabo and others, 2006) and in zones with clayey sediments where ion exchange occurs under reducing conditions or where water-rock interaction has been ongoing over a long period of time (Millot and others, 2010). High concentrations of B, Mo, and As(III) may diffuse from clayey sediments into the already suboxic or anoxic waters in the aquifer (Francois, 1988), may be advected into the aquifer as leakage, or may be extracted with the dewatering of the clayey sediments in response to large amounts of groundwater withdrawal.

The Spearman rank correlation coefficient for the relation between concentrations of the As(V) species and the concentrations of trace elements Se ($r = 0.815$), U ($r = 0.759$), Cr ($r = 0.794$) (not shown in figure), and V ($r = 0.742$) were significant, with p -values less than 0.05 (fig. 20; table 6). Among the oxic water samples for which concentrations of As species were determined, 3 of the highest 4 concentrations of V corresponded directly with 3 of the highest 4 concentrations of As(V) (fig. 20). Among all the oxic water samples, the samples with high concentrations of V generally corresponded with high concentrations of As (fig. 20); V and As concentrations were from the respective upper quartiles of the concentration values for these trace elements. These trace elements were measured in detectable concentrations in nearly all of the filtered groundwater samples and were presumably present in the oxidized oxyanion form (as As[V], selenate, uranate, chromate, and vanadate) (Hodge and others, 1998) in the oxic waters. These trace elements had higher mean rank concentrations in oxic waters as opposed to anoxic waters as determined by the Tukey test (table 4B). The chemical properties and solubility of these oxyanions are similar to those of the As(V) oxyanion, namely increasing solubility in oxic waters that are in the slightly alkaline pH range (Hodge and others, 1998); hence, the oxyanions loaded (grouped) in association with As(V) with principal component 2 (table 8A).

Relations of Uranium, Radium, Iron, and Redox Categories

The occurrence of the highest concentrations of U was most frequent in oxic waters with DO concentrations greater than 0.5 mg/L (figs. 12B and 15A) and low concentrations of Fe; in these waters, concentrations of U correlated positively with DO ($r = 0.665$) and negatively with Fe ($r = -0.634$) (table 6). In some cases, concentrations of U were substantial in mixed (redox) water, which, by definition, contains concentrations of DO greater than 0.5 mg/L. The concentration of U was positively correlated with the concentrations of the oxidized species of As (measured as As[V]) and other trace elements that also readily form soluble oxyanions (Hodge and others, 1998), specifically of As (measured as As[V]), Cr (not shown), Se, and V (likely present as chromate, selenate, and vanadate) (fig. 20). The concentration of U correlated positively with the As(V) species ($r = 0.759$) (fig. 20; table 6), as would be expected on the basis of the solubility of both U and As(V) in oxic, slightly alkaline, HCO_3^- -rich waters (Dixit and Hering, 2003; Jurgens, Fram, and others, 2009). The correlation coefficient between concentrations of U with concentrations of Se ($r = 0.866$) (fig. 21A), V ($r = 0.787$), Cr ($r = 0.741$), and Sr ($r = 0.363$) were significant (table 6). Concentrations of U and several other trace elements, such as Se and V, generally cluster together in low concentrations (mostly less than 1 $\mu\text{g/L}$) in anoxic conditions, then gradually increase from about 1.5 to more than 10 $\mu\text{g/L}$ in suboxic, mixed, and oxic conditions (fig. 21A).

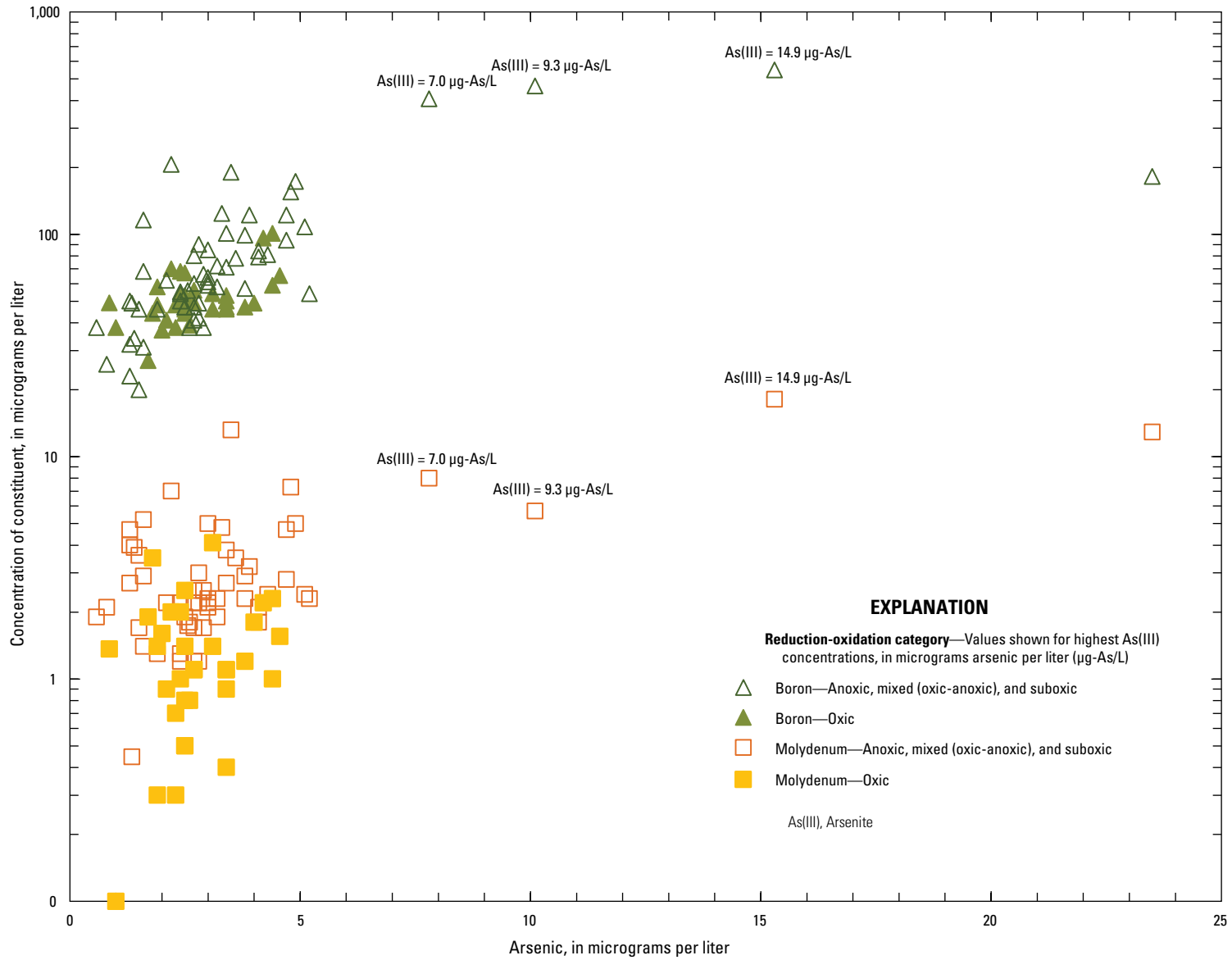


Figure 19. Selected trace elements boron and molybdenum as a function of arsenic concentration, with reduction-oxidation category indicated for the water samples from 91 municipal supply wells in Houston, Texas, 2007–11.

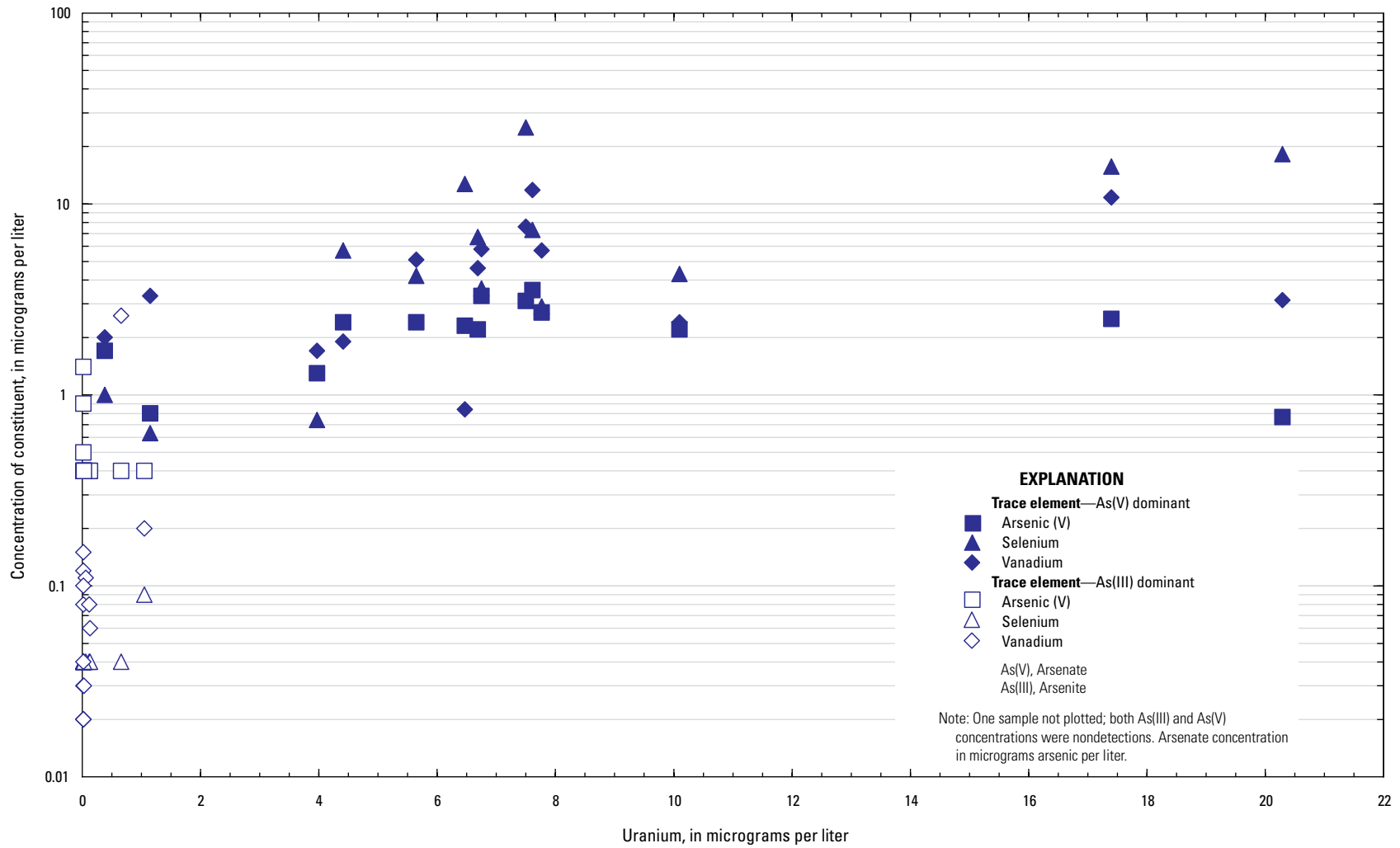


Figure 20. Concentrations of selected trace elements selenium, vanadium, and arsenic (as arsenate) as a function of uranium concentration for the water samples from 31 municipal supply wells in Houston, Texas, 2007–11, grouped by arsenic species dominance.

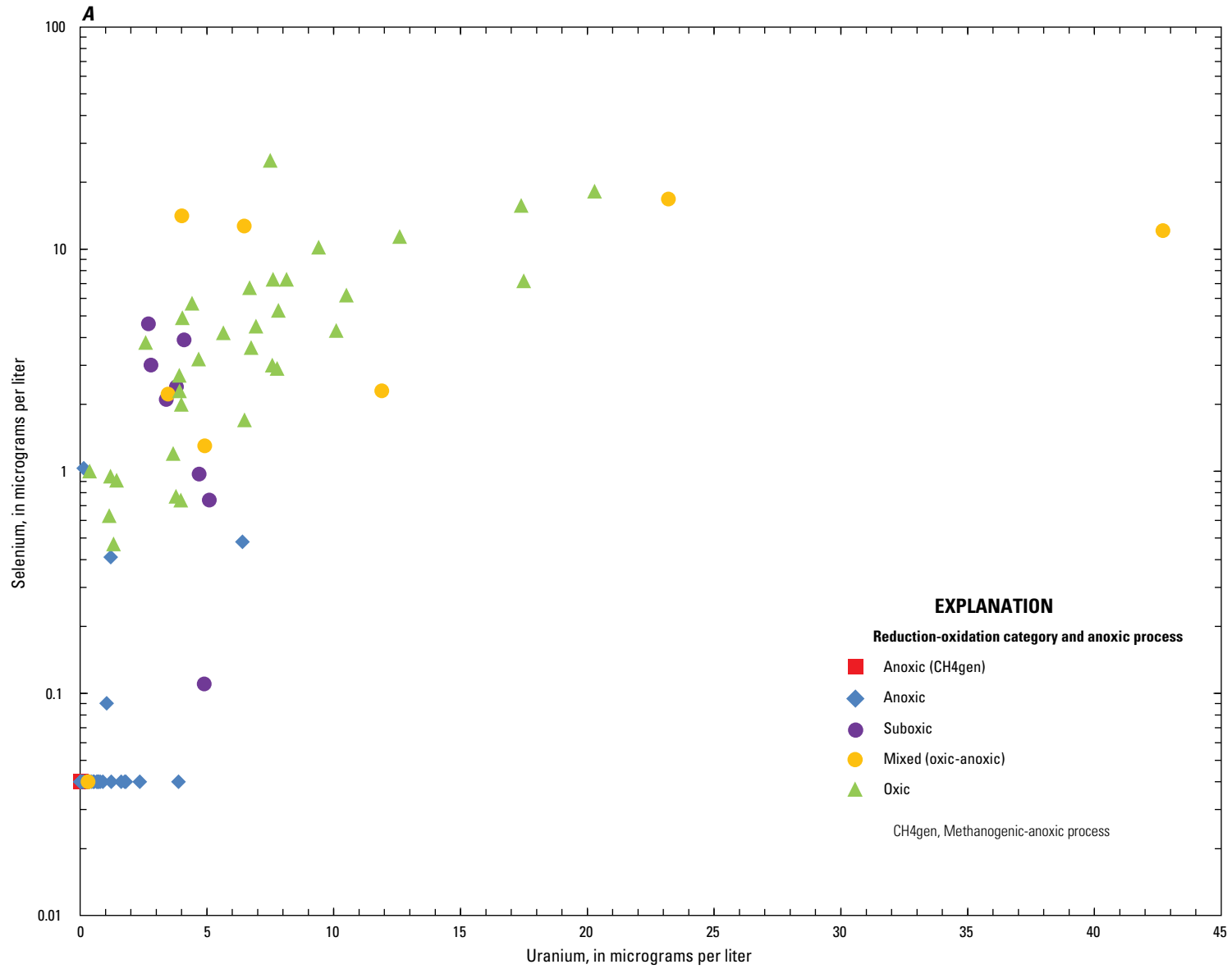


Figure 21. Concentrations of *A*, trace element selenium as a function of uranium concentration, with reduction-oxidation category and anoxic process indicated for the water samples from 91 municipal supply wells in Houston, Texas, 2007–11; and *B*, arsenic as a function of uranium concentration, with reduction-oxidation category and anoxic process indicated for the water samples from 91 municipal supply wells in Houston, Texas, 2007–11.

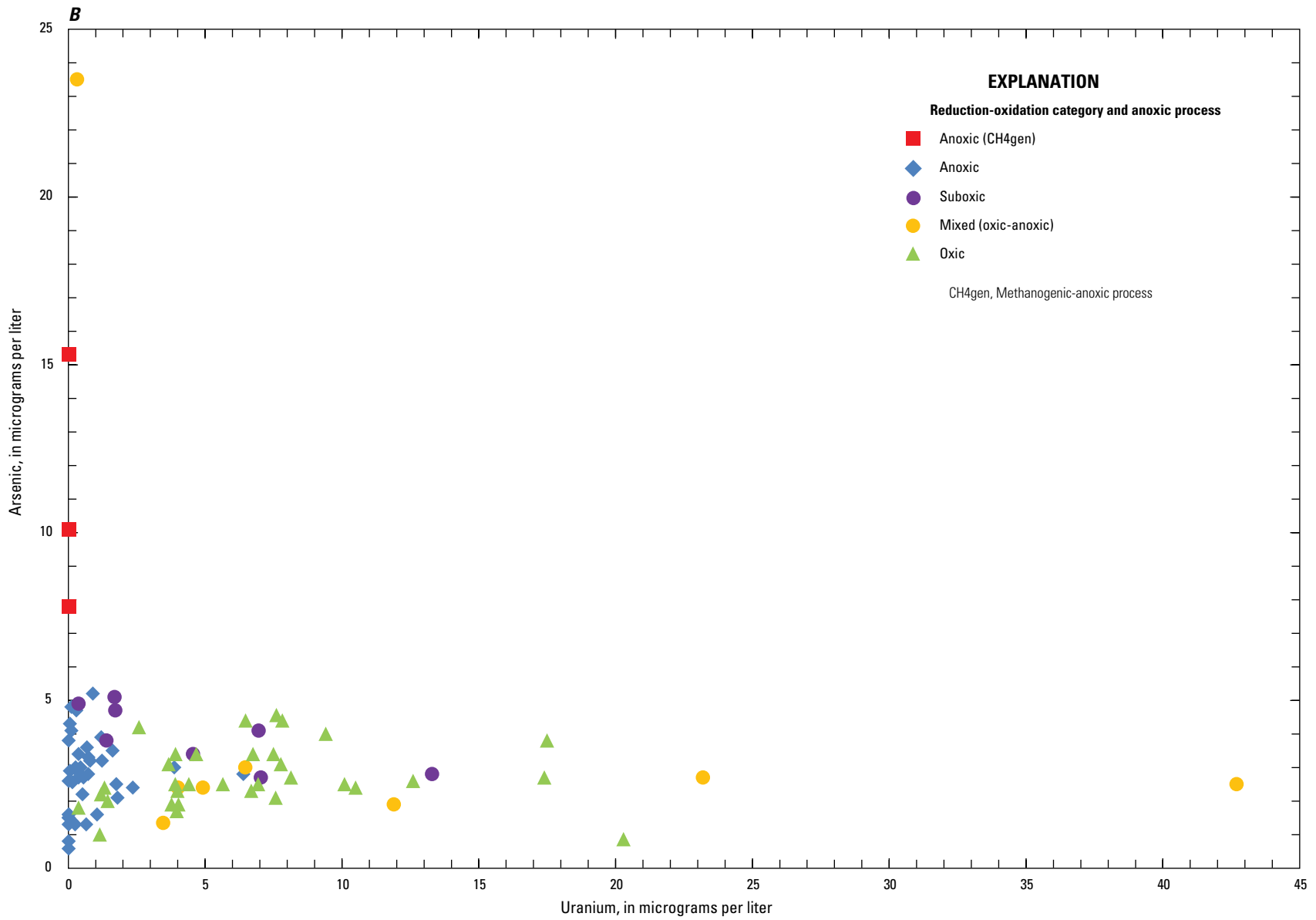


Figure 21. Concentrations of *A*, trace element selenium as a function of uranium concentration, with reduction-oxidation category and anoxic process indicated for the water samples from 91 municipal supply wells in Houston, Texas, 2007–11; and *B*, arsenic as a function of uranium concentration, with reduction-oxidation category and anoxic process indicated for the water samples from 91 municipal supply wells in Houston, Texas, 2007–11.—Continued

In contrast to the other oxyanions, the highest concentrations of total As corresponded to the lowest concentrations of U, and concentrations of total As did not cluster with low concentrations of U in the anoxic waters but rather exhibited a range in concentrations to about 5 µg/L in Fe-reducing, anoxic waters and an even greater range in methanogenic-anoxic waters (fig. 21B). The concentration of U did correlate slightly with the concentration of total As in oxic water (fig. 21B; $r=0.350$, not shown in table 6) but at lower strength of correlation than when the concentration of U was compared solely to that of As(V) ($r=0.759$) (fig. 20; table 6). The highest concentrations of U corresponded with concentrations of total As from 1 to 4 µg/L (fig. 21B).

The much higher concentrations of U compared to total As in the oxic (and mixed redox) waters (fig. 21B) indicated that the solubility of the U was somewhat greater than the solubility of As(V) in the oxic, slightly alkaline, HCO_3^- -rich waters in the Texas Gulf Coast aquifer system in Houston. One major reason for this difference in the concentrations of U and total As might be the strong solubility of U in the presence of HCO_3^- , with which it forms highly soluble, poorly sorbed carbonate-anionic complexes (Hsi and Langmuir, 1985; Jurgens, Fram, and others, 2009), even at near neutral to very slightly alkaline pH (about 7.0–7.3) water (Chapman and others, 2013). Unlike U, As(V) does not form highly soluble, poorly sorbed carbonate-anionic complexes in near neutral pH groundwater (Chapman and others, 2013). In addition, Se, V, and U oxyanions desorb slightly more efficiently from Fe hydroxides in the pH range from about 7.0 to 7.5 than does As(V) (Echevarria and others, 2001; Chapman and others, 2013). Finally, local areas of U enrichment in the aquifer matrix are known (Eargle and others, 1975), but little or no information exists concerning high As concentrations in the solid (sediment) matrix; it is conceivable that U concentrations are higher in the sediment matrix, and thus U can increase in concentrations more rapidly in the groundwater compared to As.

The highest amounts of Ra-226 were measured in groundwater samples that exhibited reducing or anoxic geochemical characteristics, with especially high concentrations of Fe that correlated with the concentrations of Ra-226 ($r=0.418$) (fig. 22; table 6). These samples were specifically designated Fe-reducing, anoxic waters (figs. 9A, 12C, and 15B), representing conditions that were the opposite of redox conditions where the concentration of U was greatest (figs. 12B and 15A). In the Fe-reducing, anoxic waters, the ratios of Ra-226 to U-238 radioactivity were much larger

than 1.0 (table 3) because of the preferential dissolution of Ra-226 compared to U-238. The opposing geochemical conditions facilitating the relative abundance of U and Ra-226 in groundwater were represented by the opposing terms for loading for component 2 (U) and component 3 (Ra-226) of the PCA (table 8B). In addition to the statistically significant positive correlation of Fe-to-Ra-226 concentrations ($r=0.418$), Mg ($r=0.487$) and Sr ($r=0.565$) were similarly correlated to Ra-226 (table 6). Many of the wells completed in the Chicot and Evangeline aquifers in northwest and southwest Houston that were characterized by producing Fe-reducing, anoxic waters provided the samples that contained among the highest concentrations of Ra-226 in association with the highest or nearly the highest concentrations of Sr, Fe, and Mg. In only one sample categorized as Fe reducing was the concentration of Ra-226 less than 1 pCi/L in samples from wells in the northwest and southwest areas—conversely, in all but one sample categorized as oxic, the Ra-226 concentrations were less than 1 pCi/L (fig. 16). The geochemistry of the groundwater samples indicated that reductive dissolution of the redox-sensitive Fe hydroxides and competitive exchange with divalent cations (Mg, Sr, and Fe) for a diminished number of the sparse sorption sites were the processes that likely limited Ra-226 sorption to aquifer materials, resulting in the increase in Ra concentrations (Miller and Sutcliffe, 1985; Szabo and others, 2012). Once dissolved, the divalent Ra cation does not hydrolyze except under the most alkaline conditions where the pH is greater than about 10 (Langmuir and Riese, 1985). Amorphous Fe hydroxide can adsorb considerable amounts of Ra, more than clay minerals (Ames, McGarrah, and Walker, 1983; Ames, McGarrah, and others, 1983). The ongoing geochemical processes thus effectively mobilized (Fe-reducing, anoxic) or immobilized (oxic) Ra-226 in groundwater in the Gulf Coast aquifer system in Houston. Reductive dissolution of metal hydroxides had diminished overall sorption capacity, liberating the relatively weakly sorbed Ra-226 and Sr.

The process of reductive dissolution of Fe oxyhydroxides has been found to be the most prevalent geochemical process for mobilizing Ra to waters from sediments among aquifers nationwide (Szabo and others, 2012). The process has been described for individual aquifers, including in the midcontinent (Gilkeson and Cowart, 1987; Wilson, 2012), in the Southwestern United States (Herczeg and others, 1988), and in the Eastern United States (Szabo and Zapecza, 1991; Chapman and others, 2013).

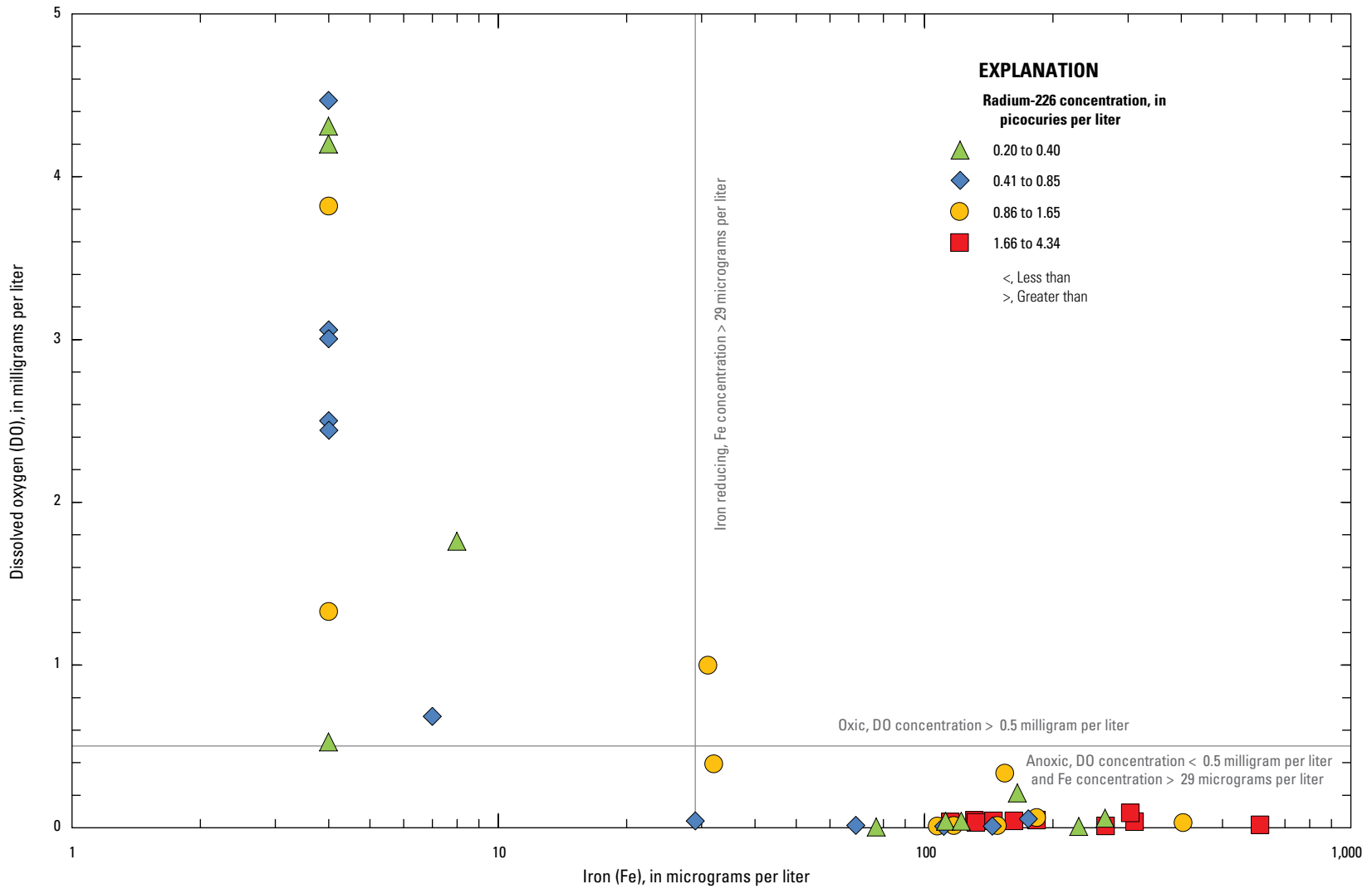


Figure 22. Concentrations of iron and dissolved oxygen, with the concentration ranges for radium-226 indicated for the water samples from 41 municipal supply wells in Houston, Texas, 2007–11.

Relations of Uranium, Radium, pH, and Predominant Cation Water Types

The chemical type of water was an important factor affecting the concentration of Ra, more so than the effect the chemical type of water has on the concentrations of U and As. Although the concentrations of all three of these constituents are controlled primarily by redox conditions and pH, the concentration of Ra-226 was also directly affected by cation-exchange reactions. The concentration of Ra-226 was significantly highest among anoxic (Fe-reducing) waters (figs. 12C, 15B; “A” Tukey class, table 4B), with detectable concentrations of SO_4 (9–17 mg/L) and the highest concentrations of Fe (more than 100 $\mu\text{g/L}$) (fig. 22; table 3). In contrast, groundwater samples with the lowest Ra-226 concentrations were characterized as methanogenic anoxic (the most reducing) and Na rich (fig. 16) rather than Fe-reducing anoxic (fig. 22). The correlation of the concentration of Ra-226 with the concentration of Fe in anoxic conditions was not significant in the low SO_4 (methanogenic-anoxic process predominant), Na-rich waters at depth (near the base of the Evangeline aquifer). Concentrations of Ra-226 vary depending on geochemical conditions, including differences in the degree of completion of cation-exchange reactions (Ca exchange for Na), which vary depending on location and depth in the aquifer system.

The fate of Ra in the deepest part of the Evangeline aquifer was controlled by the same cation-exchange reactions that control water-chemistry evolution along flow paths, and Ra-226 concentration in groundwater effectively was limited by the same geochemical processes that govern the concentrations of Ca, Mg, Na, and other constituents. In this deep groundwater, the concentrations of the divalent major cations (Ca and Mg) and common alkaline earth divalent cations (Sr and Ba) decreased substantially as the concentrations of Na increased (tables 4C and 8B). With increasing Na concentrations, decreases in Ra-226 were observed (fig. 16). In laboratory studies, montmorillonite, a clay mineral with considerable cation-exchange capacity, removed about 99 percent of the Ba (Laudelot and others, 1968) and Ra (Ames, McGarrah, and Walker, 1983) from aqueous solutions. An example of the removal of Ba and Ra in the Gulf Coast aquifer system through cation-exchange reactions is evident in the sample collected from well TS-60-62-604, which is completed to the deepest part of the Evangeline aquifer. The lowest combined Ra (Ra-226 plus Ra-228) concentration (0.246 pCi/L, Oden and others, 2010) was in the water in this sample, one of the highest Na concentrations (136 mg/L, Oden and others, 2010), as well as one of the lowest Ba concentration (146 $\mu\text{g/L}$, Oden and others, 2010). For this sample, Na was the dominant cation with a high Na-to-Cl ratio (the sample contained small amounts of K and SO_4 compared to Na and Cl; fig. 8A).

The correlation of the concentration of Ra-226 with the concentration of Fe in anoxic conditions was not significant in the low SO_4 (methanogenic or SO_4 -reducing processes predominant), Na-rich waters at depth (near the base of the

Evangeline aquifer). The concentration of Fe is relatively low in these waters, typically about 100 $\mu\text{g/L}$. Iron is likely removed from the water, precipitated to form amorphous Fe sulfides (Slowey and Brown, 2007), or the Fe does not enter into solution once sulfide becomes available until all the associated aqueous SO_4 is reduced (Kirk and others, 2004) and removed as the amorphous solid. The geochemistry of Ra and Fe is thus decoupled in SO_4 -reducing waters because different (unrelated) chemical processes controlled the concentrations of each (sequestration by cation exchange for Ra and by Fe-sulfide precipitation for Fe, respectively).

The concentrations of Ra-226 greater than 1 pCi/L in samples collected in the southwest Houston area were collected from wells completed in the “lowerCHCT, upperEVGL” or “middleEVGL” aquifers, which were anoxic (Fe reducing) and strongly mineralized with relatively abundant Na and Cl. The high concentrations of Na mostly were indicative of saltwater sources because the molar ratios of Na and Cl were close to seawater (0.86) and thus not indicative of cation-exchange reactions (Appelo, 1994) that effectively limited the concentrations of Ra-226 (fig. 16) and limited Ca and Mg content (fig. 8C). In the southwest area, the Ra-226 concentrations were greater than 2 pCi/L in four of the samples, all of which were anoxic and contained Na in concentrations of 60 mg/L or more (fig. 16C); 2 of these 4 samples were of the Na-Cl water type (fig. 8C). There was no correspondence of Na concentration to cation-exchange-dominated, methanogenic-anoxic conditions in the southwest Houston area. In addition, about half the samples collected from wells in the southwest Houston area were primarily oxic, even at considerable depth, and many of those samples contained elevated U, whereas concentrations of Ra-226 were mostly less than 1 pCi/L.

The importance of geochemical reactions in controlling, and in many cases limiting, the solubility of U and Ra-226 in groundwater in this aquifer system also is illustrated by the distribution of the dissolved concentrations of Rn-222, which differs from that of the U and Ra-226. The concentration of dissolved Rn-222 was related to the concentration of U and Ra-226 in the solids of the adjacent strata near the well open interval; Rn-222 is a soluble noble gas derived from the adjacent strata by radioactive decay (fig. 3) and did not depend on the aqueous geochemistry (Hall and others, 1985; Wanty and others, 1992; Szabo and others, 1997). In general, Rn-222 concentrations were highest among the anoxic samples, but those rarely have detectable U concentrations because U is insoluble in anoxic waters. In similar fashion, the Rn-222 concentrations did not correspond to those of Ra-226 when the geochemistry was not favorable for Ra solubility; for example, the Ra-226 concentration in the sample from well LJ-65-13-222 was a result of cation-exchange reactions—the Ra-226 concentration was much less than the 25th percentile, and the Rn-222 concentration was 800 pCi/L, a value that was elevated relative to the median. Geochemical control (limited by cation exchange) of the Ra-226 concentration is indicated, but the concentration of dissolved Rn-222 was not similarly limited.

Relations of Radioactivity Among Uranium, Radium, and Gross Alpha-Particle Activity

Uranium and Ra-226 were the primary sources of the measured gross alpha-particle activity, especially when this activity was measured 30 days after sample collection, allowing time for the decay of short-lived radionuclides. The occurrence of and relations among isotopes of Ra and U were controlled primarily by redox (figs. 12B, C; table 3) in the Texas Gulf Coast aquifer system.

In most cases, the gross alpha-particle activity measured at both 72 hours and 30 days after sample collection was greatest in the oxic and mixed waters in which the source of that radioactivity was primarily U. Especially in oxic waters, as the U concentration increased, so did the gross-alpha-particle activities (fig. 23). Most of the 10 samples with the highest gross alpha-particle and beta-particle activities measured 30 days after sample collection also contained some of the highest U concentrations, with U concentrations greater than 10 $\mu\text{g/L}$ measured in 5 of those 10 samples (fig. 17), where 10 $\mu\text{g/L}$ represent the 90th percentile of the U concentrations.

The isotopes of U were the predominant sources of gross alpha-particle activity in most of the samples (figs. 17 and 23A), but Ra-226 was the predominant source of gross alpha-particle activity in some of the anoxic water samples. Gross alpha-particle activities greater than 10 pCi/L were measured in several anoxic samples, but the associated U concentrations were less than 5 $\mu\text{g/L}$ (fig. 17). In these cases, the alpha activity was originating from Ra-226 (after 30 days) or a combination of Ra-226 and Ra-224 (and perhaps other unmeasured short-lived radionuclides) if gross alpha-particle activity was measured within 72 hours after sample collection (figs. 17 and 23A). In figure 23A, the gross alpha-particle activities measured at 72 hours after sample collection were plotted as a function of the Ra-226 and U concentrations for the 41 samples that included Ra-226 measurements. When gross alpha-particle activity exceeded 4.5 pCi/L for this sample set, the U concentrations substantially exceeded the corresponding Ra-226 concentrations in the oxic and mixed samples, whereas the opposite occurred for the anoxic (Fe reducing) samples (Ra-226 concentrations substantially exceeded the corresponding U concentrations) (fig. 23A). Of the anoxic samples with considerable gross alpha-particle activity, those selected for Ra-226 analysis had, in most cases, Ra-226 concentrations (activities) that were about equal to or considerably greater than the associated U concentration (or calculated activity ratio, as converted from the measured abundance of the U-238 mass) (fig. 23A; table 3). If the two isotopes were in equilibrium concentration in solution, then the activity ratio is 1:1, but in Fe-reducing, anoxic water, the Ra-226-to-U-238 activity ratio was much

greater than 1:1 because of the preferential dissolution of the Ra-226 isotope compared to the U-238 isotope in those geochemical conditions (table 3). For the methanogenic-anoxic samples, there was very little radioactivity present in any of the samples, represented by the gross alpha activities and associated Ra-226 and U concentrations that were all uniformly low (fig. 23A). The U concentrations were low because the samples were highly reducing; the Ra-226 concentrations were low because of the ongoing effects of cation-exchange reactions.

For more than half the samples (52 of 91 samples), the differences between activities determined at the two different time intervals for counting (72 hours and 30 days) were within 5.5 pCi/L or less (fig. 23B), or the 95th percentile of the CSU (McCurdy and others, 2008) for the gross alpha-particle activity (72-hour count). The median difference was 3.86 pCi/L. Of these 52 samples, 22 were within the uncertainty ranges defined by the associated CSU. The median value for the respective CSU for the gross alpha-particle activity for the count completed within 72 hours of sample collection was 1.50 pCi/L, and the 95th-percentile value was 2.76 pCi/L. Doubling the 95th-percentile value of the respective CSU for the gross alpha-particle activity (2.76 pCi/L times 2, rounded to 5.5 pCi/L) represents a reasonable estimate for the analytical differences among sample results that are likely to overlap within the bounds of the respective CSU; differences for sample results outside these bounds likely represent differences that cannot be attributed to counting uncertainty. The bounds of the 95th-percentile value of the respective CSU of 5.5 pCi/L were included on figure 23B to help the reader quickly identify those sample differences that most likely were not attributable to the counting uncertainty. Actual overlap within the uncertainty ranges, however, can only be determined on a sample-by-sample basis.

The generally small differences in gross alpha-particle emissions for more than half of the 72-hour- and the 30-day-count samples are consistent with the assumption that the concentrations of short-lived radionuclides such as Ra-224 were low, no greater than about 1 pCi/L. The measured concentrations of Ra-228 did not exceed 1.1 pCi/L for the subset of 28 samples with measured Ra-228 concentrations, and most concentrations were less than 1 pCi/L. Because Ra-224 is a progeny of Ra-228, similar concentrations of the two isotopes are often measured in groundwater (Szabo and others, 2005, 2012); thus, Ra-224 was unlikely a major source of gross alpha-particle activity in most of these water samples. The gross alpha-particle activity from the two measurements for these samples with minimal change over the 30-day holding period must be from one or more long-lived isotopes that do not change in activity in the 30-day period (such as isotopes of U).

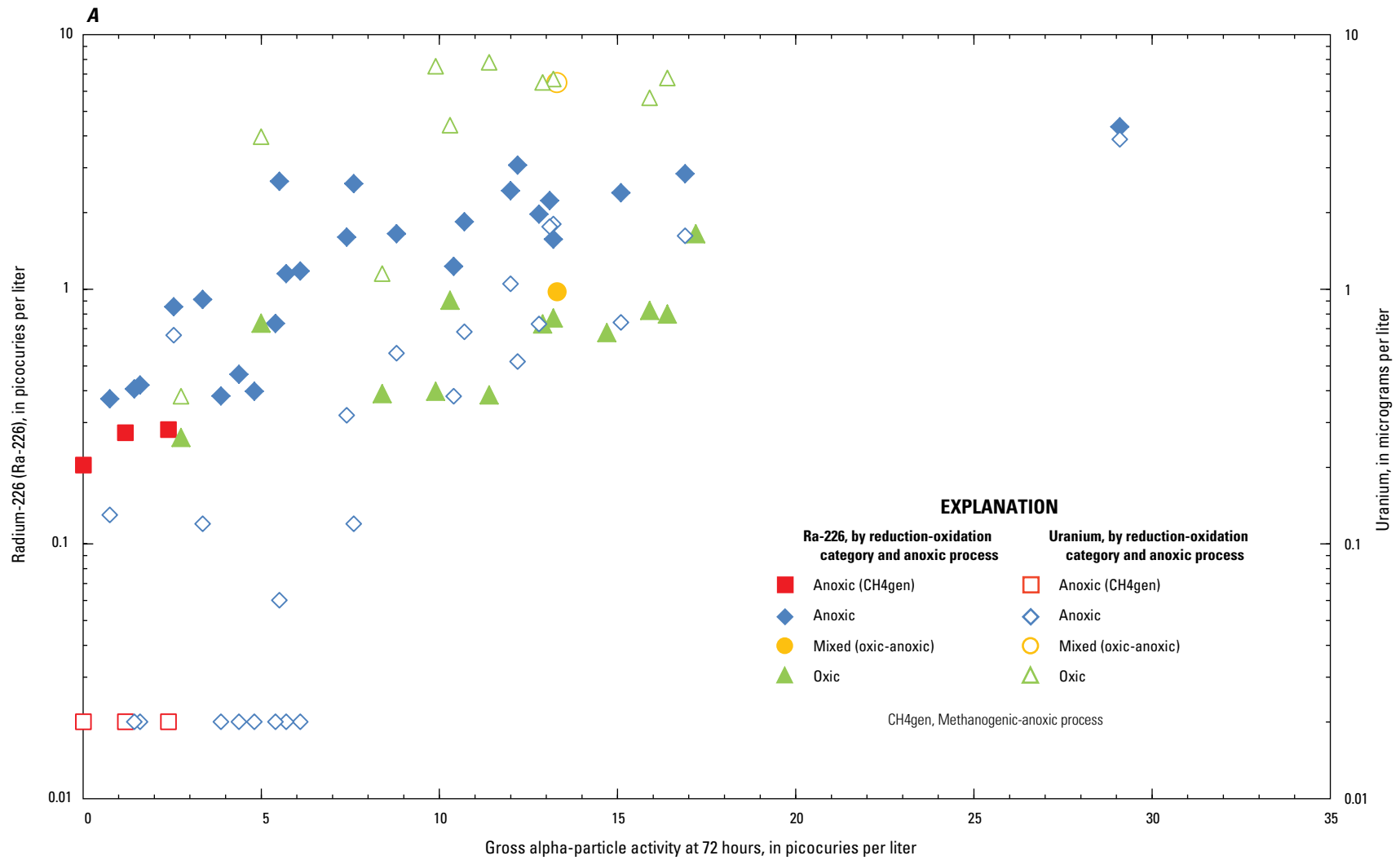


Figure 23. Radium-226 and uranium as a function of gross alpha-particle activity, *A*, measured 72 hours after sample collection, with reduction-oxidation category and anoxic process indicated for the water samples collected from 41 municipal supply wells in Houston, Texas, 2007–11; and *B*, the difference between gross alpha-particle activity measured 72 hours after sample collection and measured 30 days after sample collection as a function of uranium concentration, with reduction-oxidation category and anoxic process indicated for the water samples from 91 municipal supply wells in Houston, Texas, 2007–11.

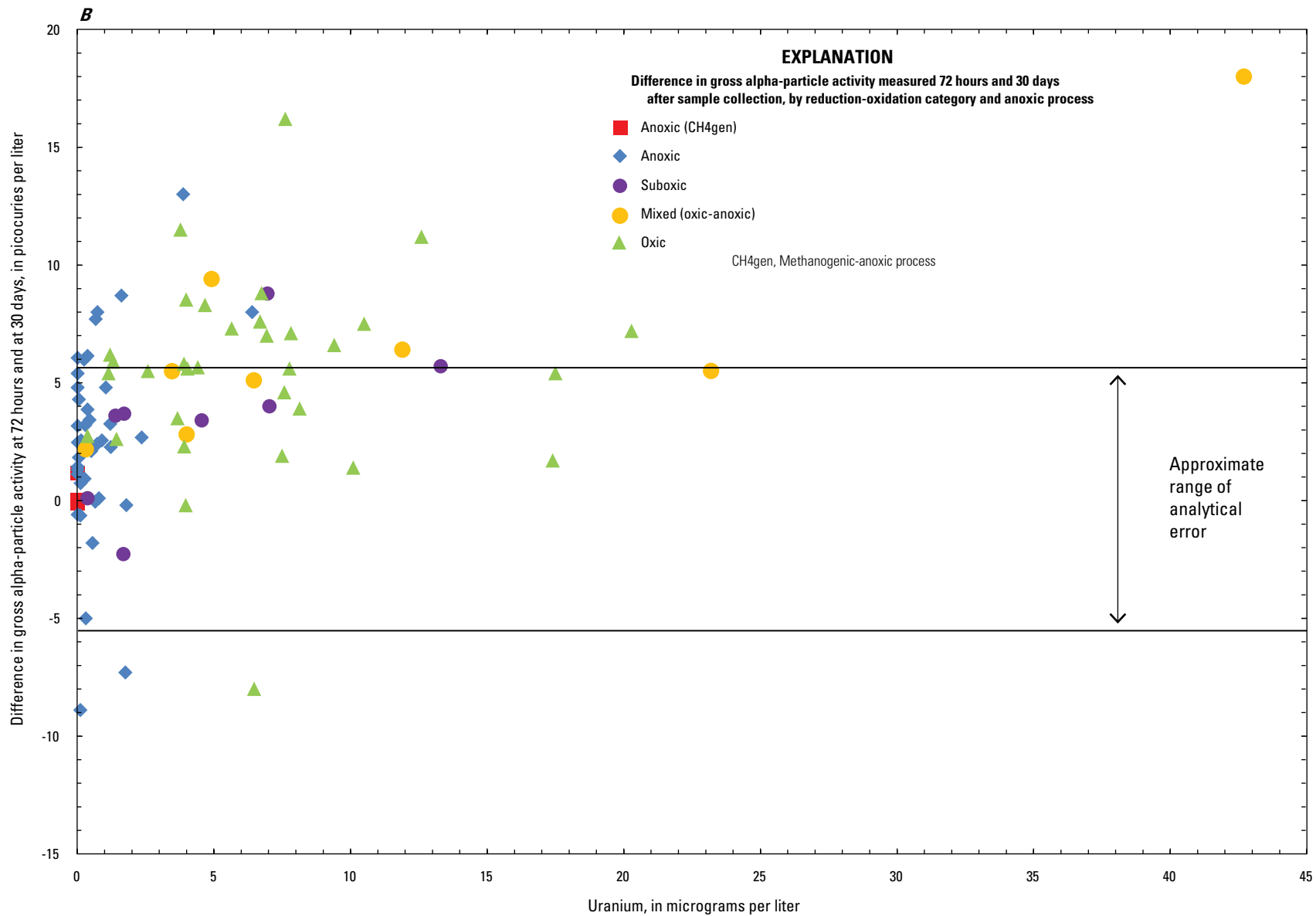


Figure 23. Radium-226 and uranium as a function of gross alpha-particle activity, *A*, measured 72 hours after sample collection, with reduction-oxidation category and anoxic process indicated for the water samples collected from 41 municipal supply wells in Houston, Texas, 2007–11; and *B*, the difference between gross alpha-particle activity measured 72 hours after sample collection and measured 30 days after sample collection as a function of uranium concentration, with reduction-oxidation category and anoxic process indicated for the water samples from 91 municipal supply wells in Houston, Texas, 2007–11.—Continued

In 39 of the 91 samples, a difference of more than 5 pCi/L was measured when subtracting the gross alpha-particle activity count measured 30 days after sample collection from the gross alpha-particle activity count measured 72 hours after sample collection (fig. 23B). Some differences in gross alpha-particle activities were negative; that is, the measured gross alpha-particle activity was greater after 30 days than the gross alpha-particle activity measured 72 hours after sample collection (fig. 23B). Water samples with relatively high Ra-226 concentrations can have an ingrowth of progeny from the Ra-226 isotope that may result in an increase in alpha activity of the sample over a 30-day period (Arndt and West, 2007). Differences in gross alpha-particle activity of more than 5 pCi/L cannot be readily accounted for among eight samples that contained U concentrations greater than 10 µg/L (fig. 23B).

The differences in gross alpha-particle activity in the respective 72-hour and 30-day counting time intervals can be used as a screening tool to try to identify samples that have the possibility of containing notable concentrations of short-lived Ra-224 or other radionuclides, but assessing these differences does not constitute an accurate measurement of short-lived radionuclide concentrations. Measurement of short-lived radionuclide concentrations might be needed to determine the source of the radioactivity not accounted for by alpha radioactivity from U and Ra-226. Concentrations of short-lived radionuclides are likely not large and may be difficult to precisely determine (Rosen and others, 2013). One candidate is the alpha-particle emitting polonium-210 (Po-210) radionuclide that also is part of the U-238 decay series (fig. 3) and derives from the decay of a short-lived progeny of Rn-222 (Hall and others, 1985). Concentrations of Po-210 on the order of less than 1 to about 5 pCi/L have been detected in samples collected from aquifers in the eastern part of the United States along the Atlantic Coastal Plain (Focazio and others, 2001; Arndt, 2010) and in anoxic samples collected from aquifers in the southern part of the United States near the Gulf of Mexico (Mullin, 1982; Rosen and others, 2013).

In 54 of the 91 samples collected with measurable gross beta-particle activity, a greater activity for the 30-day count than the 72-hour count also was noted, although the differences generally were small, about 3 to 5 pCi/L. In some of the water samples with notable differences in gross beta-particle activity with time, the concentrations of U were elevated (including the sample from well LJ-65-04-729). In the samples with abundant U, detectable amounts of beta-particle emitting progeny (Th-234 and protactinium-234) had ingrown in the sample during the 30 days after sample collection from the abundant U-238. Evidence for this ingrowth process in U-rich environmental samples was first documented by Welch and others (1995). The increase in gross beta-particle activity 30 days after sample collection is an indicator of the abundant presence of U in many of the samples.

Implications for Occurrence of Arsenic and Radionuclides in the Gulf Coast Aquifer System

The occurrence of As and radionuclides in water in the Gulf Coast aquifer system is a result of the natural processes of the chemical evolution of the aquifer water as it reacts with aquifer solids while percolating along flow paths through the sands and clays of the aquifer. Water in the aquifer system is vertically stratified by geochemistry; the composition of the water changes in response to the ongoing chemical (water-rock) reactions. Stratification is by major-ion water type and by redox as concentrations of redox-associated compounds, such as Mn, Fe, and sulfide, change as electron donors in the aquifer are consumed. This geochemical stratification varies by depth and lateral position in the aquifers as chemical reactions proceed along flow paths from recharge at aquifer outcrop areas to discharge in the Gulf of Mexico. The redox characteristics of the water control the mobility of elements such as As, U, and, to some degree, most other trace elements because the speciation and solubility are interdependent and depend upon electrostatic interactions (adsorption) with redox-sensitive amorphous Mn- and Fe-oxides (O'Day and others, 2004; Silvester and others, 2005; Slowey and Brown, 2007; Szabo and others, 2012).

The evolution of the water-quality characteristics of the Gulf Coast aquifer system has followed different geochemical processes, such that the presence of the highest concentrations of As (as As[III]), U, and to an extent, Ra-226 generally do not co-occur. Instead, they occur independently of each other on the basis of stratified redox chemistries and water types. Figure 24 shows the extent to which the highest concentrations of these constituents do not co-occur among the 35 samples for which ORP was measured and concentrations of As, U, and Ra-226 were determined, mostly from the northeast and northwest Houston areas. The redox condition on the figure is represented by the ORP measurement in the samples, which does not in every case agree with the assigned redox category for each sample (table 3). This difference for a few samples was most likely a result of variability associated with the measurement of ORP in the field. Of the seven water samples with the highest concentrations of As in this group (3.8 to 15.3 µg/L), five plotted as anoxic or methanogenic-anoxic based on ORP measurements, with negative redox potentials of less than -100 mV. The As species were determined for 5 of the 7 samples with the highest As concentrations, and the As(III) species were predominant. The three samples with the highest As concentrations, greater than 7 µg/L, with the most negative redox potential, less than -200 mV (the most anoxic), had the lowest concentrations of both U and Ra-226. Three of the four samples with the next-highest concentrations of As (3.8 to 4.8 µg/L) plotted as anoxic

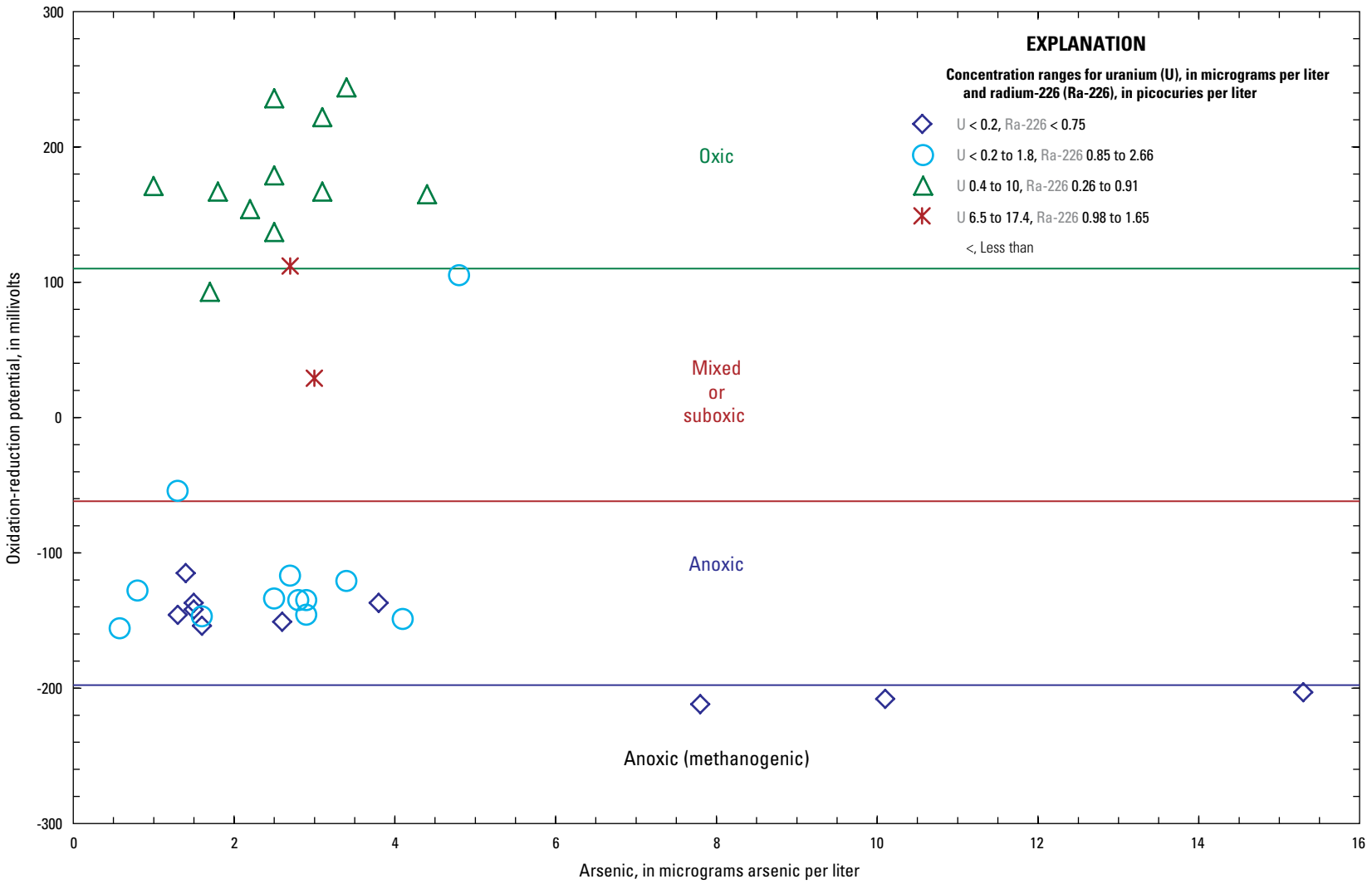


Figure 24. Concentrations of arsenic and the oxidation-reduction potential, with the concentration ranges for uranium and radium-226 indicated for water samples from 41 supply wells, Gulf Coast aquifer system, in Houston, Texas, 2007–11.

or mixed, and low concentrations of U were measured. Among these three samples, the concentrations of Ra-226 varied considerably, ranging from less than 0.75 pCi/L to a considerable (2.59 pCi/L) Ra-226 concentration (accompanied by an As concentration of 4.1 µg/L). In the sample with an As concentration of 4.8 µg/L, U was not detected; the concentration of Ra-226 was low; and with a positive ORP (105 mV), it was plotted as mixed or suboxic. This sample perhaps represents groundwater where the mixing of waters with differing redox characteristics might be influencing the geochemistry; the sample, LJ-65-20-421, was categorized as anoxic based on the concentrations of redox-sensitive species (table 3). The As(III) species was predominant in this sample. In the fourth sample, with an As concentration of 4.4 µg/L, the concentration of U was 6.48 µg/L, which was about equal to the median U concentration for all the samples; the Ra-226 concentration was 0.732 pCi/L; and with a positive ORP (165 mV), it was plotted as oxidic. This sample, LJ-65-21-148, was categorized as oxidic based on the DO and low iron concentrations (table 3). The As species were not determined for this sample.

Among the samples with the oxidizing redox conditions (with strongly positive ORP values greater than 110 mV and categorized as oxidic [table 3]), concentrations of U ranged as much as 17.4 µg/L and were generally greater than or equal to 6 µg/L. Low concentrations of Ra-226 (all but one of the samples less than 0.9 pCi/L) and As (about 3 µg/L or less) were in the oxidic water samples, with the one sample with As concentration of 4.4 µg/L as the exception. These oxidizing samples all contained only the As(V) species. Lastly, all but two of the samples with the highest Ra-226 concentrations plotted as anoxic with negative ORP values less than -100mV and were greater than 0.9 pCi/L. The two exceptions were the samples that plotted as mixed or suboxic with ORP values of -54 and 105mV, respectively. These samples either do not contain detectable U or contain small amounts of U (maximum, 1.8 µg/L) with low but detectable concentrations of As of 3.8 µg/L or less, except in two samples, which had As concentrations of 4.1 and 4.8 µg/L.

The two samples that were exceptions are indicated in figure 24 and were most likely representative of wells with mixed redox conditions. One of these samples, LJ-65-05-814, was classified as having mixed redox conditions on the basis of the concentrations of DO and Fe that were greater than the respective threshold values (table 3); this sample has an ORP very close to zero and is different in its chemistry from the samples in the other groups. As, U, and Ra-226 were all detected in this water sample but not in high concentrations, a result that is consistent with “mixing” of waters from multiple sources. Samples with mixed redox have been identified on the basis of the detectable concentration of more than one dissolved redox species, each typically representative of water with a specific redox reaction predominant (McMahon and Chapelle, 2008). This sample also contained both the As(V) and As(III) species (the concentration of the As[III] was near the LRL and only estimated). In this manner, the individual

trace elements with solubilities that are optimal in water with a specific redox reaction also are all mutually detectable in samples with mixed redox. Such mixing is common where long open intervals in supply wells intercept redox zones defined by depth stratification. The other sample that is the exception to these noted patterns of sample groupings, LJ-65-20-422, is anomalous in that it has a positive ORP (+112 mV) and was classified as oxidic (concentrations of DO were detected but those of Fe were not, table 3), but it also contained elevated concentrations of both Ra-226 (1.65 pCi/L) and U (17.4 µg/L) (fig. 24). The As concentration in this sample was detected at a relatively low concentration, with As(V) as the predominant species. This sample also might be affected by mixing, but it is unclear on the basis of the results from this one-time sampling of the groundwater from this well.

The general absence of co-occurrence of high concentrations of As, U, and Ra-226 is controlled by differences in their chemical properties. The solubility of these elements in groundwater depends on the chemistry of water types and redox characteristics that vary widely by depth and distance throughout the Gulf Coast aquifer system in Houston.

Chemical evolution and reduction processes occur along the flow paths as residence time increases, changing the geochemistry of the groundwater. In general, as oxidic water from shallow depths penetrate farther into the aquifer system, oxidized species, whether in solution or bound to the sediment, are converted to reduced species. The electron donor species, often common in recharging water, are in turn consumed by the redox reactions that occur sequentially from the reactions that release the most energy to those releasing lesser amounts of energy available for bacterial metabolism (Lovley and Chapelle, 1995), changing the water from oxidizing (having an abundance of available electron donors) to reducing with low availability of electron donors. The waters gradually become more enriched in those major and trace elements that increase in solubility in reducing conditions. In the middle and lower parts of the Evangeline aquifer in the northeast and northwest Houston areas with an increase in the reducing nature of the water, ongoing cation-exchange processes also occur with depth. The associated increase in pH further affects trace-element solubility, most specifically increasing solubility of the As(III) species (Dixit and Hering, 2003).

Figure 25 is a conceptual diagram illustrating the approximated distribution of geochemical types and redox categories that are strongly stratified by depth, along with associated occurrences of As and radionuclides in the Gulf Coast aquifer system. Concentrations of U coincide with oxidic conditions, resulting in about the same pattern of occurrence as other oxyanions including As (as As[V]). Ra-226 concentration generally increases in anoxic waters that typically contain abundant dissolved Fe, Mn, or both. The most anoxic waters, likely methanogenic, are coincident with Na-HCO₃ dominated, high pH waters from which Ra-226 is removed by cation exchange, but As (as As[III]) was predominant. The cation-exchange processes that result in an

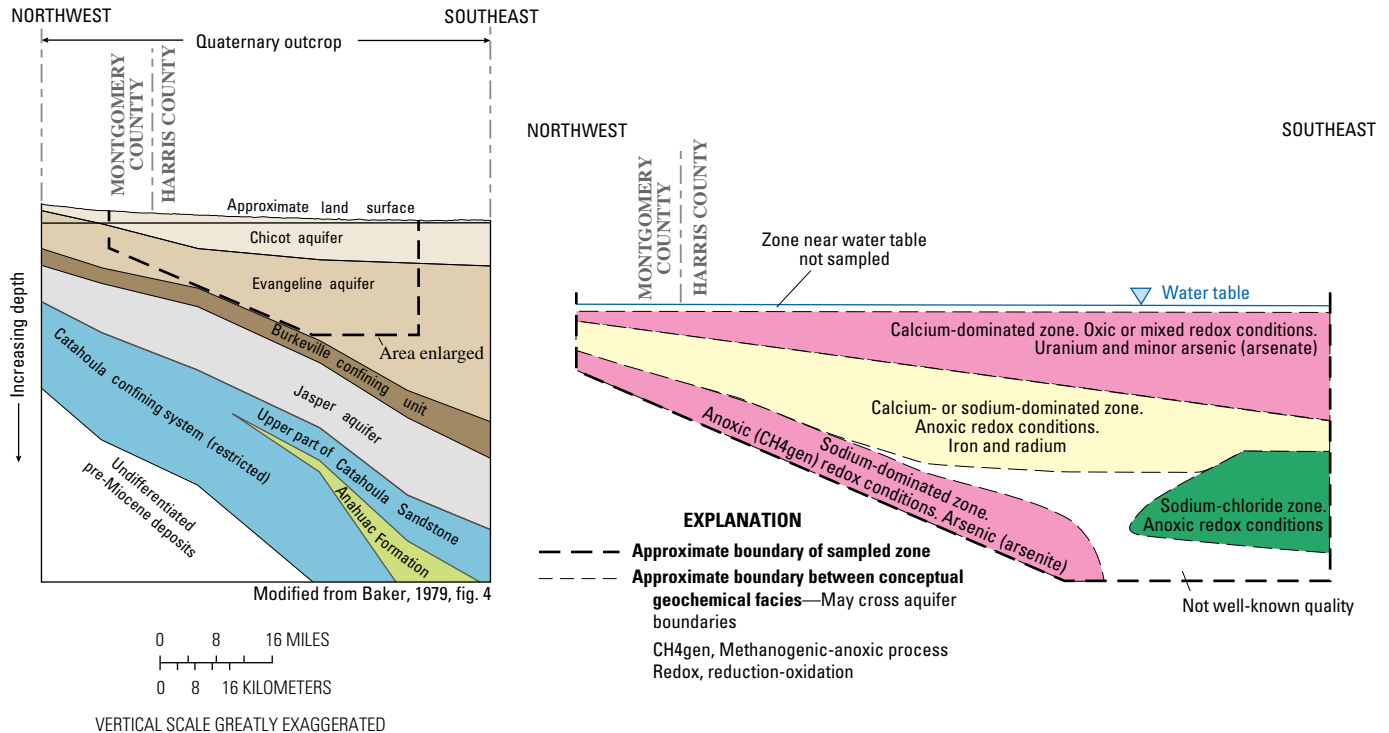


Figure 25. Conceptual diagram illustrating implications for distribution of geochemical types for occurrence of arsenic and radionuclides for a hydrogeologic section of the Gulf Coast aquifer system in part of Montgomery County and Harris County, Texas.

increase in Na concentrations and limit Ra-226 concentrations (fig. 16) also affect concentrations of all the divalent cations, including Ca (figs. 8 and 10) and Ba (table 8B), and relatively small concentrations of those divalent cations were measured near the base of the Evangeline aquifer (table 4C). The spatial distribution of these distinct zones is not characterized exactly because the aquifer system is dipping and increasing in thickness towards the Gulf of Mexico in the south and southeast. Furthermore, recharge, which takes place where the aquifers crop out, is variable (Oden and Truini, 2013), thereby affecting the orientation of flow paths and further complicating the spatial and depth distribution of geochemical types and associated occurrences of As and radionuclides. Each municipal supply well has an open interval that intercepts the different water types and redox categories found in the Gulf Coast aquifer system. The occurrence of As and radionuclides is thus determined by the positions of the well open interval within the aquifers, the aquifer thickness, and the intersection of different intervals within the well open interval with the different water types and redox zones vertically stratified in the aquifer.

Study Limitations

An evaluation of As and radionuclide concentrations in municipal supply wells throughout the study area was done in conjunction with an evaluation of how geochemical

types and redox categories are distributed both spatially and with depth in the Gulf Coast aquifer system in Houston. This information can help provide water managers with new insight into how concentrations of As and radionuclides are distributed by water types and redox categories. The water chemistry of samples collected from production wells with long open intervals represents localized mixtures that result from well pumping, and the measured water quality may not be specifically representative of various parts or zones of the aquifer (Landon and others, 2008). Compared to the relatively small-scale study area assessed in this report, an evaluation of groundwater quality from wells throughout the region screened in the Gulf Coast aquifer system, coupled with detailed information on the parts of the aquifer system intercepted by each well that was sampled, could provide the basis for assessing and understanding the possible distribution of the chemical conditions of the groundwater and As and radionuclide concentrations on a larger scale. The analysis in this report is somewhat limited by the absence of spatially distributed, discrete samples from the individual parts of the aquifer system.

The sampled municipal supply wells in this study are a combination of fully penetrating and partially penetrating wells either completed in a single aquifer (Evangeline) or a combination of aquifers (Chicot and Evangeline), with multiple well open intervals placed at a variety of depths (fig. 7). Sampled water was most likely a mixture of water

from multiple geochemical zones. The water withdrawn from fully penetrating wells in the Evangeline aquifer is most likely to be affected by this type of mixing. The fully penetrating wells contain a mixture of the reducing water presumably from the middle or the base of the aquifer and oxic or suboxic water presumably from shallow to medium depths. Waters with different chemistry may be mixed within the long boreholes or in the immediate vicinity of the boreholes in zones where changes in hydraulic heads may alter flow patterns, bringing waters from separate flow paths into contact (Landon and others, 2008). The mixing of waters with different chemistry obscures exact depth definitions of the redox zones. Retention of some distinguishing features of water-quality characteristics is possible even after the mixing occurs, although the characteristics may be diminished. An example is when oxygen and Fe are present in detectable amounts in a water sample; a mixture of oxic water characterized by the absence of detectable amounts of Fe and anoxic (Fe reducing and therefore Fe bearing) water characterized by the absence of detectable amounts of oxygen (McMahon and Chapelle, 2008).

The generalized conceptual model of the groundwater flow paths for the aquifer system and the use of a piston-flow model to calculate apparent groundwater ages are oversimplifications for the Gulf Coast aquifer system in Houston. The thick wedge of interbedded sand and clay layers influences the groundwater flow and residence times. The paleodepositional environment resulted in a highly heterogeneous sediment deposit, and localized clay lenses result in local confinement and tortuous flow paths, making simplified piston flow strongly unlikely. In addition, the large amounts of groundwater withdrawal in the study area likely alter flow paths both locally near pumping wells and more broadly throughout the study area as widespread declines in groundwater elevation altered hydraulic heads. Groundwater withdrawals have induced downward flow from local and intermediate flow systems in the regional flow system (Gabrysch, 1979), complicating the groundwater flow patterns in the aquifer system. Evaluation of results of transient tracers and ^{14}C by Oden and Truini (2013) demonstrated that the generalized concept of groundwater flow in the region is likely more complex than simple piston flow, and tracer concentrations were affected by mixing, dispersion, and preferential flow paths. Adjusted groundwater ages from wells screened in the Evangeline aquifer indicated that there was considerable groundwater-age variability, typically on the scale of 2,000 years or more, which could be explained by potentially variable lengths of flow paths from the direct recharge from the land surface where the Evangeline aquifer crops out north of where the sampled wells are located. Additional factors may also include the localized mixing of water in the Evangeline aquifer with water percolating from the overlying Chicot aquifer, a possible effect of preferential flow paths through zones of varying hydraulic conductivity among the interbedded sand and clay layers (Oden and Truini, 2013). Additionally, there also may be nearby wells with

multiple open intervals intercepting one or more aquifers in the Gulf Coast aquifer system, allowing cross-formational flow and mixing of young and old water. These flow-system heterogeneities complicate the interpretation of the water-quality results as related to the distribution of the geochemical types, redox categories, postulated residence times, and the corresponding occurrence of As and radionuclides.

Research Needs and Future Work

Geochemistry in general and redox in particular have critical effects for mobility of naturally occurring trace elements in the Gulf Coast aquifer system. Understanding the distribution of these broad geochemical properties provides benefit in designing efficient, ongoing monitoring programs as opposed to sampling randomly for individual contaminants. Defining the types and characteristics of the redox zones and determining their location and extent spatially as functions of depth, distance from outcrop, dip, texture, thickness and change in thickness of strata, positioning of the most substantial production zones within the aquifer that are intercepted by the wells, aquifer heterogeneity, recharge rates, residence time, and flow-path orientations can contribute to this understanding and are critical aspects to the areal management of the potable groundwater supplies in Houston. Such an understanding can possibly lead to improved spatial placement of wells or well open intervals to avoid the zones with greatest potential for containing particular trace elements at concentrations of concern. Once this understanding has been gained, common critical constituents or properties that are simple and quick to determine (potentially at low cost) can potentially be used as indicators of the probable presence of elevated concentrations of trace elements, including As. Simple and quick measurements that might be considered include pH, alkalinity, ORP, DO concentration, total dissolved solids, and perhaps the determination of Na and Fe concentrations. Additionally, collection of additional constituents from production wells, such as dissolved gases (methane), could be beneficial in assigning redox categories to samples collected.

Depth-dependent sampling has been used in multiple aquifer settings in the United States to collect water-quality samples at different depths while the sampled well is in production mode to identify various issues regarding contamination sources and transport or to define short-circuit pathways to municipal supply wells (Izbicki, 2004; Landon and others, 2010; Ayotte and others, 2011). Depth-dependent water-quality data may help water managers and scientists to better understand water quality produced from individual municipal supply wells, to evaluate various resource-management scenarios such as the effects of sealing a production zone or decreasing pumping, to prioritize among competing aspects of water-quality monitoring programs, and to evaluate various designs in well open interval placement and development.

Summary

Groundwater is used as the source water (the raw, ambient water withdrawn from municipal supply wells prior to water treatment) for a portion of the municipal water-supply needs of Houston, Texas. The primary sources of groundwater for the City of Houston are the Evangeline and Chicot aquifers of the Gulf Coast aquifer system. Recent changes to the U.S. Environmental Protection Agency (EPA) primary drinking-water regulations for arsenic (As) and a selected number of natural radionuclides have highlighted the necessity for municipal supply system managers to be aware of the occurrence of these constituents in their source water. During 2007–11, the U.S. Geological Survey (USGS), in cooperation with the City of Houston, collected water-quality data from 91 municipal supply wells completed in the Evangeline and Chicot aquifers of the Gulf Coast aquifer system in northeastern, northwestern, and southwestern Houston areas; hereinafter referred to as northeast, northwest, and southwest Houston areas. These data were collected as part of an ongoing study to determine concentrations, spatial extent, and associated geochemical conditions that might be conducive for mobility and transport of selected naturally occurring trace elements and radionuclides in the Gulf Coast aquifer system in Houston.

Geochemical conditions of groundwater of the Gulf Coast aquifer system were suitable in some instances for release of As and radionuclides from aquifer materials. Concentrations of arsenic ranged from 0.58 to 23.5 micrograms per liter ($\mu\text{g/L}$), with relatively low median and 75th percentile concentrations (2.7 and 3.6 $\mu\text{g/L}$, respectively). Uranium (U) concentrations ranged from less than 0.02 to 42.7 $\mu\text{g/L}$. The gross alpha-particle activity measured 72 hours after sample collection ranged from R-1.1 (nondetect, result below sample specific critical level) to 39.7 picocuries per liter (pCi/L), with a median of 10.3 pCi/L . The gross alpha particle activity ranged from R-0.94 (nondetect, result below sample specific critical level) to 25.5 pCi/L in the set of 91 samples when the measurement was completed 30 days after sample collection, with a median of 5.60 pCi/L . The Ra-226 isotope was generally predominant in the water samples. The maximum concentration of Ra-226 was 4.34 pCi/L . In five samples, the concentration of Ra-226 was greater than 2.5 pCi/L .

Differences in physiochemical property measurements (specific conductance and alkalinity) by well location (northeast, northwest, and southwest areas) indicated that the type and quality of the water withdrawn from the wells in these three areas were different. The major ions in the groundwater samples were typically as variable, as were the physicochemical properties, although the concentrations of some major ions varied more than others. The largest ranges for major-ion constituents for the 91 sampled wells were measured for the cations calcium (Ca) and sodium (Na) and for the anions bicarbonate (HCO_3^-) (as inferred from the measured alkalinity) and chloride (Cl). Approximately 62 percent of the groundwater samples were described

as Ca- and HCO_3^- -dominated water types, 36 percent as Na- and HCO_3^- -dominated water types, and 2 percent as Na- and Cl-dominated water types. A statistically significant difference between the northeast area and the other areas was detected for the Na concentrations, along with an increase in median concentrations from northeast to southwest for both dominant cations, Na and Ca. The amount of Na increased as a percentage of total ions in milliequivalents per liter, in association with an increase in the percentage of Cl in water samples from wells located in the southwest area relative to those from the northeast area. The predominant cation was Na in slightly more than 50 percent of the groundwater samples collected in the southwest. Calcium was predominant in most samples in the northeast and northwest areas, but outlying high Na concentrations were measured in a few groundwater samples where concentration of Na increased at the expense of the divalent cation Ca, without being accompanied by a similar increase in the concentration of Cl. The cation-exchange reaction of Na exchanging for divalent cations that occur on the surfaces of clay minerals was posited to be a process occurring along groundwater flow paths. These water-composition data indicate that there is a source of saltwater to the south or southwest of the study area, and at depth this source mixes with groundwater derived from recharged surface water. The saltwater mixes with the groundwater in the southwest area (closest to the Gulf of Mexico) and at depth in the northwest area.

Aquifer geochemistry also was characterized into four reduction-oxidation (redox) categories as follows: (1) 46 percent of samples were anoxic, (2) 36 percent of samples were oxic (dissolved oxygen [DO] concentration was greater than 0.5 milligrams per liter [mg/L]), (3) 9 percent of samples were mixed (criteria for more than one redox process were met), and (4) 9 percent of samples were suboxic (DO was less than 0.5 mg/L , and concentrations of the terminal electron acceptors were below threshold values). Within the anoxic category, groundwater was further characterized into four presumed predominant reduction processes: (1) iron or sulfate or both [Fe(III)/SO_4^-] reducing, (2) iron [Fe(III)] reducing, (3) iron and sulfate [Fe(III)-SO_4^-] reducing, or (4) methanogenic, as defined by composition of redox species. Three wells were presumed to be methanogenic anoxic.

Transient environmental-tracer data were used to estimate groundwater-recharge ages. The radioactive tracers tritium (not detected) and carbon-14 (generally detected in concentrations considerably less than in modern recharge) both independently indicated, along with other studies in the area, that residence time for water is in the Gulf Coast aquifer system on the order of hundreds to thousands of years.

The predominant geochemical relations in the Gulf Coast aquifer system were characterized primarily by redox reactions. The water-quality redox characteristics appear to evolve with depth and presumed residence time through the ecological succession of terminal electron-accepting processes from oxic to anoxic (Fe reducing and SO_4^- reducing) to methanogenic anoxic. Also of importance was water-rock

interaction representing reaction progress of mineral dissolution leading to mineralization (dissolution of salts) and changes in composition (water types) associated with interactions with the reactive phases of the sediment substrate (clay minerals, amorphous hydrous oxides). There is a general association of the different redox categories (oxic and anoxic [Fe reducing and methanogenic, respectively]) with the changes in water types as both the redox and nonredox reactions progress. These associated changes in water chemistry were related to residence time along flow paths and reaction rates of various sediment substrates.

Co-occurrence of water types and redox categories were related to depth and residence time. Exact depths of water types and redox zones varied spatially along likely groundwater flow paths to the point of recharge at land surface in outcrop areas. The oxic category was associated primarily with Ca-HCO₃ type water and was associated with wells with the aquifer designation of "lowerCHCT, upperEVGL," located primarily in the southwest area. The sulfidic, or methanogenic-anoxic, process was associated exclusively with the Na-HCO₃ type water and with wells with the aquifer designation of "lowerEVGL," located in the northeast and northwest areas. The samples classified as reducing (anoxic or suboxic) primarily coincided with Na-dominant groundwater in the northwest and southwest areas. With the presumed increased residence time along flow paths, results of increasing reaction progress can be noted for reduction and cation-exchange reactions. A majority of the samples collected from wells in the northeast area were Ca dominated, most likely because these wells were closest to likely recharge zones for the aquifers. The mixed redox category waters were primarily located in the northwest area from wells completed in multiple aquifers or completed in the upper, middle, and lower parts of the Evangeline aquifer.

Arsenic was about as commonly detected as U among all the samples. But unlike U that was detected most frequently in oxic conditions, As was detected with nearly equal frequency in oxic and anoxic redox conditions. Concentrations of As were correlated with an increase in anoxic conditions, an increase in pH, and an increase in Na concentration. The slightly alkaline pH conditions in the aquifer system increase mobility of As in both the arsenite (As[III]) and arsenate (As[V]) forms; hence, As was detected throughout the aquifer system. Arsenic was present as the As(III) species, with Fe-reducing and sulfidic (or methanogenic or both) anoxic water with relatively high Na concentrations. The highest concentrations of As as the As(III) species occurred in the sulfidic or methanogenic anoxic and Na-HCO₃-type water with the highest pH (7.9 or greater) in wells screened near the base of the Evangeline aquifer. Arsenic present as As(V) was associated primarily with oxic water and did not exceed 3.5 µg/L. Arsenate also was associated with near neutral to slightly alkaline water, with Na concentrations not predominant among the dissolved cations. Several trace elements corresponded with the detection of each of the inorganic As species. Concentrations of As(V) were positively

correlated with concentrations of Ca, chromium, selenium, strontium, U, and vanadium. Concentrations of As(III) were positively correlated with those of the trace element molybdenum, which does not readily precipitate from solution at the relatively low concentrations measured in these waters and does not adsorb as readily to aquifer materials, especially in moderately alkaline water, as do many other trace elements.

Uranium and Ra-226 were the primary components of the measured gross alpha-particle activity, especially when the measurement was made 30 days after sample collection. The occurrence of and relations among isotopes of Ra and U were in turn controlled primarily by redox conditions in the Gulf Coast aquifer system in Texas. Uranium was directly associated with oxic geochemical conditions optimal for its solubility. The concentration of Ra-226 was significantly highest among anoxic (Fe reducing) waters with detectable concentrations of SO₄ (9–17 mg/L) and the highest concentrations of Fe (more than 100 µg/L). The gross alpha-particle activities at both 30 days and 72 hours after sample collection were significantly higher in samples from the northwest and southwest areas and were highest in the oxic or mixed waters where the source of the radioactivity was U. Gross alpha-particle activities greater than 10 pCi/L were in several anoxic samples, but the associated U concentrations were less than 5 µg/L. In these cases, the alpha activity was likely derived from Ra-226 (after 30 days) or a combination of Ra-226, Ra-224, and perhaps other unmeasured short-lived radionuclides if gross alpha-particle activity was measured within 72 hours after sample collection. The U progeny ingrowth was the predominant source of the increase in gross beta-particle activity noted 30 days after sample collection and is an indicator of the abundance of U in many of the samples.

The evolution of the water-quality characteristics of the Gulf Coast aquifer system has followed paths such that the presence of the highest concentrations of As (as As[III]), U, and Ra-226 generally do not co-occur but rather occur independent of one another. This general absence of trace-element contaminant co-occurrence is controlled by the different geochemical properties that control the solubility of As, U, and Ra-226; therefore, their concentrations differ spatially depending on the redox condition of the aquifer from which the wells are drawing water. Because the mobility of As, U, and Ra in the Gulf Coast aquifer system in Houston are associated with specific water types and redox categories, assessment of use of selected simple geochemical surrogates as indicators of occurrence of the water type and presumed associated naturally occurring inorganic contaminant(s) is reasonable.

The spatial distribution of these distinct zones of geochemical types and redox categories was not characterized exactly because the aquifer system is dipping and increasing in thickness towards the Gulf in the south and southeast. The occurrence of As and radionuclides was thus determined by the positions of the well open intervals within the aquifers, the aquifer thickness, and the intersection of different intervals within the well open interval, with the different water types

and redox zones vertically stratified in the aquifer. The sampled municipal supply wells are a combination of fully penetrating and partially penetrating wells completed either in a single aquifer (Evangeline) or a combination of aquifers (Chicot and Evangeline), with multiple well open intervals placed at a variety of depths. Each municipal supply well has a unique spatial position in the Gulf Coast aquifer system, and the exact open interval that intercepts the water types and redox categories varies; thus, the vertically stratified water types and redox zones were intercepted somewhat differently by each well, which resulted in different geochemical signatures from well to well that did not exactly reflect the composition of any single geochemical zone in the aquifer system. Sampled water was most likely a mixture of water from multiple geochemical zones. The mixing of waters with different chemistry obscures exact depth definitions of the redox zones. Retention of some distinguishing features of water-quality characteristics was possible even after the mixing occurs, although the characteristics may be diminished. The flow system and well-completion heterogeneities complicate the interpretation of the water-quality results as related to the distribution of the geochemical types, redox categories, postulated residence times, and the corresponding occurrence of naturally occurring arsenic and radionuclides. Evaluation of As and radionuclide concentrations in production wells throughout the area in the context of how geochemical types and redox categories are distributed in the aquifer system can help provide an understanding of the distribution and co-occurrence of these constituents on the regional scale.

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