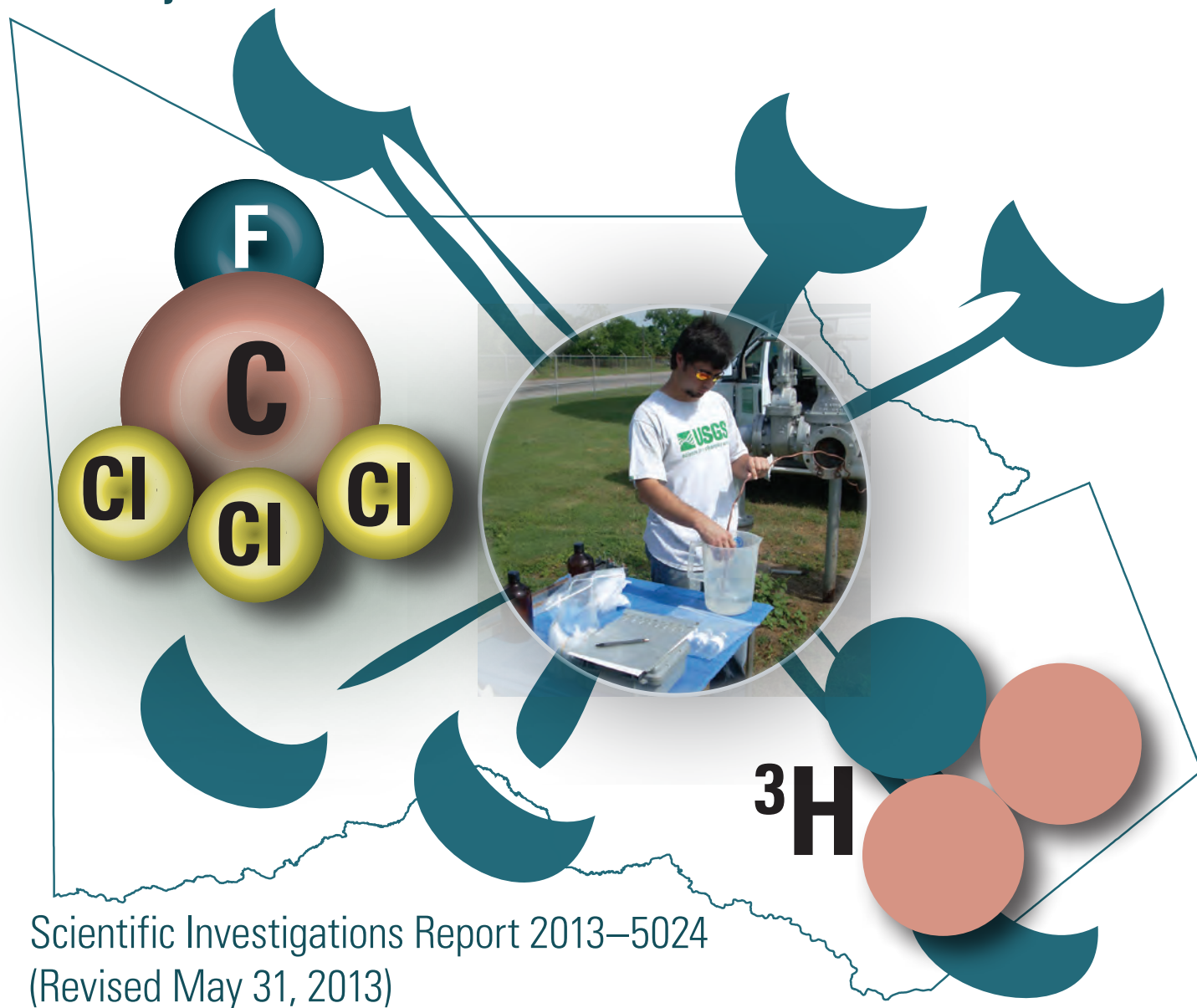


Prepared in cooperation with the Lone Star Groundwater Conservation District

Estimated Rates of Groundwater Recharge to the Chicot, Evangeline, and Jasper Aquifers By Using Environmental Tracers in Montgomery and Adjacent Counties, Texas, 2008 and 2011



Scientific Investigations Report 2013–5024
(Revised May 31, 2013)

Front cover:

Left, CFC-11 (trichlorofluoromethane) molecule.

Middle, U.S. Geological Survey scientist collects a sample for CFC analysis (in bucket).

Right, Hydrogen isotope, tritium (^3H).

Background, Sulfur hexafluoride molecule and an outline of Montgomery county, Texas.

Estimated Rates of Groundwater Recharge to the Chicot, Evangeline, and Jasper Aquifers By Using Environmental Tracers in Montgomery and Adjacent Counties, Texas, 2008 and 2011

By Timothy D. Oden and Margot Truini

Prepared in cooperation with the Lone Star Groundwater Conservation District

Scientific Investigations Report 2013–5024
(Revised May 31, 2013)

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

U.S. Department of the Interior

SALLY JEWELL, Secretary

U.S. Geological Survey

Suzette M. Kimball, Acting Director

U.S. Geological Survey, Reston, Virginia: 2013

This and other USGS information products are available at <http://store.usgs.gov/>
U.S. Geological Survey
Box 25286, Denver Federal Center
Denver, CO 80225

To learn about the USGS and its information products visit <http://www.usgs.gov/>
1-888-ASK-USGS

Any use of trade, product, or firm names is for descriptive purposes only and does not imply endorsement by the U.S. Government.

Although this report is in the public domain, permission must be secured from the individual copyright owners to reproduce any copyrighted materials contained within this report.

Suggested citation:

Oden, T.D. and Truini, Margot, 2013 (revised May 31, 2013), Estimated rates of groundwater recharge to the Chicot, Evangeline and Jasper aquifers by using environmental tracers in Montgomery and adjacent counties, Texas, 2008 and 2011: U.S. Geological Survey Scientific Investigations Report 2013–5024, 50 p., <http://pubs.usgs.gov/sir/2013/5024>.

Acknowledgments

The authors thank the San Jacinto River Authority as well as all the domestic and community-supply well owners and operators who allowed access to their wells for sample collection.

The authors also thank L. Niel Plummer and Ed Busenberg of the U.S. Geological Survey (USGS) Reston Chlorofluorocarbon Laboratory, and Mark Kasmarek, Jason Ramage, and Dexter Brown of the USGS Texas Water Science Center for their assistance in the data collection, interpretation of hydrogeology, and the interpretation of the isotope data.

Contents

Abstract	1
Introduction.....	1
Purpose and Scope	2
Description of Study Area	2
Previous Investigations.....	2
Hydrogeologic Setting.....	6
Methods.....	8
Sample Design.....	8
March–September 2008 Sample Collection.....	8
April–May 2011 Sample Collection	10
Sample Analysis.....	10
Quality Control	11
Geophysical Data Collection.....	12
Environmental Tracers	12
Chlorofluorocarbons.....	12
Sulfur Hexafluoride.....	14
Tritium	14
Helium-3 and Tritium	16
Helium-4	16
Carbon-14.....	16
Major Ion Chemistry as an Indicator of Groundwater Evolution and Travel Time	17
Dissolved Gases.....	17
Groundwater Age.....	19
Modern Environmental Tracers.....	19
Paleowaters.....	19
Environmental Tracer Data and Apparent Groundwater Age	26
Modern Environmental Tracers.....	26
Modeling of Carbon-14 with NETPATH.....	28
Estimated Rates of Groundwater Recharge.....	29
Aquifer Properties for Estimation of Groundwater Recharge Rates.....	32
Porosity.....	32
Aquifer Thickness.....	32
Distance Measurement	32
Recharge Estimates for the Unconfined Chicot, Evangeline, and Jasper Aquifers	33
Recharge Estimates for the Confined Zones of the Evangeline and Jasper Aquifers	33
Uncertainty Analysis of the Recharge Rates	33
Limitations of Estimating Recharge Rates.....	42
Summary	44
References.....	45

Appendixes (available at <http://pubs.usgs.gov/sir/2013/5024/>)

1. Environmental and quality control samples for 24 wells sampled in Montgomery County, Texas, 2011.
2. Well construction information for four additional groundwater wells sampled in the Jasper aquifer in Montgomery County, Texas, 2011.
3. Borehole geophysical data from wells in Montgomery and Walker Counties, Texas, April 2010.
4. Dissolved-gas concentrations measured in groundwater samples collected from the Evangeline and Jasper aquifers in Montgomery County, Texas, 2011.
5. Helium-4 (^4He) measured in groundwater samples collected from the Evangeline and Jasper aquifers in Montgomery County, Texas, 2011.

Figures

1. Map showing locations of wells sampled during March–September 2008 and April–May 2011 in Montgomery County and adjacent counties, Texas.....3
2. Graph showing total annual total precipitation during 1947–2008 in Houston, Texas.....4
3. Map showing soil types based on drainage class in Montgomery County, Texas, and surrounding counties.....5
4. Hydrogeologic section showing the Gulf Coast aquifer system in part of Montgomery County and adjacent counties, Texas7
5. Local geologic section showing borehole geophysical data in Montgomery County, Texas13
6. Graph showing atmospheric concentrations of chlorofluorocarbons, sulfur hexafluoride, and tritium in precipitation data in Waco, Texas, decayed to 200815
7. Map showing water chemistry in the Chicot, Evangeline, and Jasper aquifers in April–May 2011, Montgomery, Walker, and Waller Counties, Texas18
8. Diagram showing conceptual approaches to radiocarbon dating of dissolved inorganic carbon in groundwater20
9. Map showing adjusted carbon-14 ages from wells developed into the Chicot, Evangeline, and Jasper aquifers in Montgomery, Waller, and Walker Counties, Texas30
10. Diagram showing conceptual model of idealized flow through an unconsolidated aquifer.....31
11. Map showing recharge estimates at wells completed in the Chicot aquifer in Montgomery County, Texas, during March–September 2008 and April–May 2011.....35
12. Map showing recharge estimates at wells completed in the Evangeline aquifer in Montgomery County, Texas, during March– September 2008 and April–May 201137
13. Recharge estimates at wells completed in the Jasper aquifer in Montgomery, Walker, and Waller County, Texas, during March–September 2008 and April–May 2011.....39
14. Scatter plot showing uncertainty analysis of recharge rates for unconfined wells screened in the Chicot, Evangeline, and Jasper aquifers40
15. Scatter plot showing uncertainty analysis of recharge rates for confined wells screened in the Evangeline and Jasper aquifers41

Tables

1. Wells sampled in Montgomery, Walker, and Waller Counties Texas March–September 2008 and April–May 2011	9
2. Geophysical logging methods used at wells where borehole geophysical data were collected in April 2010.....	12
3. Summary of recharge temperatures and field water temperatures for wells sampled in and around Montgomery County, Texas during March–September 2008 and April–May 2011	19
4. Summary of adjusted carbon-14 ages and mineral mass transfer in the Chicot, Evangeline, and Jasper Aquifers, Montgomery County, Texas.....	22
5. Sensitivity analysis for modeled carbon-14 adjusted ages for selected wells within the Chicot, Evangeline, and Jasper Aquifers, Montgomery County, Texas.....	24
6. Apparent groundwater age derived by using samples collected during March–September 2008 from wells completed in the Chicot, Evangeline or Jasper aquifer, and the environmental tracer used for apparent age determination, Montgomery County, Texas.....	26
7. Comparison of apparent ages determined from environmental tracers for groundwater samples collected during March–September 2008 from wells completed in the Chicot aquifer in Montgomery County, Texas	27
8. Apparent groundwater ages and recharge estimates derived by using samples collected during March–September 2008 and April–May 2011 from wells completed in the Chicot aquifer in Montgomery County, Texas	34
9. Apparent groundwater ages and recharge estimates derived by using samples collected during March–September 2008 and April–May 2011 from wells completed in the Evangeline aquifer in Montgomery County, Texas	36
10. Apparent groundwater ages and recharge estimates derived by using samples collected during March–September 2008 and April–May 2011 from wells completed in the Jasper aquifer in Montgomery, Walker, and Waller County, Texas.....	38
11. Recharge methods and estimates of annual recharge rates previously determined for four wells completed in the Chicot aquifer in Montgomery County, Texas	43
12. Comparison of recharge rates determined in Montgomery County during March–September 2008 by using environmental age tracers with recharge rates from previous studies that used various methods in the Gulf Coast aquifer system in Montgomery County and adjacent counties in Texas.....	43

Conversion Factors

Inch/Pound to SI

Multiply	By	To obtain
Length		
inch (in.)	2.54	centimeter (cm)
foot (ft)	0.3048	meter (m)
mile (mi)	1.609	kilometer (km)
Volume		
cubic inch (in ³)	16.39	cubic centimeter (cm ³)
Flow rate		
inch per hour (in/h)	0.0254	meter per hour (m/h)
inch per year (in/yr)	2.54	centimeter per year (cm/yr)
Pressure		
atmosphere, standard (atm)	101.3	kilopascal (kPa)
Radioactivity		
picocurie per liter (pCi/L)	0.313	Tritium units (TU)

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

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

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

$$^{\circ}\text{C}=(^{\circ}\text{F}-32)/1.8$$

Vertical coordinate information is referenced to the North American Vertical Datum of 1988 (NAVD 88) and the National Geodetic Vertical Datum of 1929 (NGVD 29). Horizontal coordinate information is referenced to the North American Datum of 1927 (NAD 27) and the North American Datum of 1983 (NAD 83). Altitude, as used in this report, refers to distance above the vertical datum.

Acronyms and Chemical Abbreviations and Units

CFC	Chlorofluorocarbon
DG	Dissolved gases
LSGCD	Lone Star Groundwater Conservation District
NACP	North Atlantic Coastal Plain
USGS	U.S. Geological Survey
³ H	tritium
³ He/ ³ H	helium-3/tritium
⁴ He	helium-4
SF ₆	sulfur hexafluoride
¹⁴ C	carbon-14, radio-isotope of carbon
cm ³ /g STP H ₂ O	cubic centimeter per gram at standard temperature and pressure water
pCi/L	picocurie per liter
TU	tritium units

Estimated Rates of Groundwater Recharge to the Chicot, Evangeline, and Jasper Aquifers By Using Environmental Tracers in Montgomery and Adjacent Counties, Texas, 2008 and 2011

By Timothy D. Oden and Margot Truini

Abstract

Montgomery County is in the northern part of the Houston, Texas, metropolitan area, the fourth most populous metropolitan area in the United States. As populations have increased since the 1980s, groundwater has become an important resource for public-water supply and industry in the rapidly growing area of Montgomery County. Groundwater availability from the Gulf Coast aquifer system is a primary concern for water managers and community planners in Montgomery County and requires a better understanding of the rate of recharge to the system. The Gulf Coast aquifer system in Montgomery County consists of the Chicot, Evangeline, and Jasper aquifers, the Burkeville confining unit, and underlying Catahoula confining system. The individual sand and clay sequences of the aquifers composing the Gulf Coast aquifer system are not laterally or vertically continuous on a regional scale; however, on a local scale, individual sand and clay lenses can extend over several miles. The U.S. Geological Survey, in cooperation with the Lone Star Groundwater Conservation District, collected groundwater-quality samples from selected wells within or near Montgomery County in 2008 and analyzed these samples for concentrations of chlorofluorocarbons (CFCs), sulfur hexafluoride (SF_6), tritium (^3H), helium-3/tritium ($^3\text{He}/^3\text{H}$), helium-4 (^4He), and dissolved gases (DG) that include argon, carbon dioxide, methane, nitrogen and oxygen. Groundwater ages, or apparent age, representing residence times since time of recharge, were determined by using the assumption of a piston-flow transport model. Most of the environmental tracer data indicated the groundwater was recharged prior to the 1950s, limiting the usefulness of CFCs, SF_6 , and ^3H concentrations as tracers. In many cases, no tracer was usable at a well for the purpose of estimating an apparent age. Wells not usable for estimating an apparent age were resampled in 2011 and analyzed for concentrations of major ions and carbon-14 (^{14}C). At six of these wells, additional ^4He and DG samples were collected and analyzed.

Recharge rates estimated from environmental tracer data are dependent upon several hydrogeologic variables and have inherent uncertainties. By using the recharge estimates derived from samples collected from 14 wells completed in the Chicot aquifer for which apparent groundwater ages could be determined, recharge to the Chicot aquifer ranged from 0.2 to 7.2 inches (in.) per year (yr). Based on data from one well, estimated recharge to the unconfined zone of the Evangeline aquifer (outcrop) was 0.1 in./yr. Based on data collected from eight wells, estimated rates of recharge to the confined zone of the Evangeline aquifer ranged from less than 0.1 to 2.8 in./yr. Based on data from one well, estimated recharge to the unconfined zone of the Jasper aquifer (outcrop) was 0.5 in./yr. Based on data collected from nine wells, estimated rates of recharge to the confined zone of the Jasper aquifer ranged from less than 0.1 to 0.1 in./yr. The complexity of the hydrogeology in the area, uncertainty in the conceptual model, and numerical assumptions required in the determination of the recharge rates all pose limitations and need to be considered when evaluating these data on a countywide or regional scale. The estimated recharge rates calculated for this study are specific to each well location and should not be extrapolated or inferred as a countywide average. Local variations in the hydrogeology and surficial conditions can affect the recharge rate at a local scale.

Introduction

Montgomery County is in the northern part of the Houston, Texas, metropolitan area, the fourth most populous metropolitan area in the United States (U.S. Census Bureau, 2011a). As populations have increased since the 1980s, groundwater has become an important resource for public-water supply and industry. Groundwater is withdrawn from the Gulf Coast aquifer system, which comprises, in descending order, the Chicot aquifer, Evangeline aquifer, Burkeville

confining unit, Jasper aquifer, and the Catahoula confining system. A good understanding of the rate of recharge is important to water managers to help them ensure that the amount of groundwater withdrawn from the Gulf Coast aquifer system in Montgomery County is sustainable.

The Lone Star Groundwater Conservation District (LSGCD) was created in 2001 by the 77th Texas Legislature and was charged with managing and protecting the groundwater resources of Montgomery County. The U.S. Geological Survey (USGS) has worked cooperatively with the LSGCD since 2001 to monitor and appraise the Gulf Coast aquifer system. Water-level measurements are recorded and periodic water-level change maps are produced to provide short- and long-term analyses of the effects of groundwater withdrawal on the regional aquifer flow system. In 2003, the LSGCD set a maximum amount of sustainable yield for the Gulf Coast aquifer system in Montgomery County equal to previously determined estimates of recharge (Lone Star Groundwater Conservation District, 2008). In 2007, the LSGCD began planning for an alternative source of water, so further detailed information on recharge was needed in Montgomery County, especially for the different aquifers within the Gulf Coast aquifer system. Accordingly, the USGS, in cooperation with the LSGCD, estimated rates of groundwater recharge in 2008 and 2011 to the Gulf Coast aquifer system, namely the Chicot, Evangeline and Jasper aquifers, at selected wells by using a combination of different environmental tracers in Montgomery County.

Purpose and Scope

The purpose of this report is to document groundwater recharge rates estimated by using environmental tracers at selected wells screened in the Gulf Coast aquifer system in Montgomery County. This report provides an overview of the hydrogeology, estimates of recharge rates at selected wells, and a discussion of the appropriate use and limitations of the recharge rates documented in this report. Recharge rates are provided on a well-by-well basis because the data did not support a determination of the average rate of recharge for Montgomery County.

Description of Study Area

Montgomery County is rapidly growing and includes Magnolia, Conroe, and The Woodlands (fig. 1). From April 1, 2000 to July 1, 2009, the population of Montgomery County increased from 293,767 to 447,718 (U.S. Census Bureau, 2011b), making it one of the fastest growing counties in the Houston area. Montgomery County is forecasted to remain one of the fastest growing counties in the Houston area, more than doubling its 2000 population to about 750,000 by 2035 (Houston–Galveston Area Council, 2006). Land use in Montgomery County was historically mostly forest and rangeland.

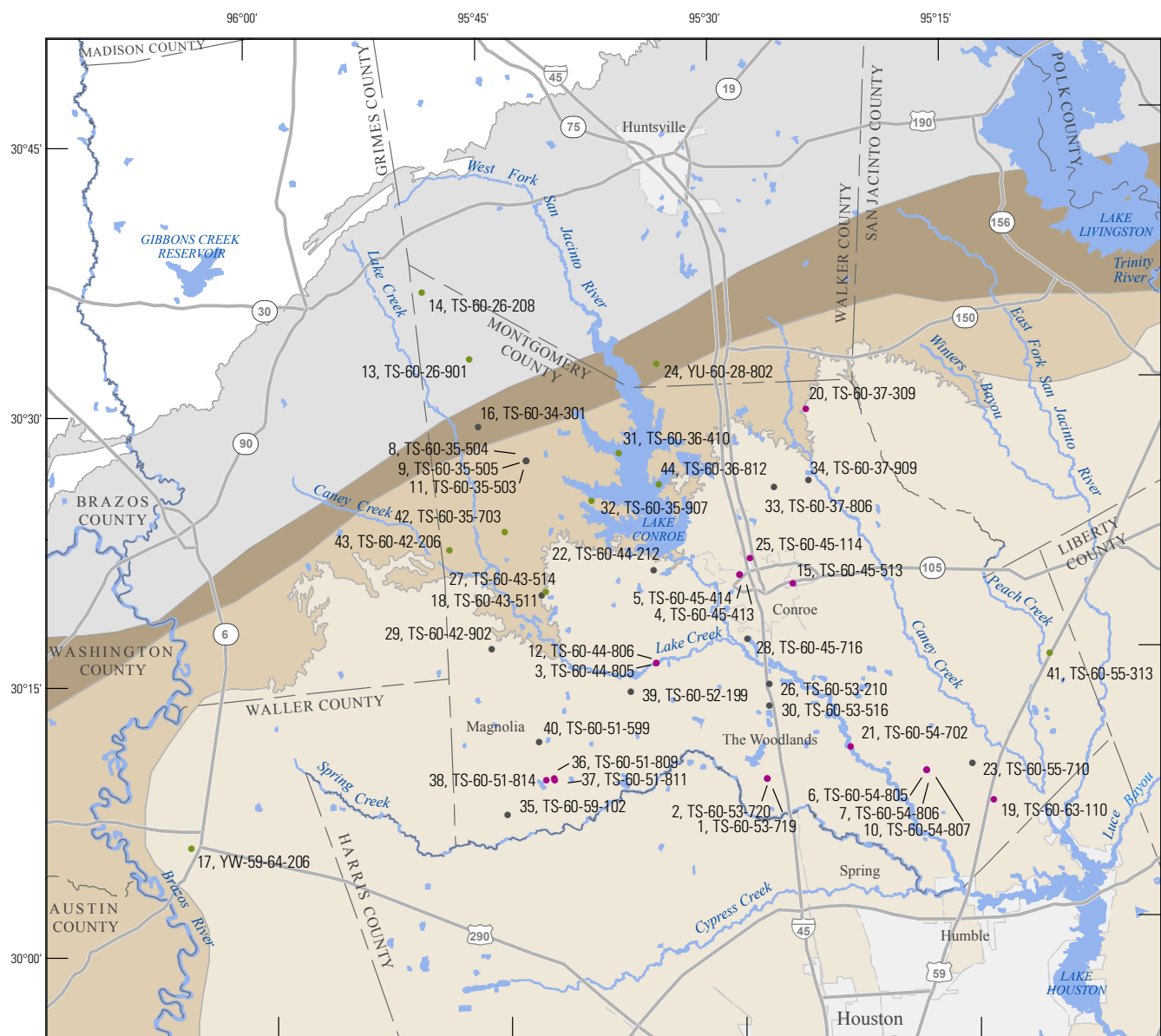
The topography of Montgomery County ranges from generally flat toward the coast and near larger streams to rolling hills in the northern part of the county. Land-surface altitude ranges from about 79 feet (ft) above North American Vertical Datum of 1988 (NAVD 88) in the southeastern corner of the county to about 330 ft in the northwestern corner (U.S. Department of Agriculture, 1972). Montgomery County is entirely within the San Jacinto River drainage basin, which trends from the northwest to the southeast. Streams in Montgomery County include Lake Creek, West Fork San Jacinto River, Peach Creek, and Caney Creek (fig. 1). Lake Conroe impounds the West Fork of the San Jacinto River upstream from Conroe. Montgomery County has a humid subtropical climate characterized by hot, humid summers and cool winters. The average annual precipitation in the Houston area was 51.67 inches (in.) during 1947–2008 (National Climatic Data Center, 2010). Substantial droughts (operationally defined for the purposes of this report as years with less than 30 in. of precipitation) occurred in 1954, 1956, and 1988 (fig. 2).

Montgomery County has complex soil types with different infiltration rates, primarily related to the drainage network (fig. 3). Although the infiltration rates of the soils in Montgomery County range from high to low, the predominant soil associations are poorly to moderately drained soils consisting primarily of clay or clay-pan features in the underlying geology (fig. 3). Permeability of the soils is highly variable, as presumed from the drainage rates ranging from about 20 in. per hour (hr) in well drained soils to less than 0.06 in./hr in poorly drained soils (U.S. Department of Agriculture, 1972). The higher permeability soils are generally associated with the major river drainages of the West Fork San Jacinto River and Lake Creek.

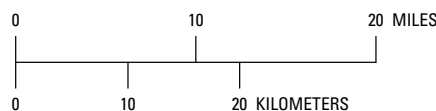
Previous Investigations

Groundwater recharge is a component of conceptual groundwater flow models and water-budget calculations, and recharge in these models is rarely measured empirically. Typically, recharge rates are estimated on the basis of other groundwater flow components such as river base flow, withdrawal rate, and groundwater-level fluctuations. Several approaches to estimating recharge have been attempted in the Gulf Coast aquifer system underlying the greater Houston area including the numerical groundwater flow models developed by Ryder (1988), Williamson and others (1990), Kasmarek and Strom (2002), and Kasmarek and Robinson (2004).

Previous estimated recharge rates, derived from calibrated models of the regional flow system in the Montgomery County area, were determined and ranged from 0.0 to 6.0 in. per year (yr) (Ryder, 1988) and from 0.0 to 0.7 in./yr (Williamson and others, 1990). Results from both studies associated smaller recharge rates with the far downdip areas along the Texas Gulf of Mexico coast where the aquifer system discharges through diffuse upward leakage into the



Base from U.S. Geological Survey 1:24,000-scale digital data
Albers Equal Area Projection, Texas Mapping System
North American Datum of 1983



Aquifer data from Strom and others, 2003 a,b,c
and Kasmarek and Robinson, 2004

EXPLANATION

- Chicot aquifer
- Evangeline aquifer
- Burkeville confining unit
- Jasper aquifer

- Sampled monitor well and contributing aquifer**
— Map identifier and state well number (see tables 1, 8, 9, and 10)
- Chicot aquifer
 - Evangeline aquifer
 - Jasper aquifer



Figure 1. Locations of wells sampled during March–September 2008 and April–May 2011 in Montgomery County and adjacent counties, Texas.

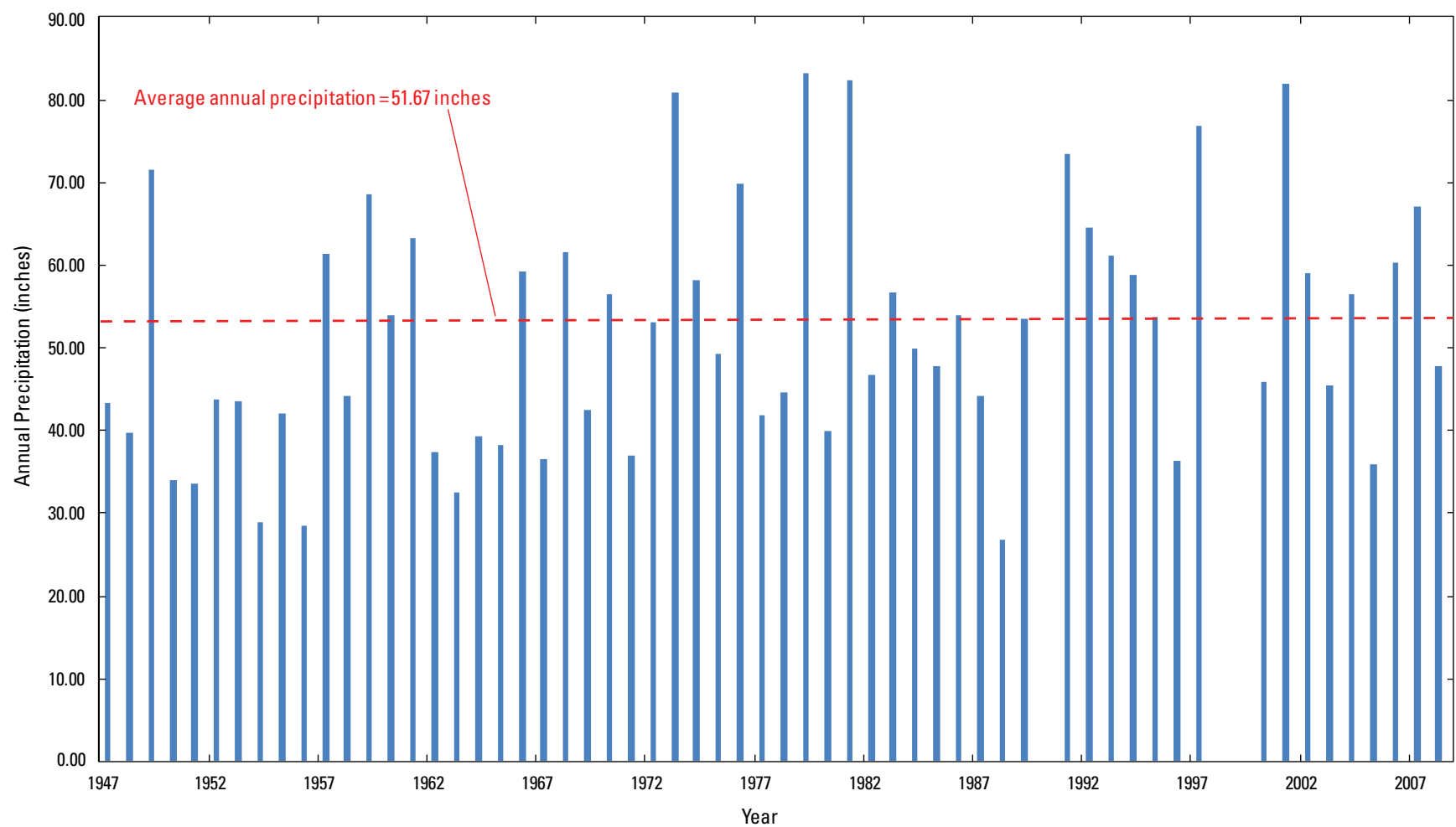


Figure 2. Total annual precipitation during 1947–2008 in Houston, Texas (National Climatic Data Center, 2010).

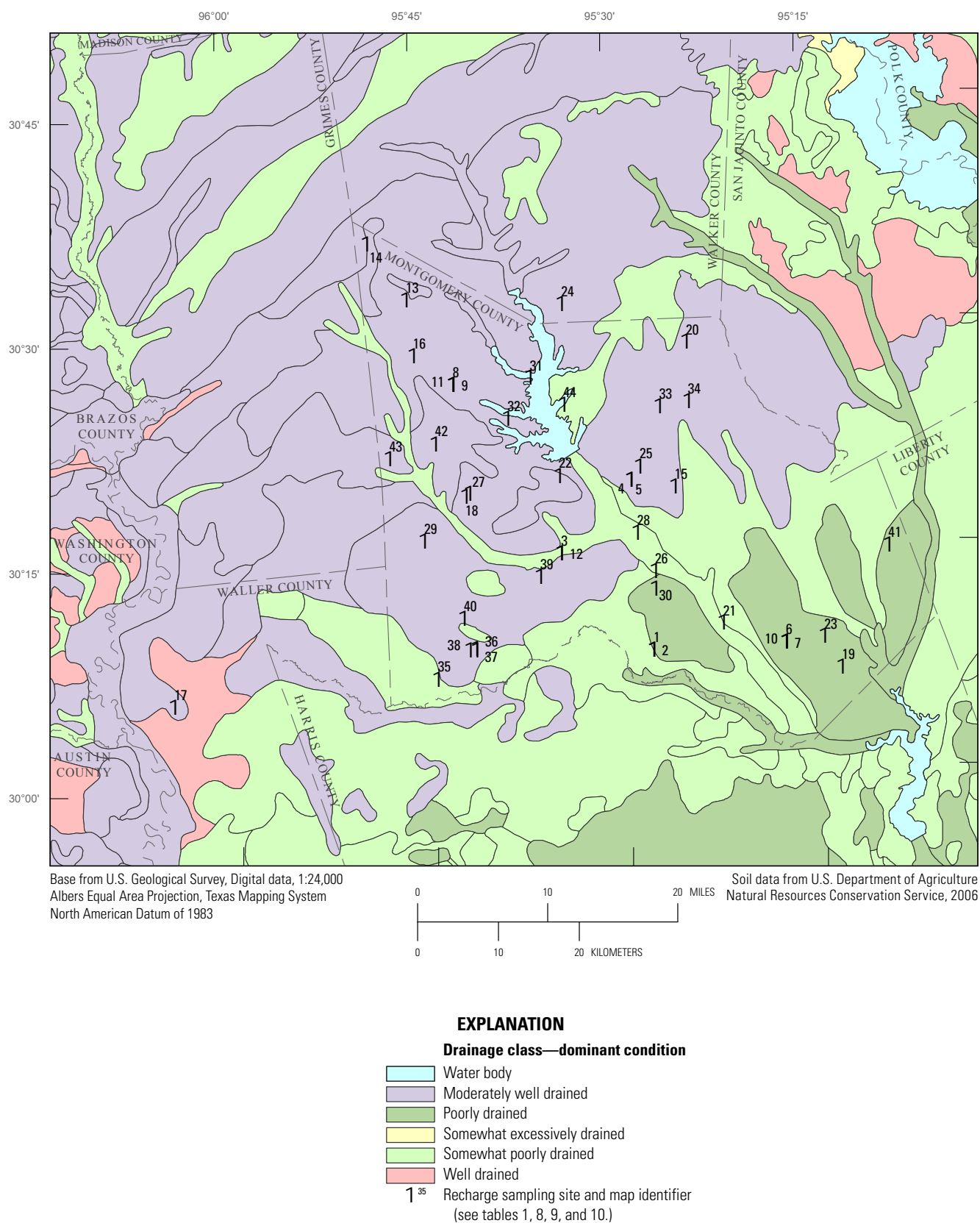


Figure 3. Soil types based on drainage class in Montgomery County, Texas, and surrounding counties.

Gulf of Mexico; larger recharge rates were associated with more transmissive updip outcrop areas of the aquifer system.

Unpublished analyses done in the 1990s by USGS hydrologists (R.K. Gabrysch and F. Liscum, U.S. Geological Survey, retired, written commun., 1995) estimated the potential recharge in the Houston area by using 30 years of streamflow data and water-budget information. Their analyses indicated that area-weighted runoff was about 7 in./yr less in four stream basins on outcrops of water-bearing units of the Gulf Coast aquifer system (Chicot and Evangeline aquifers, which are discussed in the “Hydrogeologic Setting” section) than in two stream basins on outcrops of the confined zones of the two aquifers. These results indicated that recharge on outcrops of the unconfined zones of the Chicot and Evangeline aquifers is substantially larger compared to recharge on outcrops of the confined zones.

In other studies, Noble and others (1996) sampled 41 wells screened in the Chicot and Evangeline aquifers for environmental tritium concentrations in northern Harris and Montgomery Counties and estimated a maximum recharge rate of 6 in./yr using a tritium front method assuming a uniform porosity of 23 percent. Scanlon, Dutton, and Sophocleous (2002) did a literature review to estimate that the recharge rate to the Gulf Coast aquifer system along the Texas Gulf of Mexico coast ranged from 0.0004 to 2 in./yr. Nolan and others (2007) showed how estimated recharge rates varied depending on methodology and concluded that utilizing multiple methods is beneficial because each method has advantages and disadvantages. Scanlon and others (2011) conducted a data compilation and analysis for estimation of groundwater recharge to the Gulf Coast aquifer in Texas, including Montgomery County. Their results for the Chicot aquifer in Montgomery County showed a range of 0.8–4.8 in./yr by using well hydrograph analysis and groundwater chloride mass balance.

Hydrogeologic Setting

The Gulf Coast aquifer system in Montgomery County consists of the Chicot aquifer, Evangeline aquifer, Burkeville confining unit, and Jasper aquifer and the underlying Catahoula confining system. The Chicot aquifer is unconfined in Montgomery County and consists of Pleistocene and Holocene-age sediments (Baker, 1979). The underlying Evangeline aquifer consists of Miocene- and Pliocene-age sediments. Underlying the Evangeline aquifer is the Jasper aquifer, which consists of Miocene-age sediments (Baker, 1979) and is separated from the Evangeline aquifer by the Burkeville confining unit. At the base of the Gulf Coast aquifer system, the Catahoula confining system consists of Oligocene-age sediments; it contains small amounts of freshwater in shallow restricted sands near the outcrop area to the north (Baker, 1979). Detailed information on the hydrogeology of the area can be found in Popkin (1971),

Baker (1979 and 1986), Ryder (1988), Chowdhury and Turco (2006), and Kasmarek and others (2010).

The sediments of the Gulf Coast aquifer system were deposited by fluvial-deltaic processes and subsequently eroded and redeposited. The processes of deposition, erosion, and redeposition created a thick accretionary sediment wedge of interbedded sand and clay layers exceeding 7,600 ft near the Gulf of Mexico coast (Chowdhury and Turco, 2006). Many clay layers in the region are not laterally extensive and generally are not mappable beyond the county level (Ryder, 1996). The hydrologic units within the Gulf Coast aquifer system dip and thicken from the outcrop areas in the northwest—where they exist in outcrop—toward the southeast, becoming more deeply buried beneath overlying sediments (fig. 4). The Chicot aquifer outcrops throughout much of Montgomery County and can be differentiated from the geologically similar Evangeline aquifer on the basis of hydraulic conductivity (Carr and others, 1985, p. 10). The Chicot aquifer is thinner in Montgomery County than in counties to the south (Kasmarek and others, 2010). The Chicot and the Evangeline aquifers are hydrologically connected with no separating confining units. In central and southern Montgomery County, the Chicot aquifer is not productive for the purpose of groundwater withdrawal, and the water-bearing sediments of the Evangeline aquifer progressively thin from south to north (Kasmarek and others, 2010). The Evangeline aquifer outcrops in parts of northwest Montgomery County, whereas the Jasper aquifer outcrops northwest of Montgomery County. There is little information available on the thickness and spatial characteristics of the Catahoula confining system in Montgomery County.

Water recharges the aquifers in the unconfined outcrop areas, moves downward and coastward through the interbedded sands, and discharges into streams (as base flow) by upward leakage to shallow aquifers or into the Gulf of Mexico (Ryder, 1996). Much of the water that infiltrates into the saturated zone flows through locally continuous shallow sand layers and discharges into streams; the remainder of the water flows to intermediate and deep zones of the aquifer system southeastward of the outcrop where it is captured and withdrawn by wells or naturally discharged by upward leakage in topographic lows along the coast (Kasmarek and others, 2010). In Montgomery County, groundwater withdrawal has had an appreciable effect on regional and local groundwater flow. Based on historical groundwater-level change, major areas of withdrawal include Conroe, The Woodlands, and Magnolia (Kasmarek and others, 2010). Compared to predevelopment conditions, large areas of decreased groundwater levels in these populated areas have induced flow between the Chicot and Evangeline aquifers and caused flow directions to reverse (Kasmarek and others, 2010) that imply aquifer dewatering.

Methods

In total, 32 sample sites with 40 existing groundwater wells in or near Montgomery County were selected for sampling in 2008. Well nests at seven sites contained two or more closely spaced wells. Wells screened in the Gulf Coast aquifer system were selected for sampling in Montgomery, Waller, and Walker Counties—38 wells were in Montgomery County, 1 well was in Waller County, and 1 well was in Walker County (fig. 1 and table 1). Groundwater-quality samples and physicochemical properties were collected once from each of the 40 wells during March–September 2008; water-level data were collected from those wells where it was possible to insert either a steel tape or an electric water-level contact tape (e-line). Groundwater-quality samples were analyzed for chlorofluorocarbons (CFCs), sulfur hexafluoride (SF_6), tritium (^3H), helium-3/tritium ($^3\text{He}/^3\text{H}$), helium-4 (^4He), and dissolved gases (DG). Water samples were collected and processed onsite by using methods designed to minimize changes to the water-sample chemistry or contamination from the atmosphere. Replicate samples for quality assurance and quality control were collected with each environmental sample (Oden, 2011).

In the spring of 2011, 20 of the sites sampled in 2008 were resampled, along with 4 additional sites that were added to the study for a total of 24 sites sampled in 2011. The four wells were added to the study because previously sampled wells in 2008 that were to be resampled were either down for maintenance in 2011 (two wells) or as replacements for wells that were not available in 2011 (two wells). Groundwater-quality samples were collected and physicochemical properties and water-level data (when accessible) were measured once from each of the 24 wells during April–May 2011 (appendix 1). Groundwater-quality samples were analyzed for major ions and carbon-14 (^{14}C) at all 24 wells. At the four wells added in 2011 DG and ^4He were also collected. Water samples were collected and processed onsite by using methods designed to minimize changes to the water-sample chemistry, contamination, and in the case of ^4He and dissolved gases, exposure to the atmosphere. Blank and replicate samples for quality assurance and quality control were collected for major ions and replicate analysis only for ^{14}C , DG, and ^4He .

Sample Design

Existing groundwater wells in or near Montgomery County that met the following screening criteria were considered for the initial sampling in 2008:

1. The well depth was known in the targeted aquifer;
2. The length of open interval was small as possible (ideally less than 30 ft) to facilitate the collection of discrete samples of uniform age rather than samples representing groundwater of different ages; and
3. The well was completed in a single aquifer unit.

After the initial screening, wells were selected to provide an areal distribution across the study area. Wells with relatively short open intervals (less than 30 ft) were preferred. In a few instances to meet spatial distribution, wells with open intervals greater than 30 ft were selected. Well depths for the 40 selected wells ranged from 52 to 1,240 ft with a median depth of 170 ft. Open intervals for the wells ranged from 10 to 118 ft. Well construction information is documented in a previous report (Oden, 2011).

The four additional wells sampled in Montgomery County in 2011 met the newly developed screening criteria:

1. The well depth was known;
2. The well was completed solely in the Jasper aquifer; and
3. The well had an open interval of less than 75 ft.

The four wells had well depths ranging from 581 to 1,639 ft, and open intervals ranged from 20 to 75 ft (appendix 2).

March–September 2008 Sample Collection

Groundwater samples were collected once from 40 wells during March–September 2008 by using procedures described in the USGS “National Field Manual for the Collection of Water-Quality Data” (U.S. Geological Survey, variously dated) and provided by the USGS Chlorofluorocarbon Laboratory, Reston, Virginia (U.S. Geological Survey, 2009a). Groundwater-quality samples, physicochemical properties, and water-level data (when access allowed) were collected. Groundwater-quality samples were collected and analyzed for concentrations of CFCs, SF_6 , ^3H , $^3\text{He}/^3\text{H}$, ^4He , and DG. Water levels in wells were measured manually at the time

Table 1. Wells sampled in Montgomery, Walker, and Waller Counties Texas March–September 2008 and April–May 2011.

Map identifier/ sample sequence	Station number	Station name	Aquifer	County	Year sampled
1	300824095274703	TS-60-53-719	Chicot	Montgomery	2008
2	300824095274702	TS-60-53-720	Chicot	Montgomery	2008
3	301505095343702	TS-60-44-805	Chicot	Montgomery	2008, 2011
4	301948095290003	TS-60-45-413	Chicot	Montgomery	2008
5	301948095290004	TS-60-45-414	Chicot	Montgomery	2008
6	300833095173201	TS-60-54-805	Chicot	Montgomery	2008, 2011
7	300833095173202	TS-60-54-806	Chicot	Montgomery	2008
8	302636095422802	TS-60-35-504	Burkeville ¹	Montgomery	2008
9	302636095422803	TS-60-35-505	Burkeville ¹	Montgomery	2008
10	300833095173203	TS-60-54-807	Chicot	Montgomery	2008
11	302636095422801	TS-60-35-503	Burkeville ¹	Montgomery	2008, 2011
12	301505095343703	TS-60-44-806	Chicot	Montgomery	2008
13	303222095455301	TS-60-26-901	Jasper	Montgomery	2008
14	303610095484501	TS-60-26-208	Jasper	Montgomery	2008
15	301912095253701	TS-60-45-513	Chicot	Montgomery	2008, 2011
16	302836095452701	TS-60-34-301	Evangeline	Montgomery	2008
17	300542096045403	YW-59-64-206	Jasper	Waller	2008, 2011
18	301904095414801	TS-60-43-511	Evangeline	Montgomery	2008, 2011
19	300642095131701	TS-60-63-110	Chicot	Montgomery	2008
20	302850095241801	TS-60-37-309	Chicot	Montgomery	2008
21	300958095221901	TS-60-54-702	Chicot	Montgomery	2008
22	302014095343201	TS-60-44-212	Evangeline	Montgomery	2008
23	300849095143301	TS-60-55-710	Evangeline	Montgomery	2008, 2011
24	303143095334801	YU-60-28-802	Jasper	Walker	2008, 2011
25	302040095281701	TS-60-45-114	Chicot	Montgomery	2008, 2011
26	301338095272301	TS-60-53-210	Evangeline	Montgomery	2008
27	301917095413101	TS-60-43-514	Jasper	Montgomery	2008, 2011
28	301614095284201	TS-60-45-716	Evangeline	Montgomery	2008, 2011
29	301612095450901	TS-60-42-902	Evangeline	Montgomery	2008
30	301228095272501	TS-60-53-516	Evangeline	Montgomery	2008, 2011
31	302651095362901	TS-60-36-410	Jasper	Montgomery	2008, 2011
32	302412095382101	TS-60-35-907	Jasper	Montgomery	2008, 2011
33	302436095263501	TS-60-37-806	Evangeline	Montgomery	2008
34	302452095242001	TS-60-37-909	Evangeline	Montgomery	2008, 2011
35	300658095443101	TS-60-59-102	Evangeline	Montgomery	2008
36	300853095412701	TS-60-51-809	Chicot	Montgomery	2008, 2011
37	300849095412601	TS-60-51-811	Chicot	Montgomery	2008, 2011
38	300849095415701	TS-60-51-814	Chicot	Montgomery	2008, 2011
39	301332095361901	² TS-60-52-199	Evangeline	Montgomery	2008, 2011
40	301057095421901	² TS-60-51-599	Evangeline	Montgomery	2008, 2011
41	301443095091801	TS-60-55-313	Jasper	Montgomery	2011
42	302240095440101	TS-60-35-703	Jasper	Montgomery	2011
43	302145095473901	TS-60-42-206	Jasper	Montgomery	2011
44	302459095335801	TS-60-36-812	Jasper	Montgomery	2011

¹Wells listed in U.S. Geological Survey database as being in Evangeline, but determined to be completed in Burkeville confining unit.²Final State well number assignment pending Texas Water Development Board.

of sampling, when possible, by using an electric tape or steel tape. In some wells with pumps, when water levels were not obtained because of either a lack of access point or an obstruction in the well, the most recent water-level measurement stored in the USGS National Water Information System (NWIS) Groundwater Site Inventory (GWSI) database (Oden, 2011) was used.

Observation wells were pumped by using an electric, portable, submersible, positive displacement pump (Grundfos Redi-flo2, Redi-flo-3 or Fultz SP400R) constructed of stainless steel and Teflon. When practical, the intake on the portable submersible pump was set at a position about 10 times the diameter of the well above the top of the first screen in the well. Additionally, a stainless steel splitter was installed on top of the pump, above the check valve, allowing water to simultaneously discharge for physicochemical properties monitoring and waste through Teflon or polyethylene tubing and to discharge for sample collection through a refrigeration-grade copper line. Water was pumped from domestic and municipal wells by using existing pumps, and samples were collected at the wellhead prior to installation of any pressure tanks or filtering or other treatment devices. Prior to any treatment, a connection was made for purging and sampling by using a brass connector with compression fitting to refrigeration-grade copper tubing.

Before sample collection, one to three casing volumes were purged from the well, depending on well type, either observation or supply. For wells that are continuously pumped (or pumped regularly every few hours) such as those used for public supply, domestic supply, or industrial purposes, purging less than three casing volumes is permissible (U.S. Geological Survey, variously dated, chapter A4). The purge procedure removes stagnant water in the well, reduces chemical artifacts of well installation or well construction materials, or mitigates effects of infrequent pumping. After purging was complete, the physicochemical properties of dissolved oxygen, pH, specific conductance, and water temperature were measured until readings were stable (Oden, 2011). Once readings stabilized, water samples were collected in new, precleaned bottles. Water samples were collected and processed onsite by using methods designed to minimize changes to the water-sample chemistry or contamination from the atmosphere. So there would be no degradation of water samples and to maintain initial concentration of compounds between the time of sample collection and laboratory analyses, bottle lids were taped on, copper tubes were crimped shut, and samples were stored according to the laboratory protocols, which might include storing upside down, or storing either chilled or at room temperature.

All equipment used for the collection of the environmental tracers during March–September 2008 was cleaned with tap water and a native water rinse. The external parts of the submersible pump were rinsed with tap water, and the interior of sample and discharge lines was rinsed multiple times with native water prior to collection. The introduction of solvents to the cleaning procedures, such as methanol or

detergents, was not done as it could have affected quality of the samples.

April–May 2011 Sample Collection

Groundwater-quality samples were collected once from 24 wells during April–May 2011 and analyzed for concentrations of major ions and ^{14}C , with 6 samples analyzed for ^4He and DG. Samples were collected and processed by using the same procedures as in 2008 with the exception of using low-density polyethylene (LDPE) tubing for sampling lines rather than copper.

Samples for major ions, field alkalinity, and ^{14}C were collected through a preconditioned (2 liters [L] of deionized water [DIW] passed through a filter), 0.45-micron pore size, disposable capsule filter. Samples for ^{14}C were filtered through the preconditioned, 0.45-micron pore size, disposable capsule filter with an additional 10–12 in. long piece of CFlex tubing on the outflow to allow for bottom filling of a 1-L glass bottle, leaving about 1 cubic centimeter (cc) of headspace in the bottle and closing the bottle with a polyseal cone cap. To prevent degradation of water samples and maintain the initial concentration of compounds between the time of sample collection and laboratory analyses, bottle lids for ^{14}C were taped on, and samples for cations were chemically treated with 2 milliliters of Ultrex 7.5–7.7N nitric acid then were stored according to the laboratory protocols, which include storing chilled (^{14}C) or at room temperature (major ions). Samples were shipped overnight once a week to analyzing laboratories after being chilled to 4 °C or less.

All equipment used for the collection of the samples was cleaned with 0.1-percent nonphosphate detergent rinse, tap water rinse, and DIW as described in the USGS National Field Manual (U.S. Geological Survey, variously dated, chapter A3). LDPE tubing used for domestic wells was precleaned in the laboratory, then cut to length in the field with clean tubing cutters, then discarded after a one-time use. The same cleaning procedures were used for immediate cleaning of sample equipment that had portable pumps. Sample equipment for use with the portable pumps was cleaned immediately after use at the site.

Sample Analysis

SF₆ and CFC analyses were done at the USGS Chlorofluorocarbon Laboratory in Reston, Va., by using a purge-and-trap gas chromatography procedure with an electron capture detector (ECD) documented by Busenberg and Plummer (1992, 2000). $^3\text{He}/^3\text{H}$ analyses were done at the Noble Gas Laboratory of Lamont-Doherty Earth Observatory (LDEO) of Columbia University, Palisades, New York, by using ^3He -ingrowth with mass spectrometry for ^3H (Clarke and others, 1976) and mass spectrometry for ^3He as described in Schlosser and others (1988) and Ekwurzel and others (1994). ^3H analyses were done at the USGS Tritium Laboratory,

Menlo Park, California, by using electrolytic enrichment (Östlund and Werner, 1962) and liquid scintillation (Thatcher and others, 1977). Sample analysis for ^4He and dissolved gases was done at the USGS Dissolved Gas Laboratory, Reston, Va., by using gas chromatography as described in Busenberg and others (1993) and Busenberg and others (2001). Major ion samples (calcium, magnesium, potassium, sodium, laboratory alkalinity, chloride, fluoride, silica, sulfate, and iron) were analyzed at the USGS National Water Quality Laboratory in Lakewood, Colorado, by using methods described in Fishman and Friedman (1989), Fishman (1993), and American Public Health Association, American Water Works Association, and Water Environment Federation (1998). ^{14}C analysis was conducted by a USGS contract laboratory, Woods Hole Oceanographic Institution, National Ocean Sciences Accelerator Mass Spectrometry (NOSAMS) Facility, in Woods Hole, Massachusetts, by using accelerator mass spectrometry (AMS) (Woods Hole Oceanographic Institution, 2011). Field alkalinity samples were collected and measured by field personnel and processed by using methods described in Rounds (2006).

Quality Control

No blank samples were collected as part of the study for the sampling completed in March–September 2008 because water free of environmental tracers and DG is not easily prepared or available (L. Niel Plummer, U.S. Geological Survey, written commun., 2009). For quality assurance, all samples were collected and analyzed as replicate samples (Oden, 2011) in accordance with standard procedures for collecting the environmental tracers specific to this report. A summary of replicate analyses and relative percent differences for environmental tracers (CFCs, SF_6 , ^3H , $^3\text{He}/^3\text{H}$, ^4He , and DG) is not included in this report. Although samples were collected as replicate samples, all values were analyzed, reviewed, and included in the determination of apparent groundwater ages. Summary statistics for environmental tracers (CFCs, SF_6 , ^3H , $^3\text{He}/^3\text{H}$, ^4He , and DG) are not provided. The evaluation of an individual analyte in relation to its replicate, for example CFCs, is also dependent upon the SF_6 or $^3\text{He}/^3\text{H}$ result provided, or both. Even if a result for CFCs appears valid, it may be contradicted by evidence in one of the other environmental tracers, therefore making the result not valid.

Quality-control (QC) samples for groundwater samples collected April–May 2011 were collected as described in “National Field Manual for the Collection of Water-Quality Data” (U.S. Geological Survey, variously dated) and analyzed by the same laboratories and methods as the environmental samples. QC samples include an equipment blank for major ions (one), field blanks for major ions (two), and sequential replicate samples (major ions [three], ^{14}C [four], ^4He , and DG [six]). QC samples were collected to evaluate any contamination, as well as bias and variability

of the water chemistry data, that might have resulted from sample collection, processing, transportation, and laboratory analysis. QC results are listed in italics in appendix 1. An equipment blank was collected prior to environmental sample collection (USGS Houston Laboratory at Shenandoah, Tex., April 7, 2011) in a controlled environment to determine if the cleaning procedures for sample containers and the equipment for sample collection and sample processing were sufficient to produce contaminant-free samples. Manganese (measured in micrograms per liter ($\mu\text{g/L}$)) was the only constituent detected in the equipment blank (0.30 $\mu\text{g/L}$) above the laboratory reporting level (LRL). Two field blanks were collected and processed at sampling sites prior to the collection of environmental samples. Constituent concentrations in field blank samples were less than the LRL except for manganese (appendix 1), which was detected in both field blanks 0.27 $\mu\text{g/L}$ (May 5, 2011) and 0.19 $\mu\text{g/L}$ (May 12, 2011). With manganese being detected in the equipment and both field blanks at low concentrations, censoring of low concentration of manganese occurred. The mean of the three detected blank concentrations (0.253 $\mu\text{g/L}$) was multiplied by three (0.76 $\mu\text{g/L}$), and all environmental sample concentrations (5) equal to or less than that value were rejected from the dataset.

Sequential replicate samples (hereafter referred to as “replicate samples” in this report) were collected during the study. Replicate samples are collected sequentially by filtering environmental samples through a preconditioned 0.45 micron disposable capsule filter, discarding the filter, attaching a new preconditioned 0.45 micron disposable capsule filter, and collecting another set of samples to provide a measure of the variability of sample processing and analysis. Replicate samples were compared to the associated environmental samples by computing the relative percent difference (RPD) for each constituent. RPD was computed by using the equation

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

where

C_1 = concentration from environmental sample; and
 C_2 = concentration from replicate sample.

RPDs of 10 percent or less indicate good agreement between analytical results if the concentrations are sufficiently large compared to the LRL. The RPD exceeded 10 percent for one of the sample pairs of major ions and for two of the sample pairs for ^{14}C . The RPD for the manganese replicate pair was 15.7 percent and was considered acceptable with concentrations in 3 $\mu\text{g/L}$ range. The large RPDs for ^{14}C are related to calculating percent difference on percent, and both replicated pairs were at or near the method detection limit, a concentration range in which a small change creates a large relative percent difference.

Geophysical Data Collection

Five observation wells from which groundwater samples were collected for this study and three additional wells at the same sampling sites containing wells sampled for this study (wells in the same well nest as those sampled) were logged in April 2010 by the USGS with borehole geophysical tools (table 2). All geophysical tools interfaced to a Century System VI log acquisition system in the logging truck by way of 0.25-inch-(6-millimeter-) diameter four conductor wireline. Standard borehole geophysical logs, including natural gamma radiation (natural gamma), fluid resistivity, conductivity, and temperature, and electromagnetic induction (induction/conductivity) are provided in appendix 3. All results are referenced to feet below land surface (land-surface datum). A description of standard borehole geophysical logging methods and interpretation is given by Keys (1990, 1997). For example, gamma counts increase with increasing clay content and resistivity increases with increasing freshwater contents in sands; however, resistivity can also be an indicator of clay content, decreasing with increasing clay content.

The borehole geophysical logging was done to gain a better understanding of the physical characteristics of the material immediately surrounding the wells and of the physical condition of each well (fig. 5). The logging survey provided additional information on the local scale complexities of the subsurface that might affect the traveltime of groundwater and, consequently, groundwater ages and recharge rates.

Environmental Tracers

Samples of CFCs, SF_6 , ^3H , and $^3\text{He}/^3\text{H}$ were used to estimate apparent ages of recently recharged (post-1940s) groundwater. Additionally, ^4He samples were collected and analyzed with the less sensitive gas-chromatography technique initially as a screening tool to evaluate suitability for $^3\text{He}/^3\text{H}$ analysis. ^{14}C data were used to estimate apparent ages of premodern groundwater recharged more than 1,000 years ago.

Chlorofluorocarbons

CFCs are stable, synthetic organic compounds that were developed in the early 1930s as safe alternatives to ammonia and sulfur dioxide in refrigeration; CFCs have been used in a wide range of industrial and refrigerant applications (Plummer and Friedman, 1999). Production of dichlorodifluoromethane (CFC-12) began in 1931, followed by trichlorofluoromethane (CFC-11) in 1936, and then by many other CFC compounds, most notably trichlorotrifluoroethane (CFC-13). The CFC-11 and CFC-12 compounds were used as coolants in air conditioning and refrigeration; blowing agents in foams, insulation, and packing materials; propellants in aerosol cans; and solvents (Plummer and Busenberg, 2000). The CFC-113 has been used primarily by the electronics industry in semiconductor chip manufacturing, in vapor degreasing and cold immersion cleaning of microelectronic components, and in surface cleaning. Probably better known as Freon, CFCs

Table 2. Geophysical logging methods used at wells where borehole geophysical data were collected in April 2010.

[PVC, polyvinyl chloride; Yes, method used; No, method not used; --, Well not in table 1- see footnote]

Map identifier (fig. 1).	Station name	Logging date	Aquifer	Well depth (feet)	Casing material	Geophysical logging method		
						Natural-gamma radiation (natural gamma)	Fluid resistivity, conductivity, and temperature	Electro-magnetic induction (induction/conductivity)
--	¹ TS-60-53-718	4/29/2010	Evangeline	246	PVC	Yes	Yes	Yes
6	TS-60-54-805	4/29/2010	Chicot	165	Steel	Yes	Yes	No
23	² TS-60-55-710	4/29/2010	Evangeline	600	Steel	Yes	Yes	No
30	TS-60-53-516	4/29/2010	Evangeline	807	Steel	Yes	Yes	No
--	³ TS-60-44-807	4/29/2010	Evangeline	845	Steel	Yes	Yes	No
11	TS-60-35-503	4/30/2010	Evangeline	118	PVC	Yes	Yes	Yes
--	⁴ TS-60-45-412	4/30/2010	Chicot	261	PVC	Yes	Yes	Yes
24	YU-60-28-802	4/30/2010	Jasper	181	PVC	Yes	Yes	Yes

¹Well not sampled as part of study; however, co-located with wells TS-60-53-719 and TS-60-53-720, where samples were collected.

²Well not logged to bottom; obstruction in well reported around 285 feet below land surface.

³Well not sampled as part of study; however, co-located with wells TS-60-44-805 and TS-60-44-806, where samples were collected.

⁴Well not sampled as part of study; however, co-located with wells TS-60-45-413 and TS-60-45-414, where samples were collected.

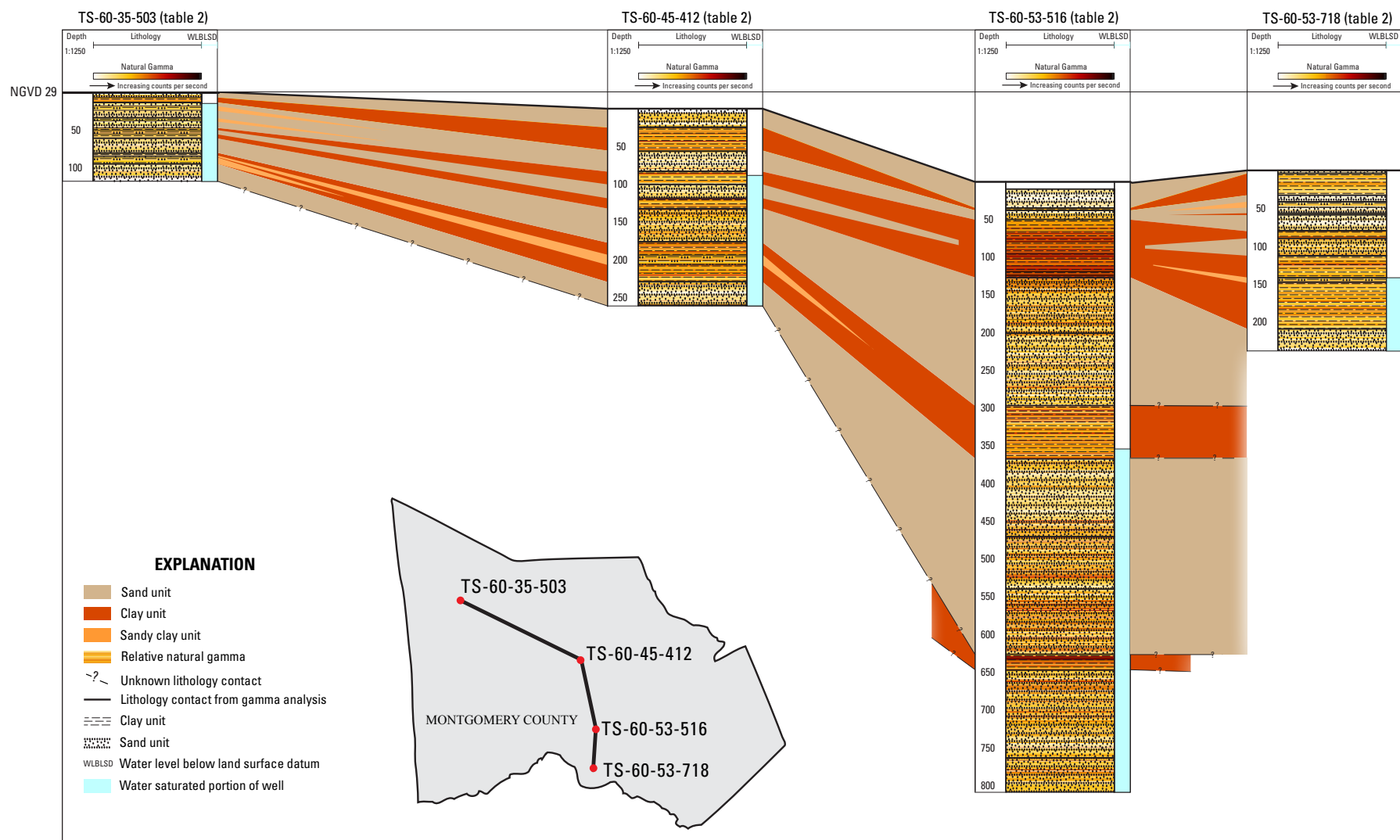


Figure 5. Local geologic section showing borehole geophysical data in Montgomery County, Texas.

are non-toxic, non-flammable, and non-carcinogenic, but they contribute to depletion of the global ozone layer (Plummer and Friedman, 1999). In 1987, 37 nations signed an agreement to limit release of CFCs and to reduce CFC emissions by 2000 (Plummer and Friedman, 1999). This agreement was strengthened in 1990 and 1992 to establish a cutoff date of 1996 to cease production of CFCs in industrialized nations. The United States ceased production on January 1, 1996, as a regulatory requirement under the U.S. Environmental Protection Agency Clean Air Act (International Atomic Energy Agency, 2006).

CFCs can be used to estimate the apparent age of water that has recharged an aquifer in approximately the last 50 to 60 years, and they also can be used to estimate the time of recharge (Plummer and Friedman, 1999). Groundwater age dating with CFCs is based on Henry's law of solubility, which is the concentration of the gas dissolved in water in equilibrium with air proportional to the partial pressure of the gas in air (Plummer and Busenberg, 2000). Under favorable conditions, sufficient concentrations of CFC-12, CFC-11, and CFC-113 can dissolve into water and allow dating of groundwater recharged since approximately 1941, 1947, and 1955, respectively. Groundwater age dating with CFC-12, CFC-11, and CFC-113 is possible because (1) the atmospheric mixing ratios of these compounds (that is, concentrations of the compounds in air) are known, and (or) have been reconstructed over the past 50 years, (2) the Henry's law solubility in water is known, and (3) concentrations of these CFCs in air and young water are relatively high and can be measured (Plummer and Busenberg, 2000). The concentrations of the CFCs in the groundwater at the time of recharge are proportional to the concentrations in the atmosphere at the same time, which are well known, and can be readily used for comparison. Atmospheric concentrations of CFC-12, CFC-11, and CFC-113 in air peaked in about 2001, 1994, and 1996, respectively (fig. 6). Because of nearly level atmospheric input functions of CFC mixing ratios (CFC-12, CFC-11, CFC-113) in the 1990s and early 2000s, it is not possible to resolve modern CFC ages as precisely as can be done with waters recharged earlier (between 1940s and 1980s), when atmospheric concentrations of CFC-12, CFC-11 and CFC-113 were increasing rapidly (Plummer and others, 2006).

Sulfur Hexafluoride

SF₆ is primarily an anthropogenic gas but can occur naturally in some minerals or rocks of igneous or volcanic origin. The primary uses of SF₆ are as an insulator in high-voltage switches and transformers and as a blanket gas in melting operations of magnesium metal production (Busenberg and Plummer, 2000). Production of SF₆ began in the 1950s and shows an upward pattern (fig. 6) that is expected to continue (Busenberg and Plummer, 1997).

Sulfur hexafluoride is a tracer and dating tool of water recharged during the last 40 years. Under favorable

conditions, detectable concentrations of SF₆ can accumulate in groundwater and allow for dating of waters since approximately 1970. Groundwater dating with SF₆ is possible because (1) the atmospheric history is well established (Maiss and Brenninkmeijer, 1998); (2) sources are identified, and there is a large contrast between a small natural background and a large anthropogenic signal; (3) the Henry's law solubility in water is known; and (4) concentrations in groundwater are sufficient to be measured (Busenberg and Plummer, 1997). The concentration of SF₆ in groundwater at the time of recharge is proportional to the concentration in the atmosphere at the same time, which is well known, and can be readily used for comparison (Busenberg and Plummer, 1997).

Tritium

The radioactive isotope of hydrogen, ³H, was used to identify modern groundwater recharge or groundwater mixtures that contain some modern groundwater recharge. ³H substitutes for a hydrogen (¹H) atom or deuterium (²H) atom in the water molecule and can serve as a tracer because water containing a ³H atom follows the same pathway through the environment as water that does not contain a ³H atom (Plummer and others, 1993); that is, transport is conservative with no retardation. The half-life of ³H is 12.32 years and commonly is measured in picocuries per liter or tritium units (TU) in which 1 TU = 3.19 pCi/L (Lucas and Unterweger, 2000). Low levels of ³H are produced naturally by the interaction of the atmosphere with cosmic rays from solar wind. Atmospheric thermonuclear weapons testing from 1952 to 1964 introduced a large amount of ³H to the atmosphere that was incorporated directly into water molecules of precipitation. Concentrations of ³H in precipitation have been decreasing since that time (fig. 6) because of the exchange of water with the oceans, short half-life of ³H, and atmospheric thermonuclear weapons testing was stopped. Because the ³H concentration in the atmosphere was high for a relatively short period (10–15 years) about 50 years ago (fig. 6), its presence in groundwater can identify water that has been recharged during the last 50 years or mixtures that contain a fraction of post-1950s water. The ³H activities in precipitation prior to thermonuclear weapons testing are not well known but probably did not exceed about 2 to 8 TU (Plummer and others, 1993). Because ³H has a half-life of 12.32 years, water derived from precipitation before thermonuclear weapons testing would contain a maximum ³H activity of about 0.12 to 0.5 TU by the early 2000s. Clark and Fritz (1997) stated that during the mid-1990s, waters with ³H activities exceeding about 30 TU contained a considerable component of recharge from the 1960s or the 1970s, and activities exceeding 50 TU indicated recharge predominantly from the 1960s.

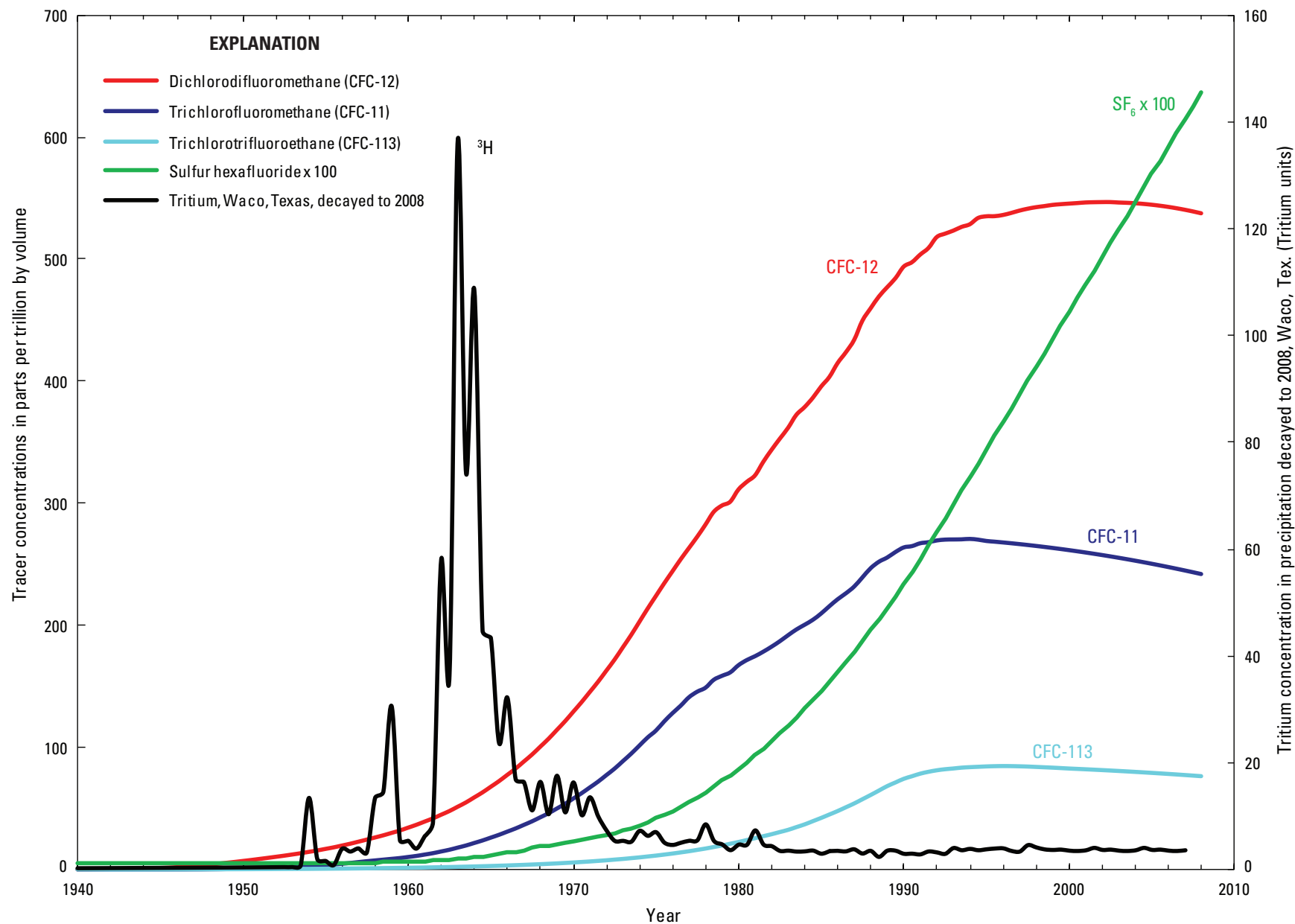


Figure 6. Atmospheric concentrations of chlorofluorocarbons, sulfur hexafluoride, and tritium in precipitation data in Waco, Texas, decayed to 2008 (International Atomic Energy Agency, 2010) (chlorofluorocarbon and sulfur hexafluoride data compiled by U.S. Geological Survey Chlorofluorocarbon Laboratory, U.S. Geological Survey, 2009b).

Helium-3 and Tritium

The radioactive decay product of ^3H is the noble gas ^3He . Simultaneous measurement of ^3H and ^3He provides an environmental tracer. Additionally, the $^3\text{H}/^3\text{He}$ ratio allows determination of the $^3\text{H}/^3\text{He}$ age of the groundwater through use of the equation of radioactive decay (Poreda and others, 1988; Schlosser and others, 1988; Schlosser and others, 1989;). For the concentration gradient of ^3He to be used in $^3\text{H}/^3\text{He}$ dating, the diffusive loss of the ^3He that is derived from the degradation of ^3H in the groundwater to the unsaturated zone must be minimal; therefore, ^3He must be confined in the aquifer. The ^3He confinement is the efficiency with which the ^3He produced by ^3H decay is retained in the aquifer. The ^3He produced in the aquifer by ^3H decay is transported to the water table by diffusion against the advective downward movement of the water; also lateral and vertical dispersion needs to be small enough not to substantively alter the $^3\text{H}/^3\text{He}$ ratio (Szabo and others, 1996).

The limitations of $^3\text{He}/^3\text{H}$ for age dating are many, but two of the important factors to consider are the presence of detectable ^3H and minimal excess ^4He . Initially, a sample would need to contain at least 1 TU to be datable by the $^3\text{He}/^3\text{H}$ method (L. Niel Plummer, U.S. Geological Survey, written commun., 2009), and water recharged prior to 1950 (prebomb) would contain less than 0.5 TU (Solomon and Cook, 2000). Another factor to consider would be the presence of helium derived from the Earth's mantle, referred to as mantle helium, or derived from uranium and thorium decay of the aquifer solids, referred to as "terrigenic helium." Excess terrigenic helium indicates water that is primarily older or contains very little younger water except where a local geological source of helium exists.

Helium-4

Water that has been in contact with the aquifer for long periods of time will accumulate ^4He (primarily from uranium and thorium decay in the aquifer), which can be used as a potential dating tool for groundwater recharged 10^1 to 10^8 years before present (Solomon and others, 1996). Samples with excess ^4He might indicate older, pre-1950s water—water that (in addition to other factors precluding $^3\text{He}/^3\text{H}$ age dating) is potentially not datable by the $^3\text{He}/^3\text{H}$ method because of excess ^4He (Solomon and Cook, 2000). Dissolved helium in groundwater is derived from terrigenic and atmospheric sources. The ^4He analysis was done primarily as an initial screening of samples collected for $^3\text{He}/^3\text{H}$ analysis; large amounts of excess ^4He indicate water that cannot be dated by the $^3\text{He}/^3\text{H}$ method, as described in the previous section. Helium accumulation in groundwater as indicated by ^4He concentration can also be another indicator of groundwater age (Solomon and others, 1996; Solomon, 2000; Hunt and others, 2010).

The concept of dating groundwater with ^4He is the longer the groundwater is in contact with the aquifer sediments, the greater the concentration of ^4He in groundwater (above air-water equilibrium) (Solomon, 2000). If external sources of ^4He are minimal (derived from the mantle or local uranium ore), then ^4He concentrations should correspond to travel times of the water. The ^4He is produced by decay of uranium-235/uranium-238 and thorium-232 in aquifer sediments. The ^4He method provides the opportunity to estimate the age of groundwater that recharged between 50 and 500 years—a range not covered by other techniques. A complicating factor is excess ^4He derived from external sources to the aquifer, such as underlying rocks or the mantle (Solomon, 2000).

The use of ^4He as an indicator of groundwater age can be difficult. A local helium accumulation rate needs to be determined, which is not always possible. Calculating a local helium accumulation rate requires data regarding the average concentration of uranium and thorium, on the flow path, along with other factors, for the aquifer (U.S. Geological Survey, 2011a, b). The quantification of the ^4He release rate can be difficult and is best suited for ^4He samples collected at sites where groundwater samples datable by other methods have been collected. The pairing of ^4He analysis with datable groundwater samples allows for the determination of the ^4He release rate (Solomon, 2000). Estimates of travel time for water from nearby wells completed in the same aquifer can be evaluated on the basis of ^4He concentration.

Carbon-14

^{14}C is an important radio-isotope tool for dating deep groundwater. It is continuously being produced by reaction of cosmic ray neutrons with nitrogen-14 (^{14}N) in the atmosphere and decays with a half-life of 5,730 years. ^{14}C is quickly oxidized to carbon dioxide (CO_2) where it is incorporated into the water cycle. With a relatively long radioactive half-life (5,730 years), ^{14}C is suitable for dating groundwaters that are thousands to tens of thousands of years old.

Dating of groundwater with ^{14}C is accomplished by measuring ^{14}C activities of dissolved inorganic and dissolved organic carbon in the water (DIC and DOC). Dissolved CO_2 , carbonic acid, bicarbonate, and carbonate are the four main species of DIC in ground water (Hem, 1985; Clark and Fritz, 1997). Groundwater cut off from the modern atmospheric reservoir can be dated by using ^{14}C if sufficient time has passed for measurable (detectable) decay of the initial ^{14}C activity (A_0) which is dependent upon the analytical capabilities of the laboratory, namely the detection capability and precision associated with it. Measured ^{14}C activities are expressed as a percent of modern carbon (pmc); the activity of modern carbon is defined as 95 percent of the ^{14}C activity in 1950 of the National Bureau of Standards (NBS) oxalic standard (Clark and Fritz, 1997), which approximates the ^{14}C activity of wood grown in 1890 that was relatively free of CO_2 from fossil-fuel sources. A discussion of how the measured ^{14}C are used to calculate the apparent ages can be found in the section "Paleowaters."

Major Ion Chemistry as an Indicator of Groundwater Evolution and Travel Time

Analytical results of major ion chemistry sampled from groundwater from wells developed into the Chicot, Evangeline, and Jasper aquifers can be characterized as predominately calcium-bicarbonate waters (fig. 7). The sediments have been described as containing limestone, calcite (CaCO_3), dolomite ($\text{CaMg}(\text{CO}_3)_2$), and gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) (Popkin, 1971), which is consistent with producing predominantly calcium-bicarbonate type waters. The relatively shallow wells and even the deeper wells to the north and east of Houston are near the updip end of the aquifer, so water is relatively dilute and has generally homogeneous composition.

Sites where the water is characterized with a slightly different signature indicate there may be other factors or processes influencing the major ion chemistry. Water from three wells (TS-60-44-805, well 3; TS-60-45-513, well 15; and TS-60-45-114, well 25) developed in the Chicot aquifer yielded very low concentrations of major ions in comparison to water from the other wells developed in the Chicot aquifer (fig. 7). This composition may indicate recent, minimally evolved recharge water, dilution occurring from mixing with a source of localized recharge, or both. Two downgradient wells in the Jasper aquifer (YW-59-64-206, well 17; and TS-60-55-313, well 41) yield elevated concentrations of sodium and low concentrations of calcium; such composition is typically characterized by cation exchange process (fig. 7). Cation exchange occurs as water moves downgradient and exchanges dissolved calcium in water for dissolved sodium held on clay mineral surfaces. Such composition is typical of long groundwater flow paths and with older water that has had long periods of contact with the clay minerals (Szabo and others, 2006).

Dissolved Gases

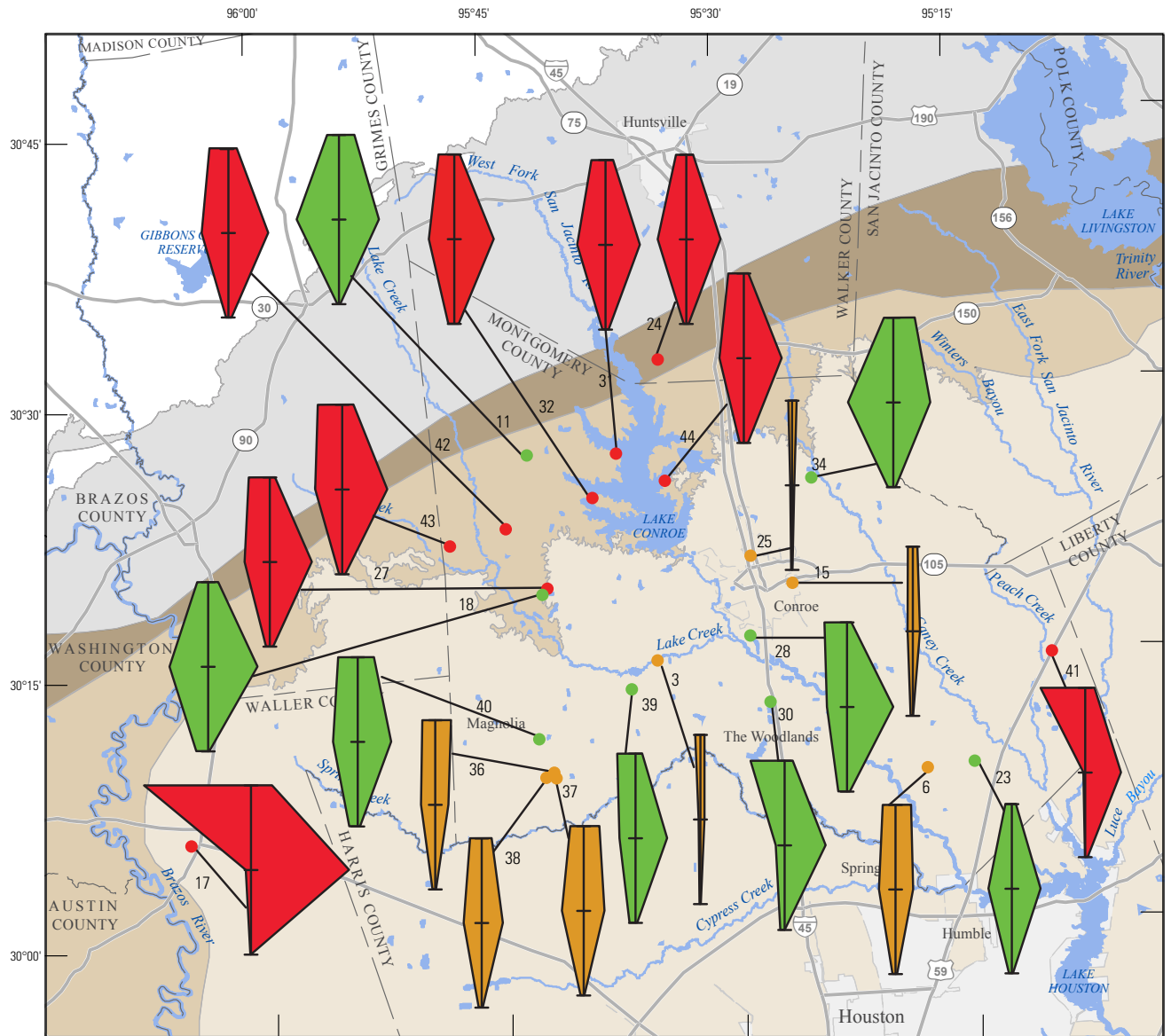
Dissolved gas concentrations, as well as the ratios of dissolved gas concentrations, can be used to calculate the recharge temperature of a groundwater sample because the solubility of gases in water varies as a function of temperature (Plummer and others, 2004). Determining the groundwater temperature is important because concentrations of CFCs (upon which groundwater ages are determined) are based on Henry's law solubility, which in turn is dependent on the groundwater temperature at the time of recharge and also altitude (pressure) at the location of recharge. Land-surface altitudes at all sites were used for recharge altitudes because actual recharge locations were unknown, but because the deposited sediments were part of a delta complex aggrading at the margin of the Gulf resulting in the relative flat topography of the study region that allowed for the assumption of minimal change in altitude with time and distance and therefore the current land-surface

altitude at each sampled site, was a reasonable approximation of recharge altitude. Gas concentrations and therefore calculated recharge temperatures and groundwater ages have little sensitivity to estimated recharge altitudes over the relatively small range in the altitude of the study area (Plummer and Busenberg, 2000).

Most dissolved gas samples contained little excess air (0.9 to 5.8 cubic centimeters [cm^3]) in groundwater samples collected from the Chicot, Evangeline, and Jasper aquifers (Oden, 2011) (0.9 to 3.1 cm^3 in samples collected from the Evangeline and Jasper aquifers, appendix 4). The small amount of excess air within the samples is consistent with diffuse rather than focused recharge. Diffuse recharge occurs over a large area as water from precipitation infiltrates and percolates through the unsaturated zone to the water table. Focused recharge occurs at discrete locations such as along a preferential pathway or location (Nimmo and others, 2002). Focused recharge can occur rapidly, resulting in larger quantities of excess air (more than about 6 cm^3) being trapped in aquifer pores and dissolving into the groundwater under recharge conditions.

Mean recharge temperatures determined from DG ranged from 10.6 to 23.5 °C in groundwater samples collected from the Chicot, Evangeline, and Jasper aquifers (Oden, 2011). Modern recharged waters should be within a few degrees of the mean annual temperature for the region. The mean annual temperature for Houston Intercontinental Airport over 30 years (1971–2000) was 20.4 °C (National Oceanic and Atmospheric Administration, 2010). The median recharge temperature at all sites was 15.7 °C (table 3). Field water temperatures measured at the time of sampling were typically higher than the recharge temperature determined by using DG, with a median difference of 8.0 °C (table 3), indicating that groundwater at the time of sampling probably recharged at lower temperatures a considerable time ago than it did at the time of this study (2008 and 2011). Another factor affecting the temperature of the groundwater was the likelihood that most recharge in the region might occur in winter and early spring, which are the coolest times of the year. In addition, groundwater temperature was not measured in situ, and the water might have warmed during the process of pumping it to the surface for sample collection.

One site located in Waller County (YW-59-64-206) had an anomalously high mean recharge temperature of 51 °C, which is a mean recharge temperature that is not plausible. Water collected from this well also contained an anomalously high concentration of methane and low concentrations of the other gases. Water from this well has most likely undergone a more complex evolution than other groundwater in the study area, and recharge temperature could not be determined accurately from the nitrogen and argon gas concentrations in this sample. Nitrogen and argon gases might have been stripped from the sample by exsolution of the methane during sampling (U.S. Geological Survey, 2011a, b). The DG data from this well with a mean recharge temperature of 51 °C was eliminated from the analysis, and the aforementioned minimum, maximum, and median recharge temperatures (table 3) do not include this outlier.



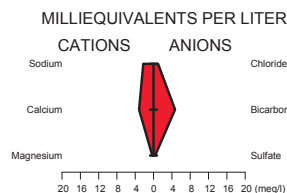
Base from U.S. Geological Survey 1:24,000-scale digital data
Albers Equal Area Projection, Texas Mapping System
North American Datum of 1983

Aquifer data from Strom and others, 2003 a,b,c
and Kasmarek and Robinson, 2004

EXPLANATION

- Chicot aquifer**
- Evangeline aquifer**
- Burkeville confining unit**
- Jasper aquifer**

- 6 - Well developed into the Chicot Aquifer
(6) - Map Identifier
- 11 - Well developed into the Evangeline Aquifer
(11) - Map Identifier
- 17 - Well developed into the Jasper Aquifer
(17) - Map Identifier



WATER CHEMISTRY DIAGRAM - Shows major chemical constituents in milliequivalents per liter (meq/L). The diagram can be used to compare and characterize types of water.



Figure 7. Water chemistry in the Chicot, Evangeline, and Jasper aquifers in April–May 2011, Montgomery, Walker, and Waller Counties, Texas.

Table 3. Summary of recharge temperatures and field water temperatures for wells sampled in and around Montgomery County, Texas during March–September 2008 and April–May 2011.

[°C, degrees Celsius]

Temperature type	Sample count	Minimum temperature (°C)	Median temperature (°C)	Maximum temperature (°C)
Recharge ¹	45	10.6	15.7	23.5
Field ²	64	20.6	23.7	31.1

¹Includes 2 wells (TS-60-55-710 and TS-60-53-516) resampled for dissolved gases in 2011.

²Includes the field water temperatures for the 20 wells resampled in 2011.

Groundwater Age

Modern Environmental Tracers

Groundwater ages are a measure of the time since the water entered the saturated zone and was isolated (through additional recharge) from the atmosphere to set the “age” (time elapsed since recharge) of the water. The age of groundwater is estimated from concentrations of dissolved chemicals or isotopes used as environmental tracers (such as CFCs, SF₆, and ³H) and comparison of the equivalent atmospheric concentration of each tracer to the atmospheric input signal for that tracer. Factors affecting the isolation time can be porosity of the unsaturated zone, recharge rate, and magnitude of water-table fluctuations (Plummer and Busenberg, 2000).

Groundwater ages commonly are termed “apparent age” because the ages are modeled by using simplifying assumptions regarding transport processes that may affect the concentration of environmental tracers (CFCs, SF₆, and ³He/³H) in the water that was recharged and isolated from the atmosphere (Plummer and Busenberg, 2000). The simplest and most common transport assumption in groundwater age dating is piston flow, in which the constituent concentration is not altered by mixing or dispersion from the point of entry to the measurement point in the aquifer. Determination of groundwater ages by using a piston-flow model is likely an oversimplification because mixing and dispersion often occur during groundwater flow (Rupert and Plummer, 2009). The effects of mixing and dispersion tracer concentrations are beyond the scope of this project, and piston flow is assumed for estimating apparent groundwater ages.

Paleowaters

¹⁴C is typically reported as percentages of modern ¹⁴C concentrations (Clark and Fritz, 1997). When ¹⁴C is used as a tool to estimate groundwater ages, the carbon is considered to represent the total DIC in the groundwater. The DIC in most groundwater flow paths will interact with the carbonate minerals and sources of ¹⁴C-free deep CO₂, resulting in a decreased pmc and apparent groundwater ages to be older than actual. To achieve more accurate estimated groundwater ages, the ¹⁴C pmc can be corrected by using a geochemical reaction path model which accounts for the sources and sinks of carbon along a flow path (Plummer and others, 1983; Plummer and others, 1991).

Chemical and isotopic data were interpreted by using the NETPATH model (Plummer and others, 1994) to adjust initial ¹⁴C activities for geochemical reactions. NETPATH uses equations of chemical mass balance, electron balance, and isotope mass balance to define possible net geochemical reactions between the initial and final water along a specified groundwater flow path. Geochemical reactions are constrained to occur among reasonable reactant and product minerals and gases, and they are consistent with the observed geochemistry and available isotopic data of the groundwater. Geochemical reaction models are then solved as an isotope-evolution problem (Wigley and others, 1978), accounting for isotope fractionation along the flow path to predict the isotopic composition at the end point in the reaction, including adjustment of the initial ¹⁴C activity for geochemical reactions (Plummer and Sprinkle, 2001).

Plummer and Sprinkle (2001, p. 144–145) described traditional and NETPATH approaches to radiocarbon dating of dissolved inorganic carbon (DIC) in groundwater for the purpose of determining adjusted ¹⁴C radiocarbon ages:

Traditionally, hydrologists have applied some of the well-known inorganic adjustment models (Ingerson and Pearson 1964; Mook 1972; Tamers 1975; Fontes and Garnier 1979; Eichinger 1983) to DIC of water from a single well to estimate adjusted ¹⁴C ages. The approach is illustrated in [figure 8.4]. This approach is well suited for geochemical systems undergoing relatively simple water–rock reactions, such as carbonate-mineral dissolution, gypsum dissolution, Ca/Na [calcium/sodium] ion exchange, CO₂ gas dissolution, and isotope exchange between soil CO₂, calcite, and DIC during recharge. Wigley [and others] (1978) present Rayleigh distillation and isotope mass-balance models to predict isotopic evolution in carbonate mineral water systems where both dissolution (incoming carbon) and precipitation (outgoing carbon with isotopic fractionation, including gas evolution) reactions occur, and they propose a general approach for constructing radiocarbon adjustment models for evolutionary waters.

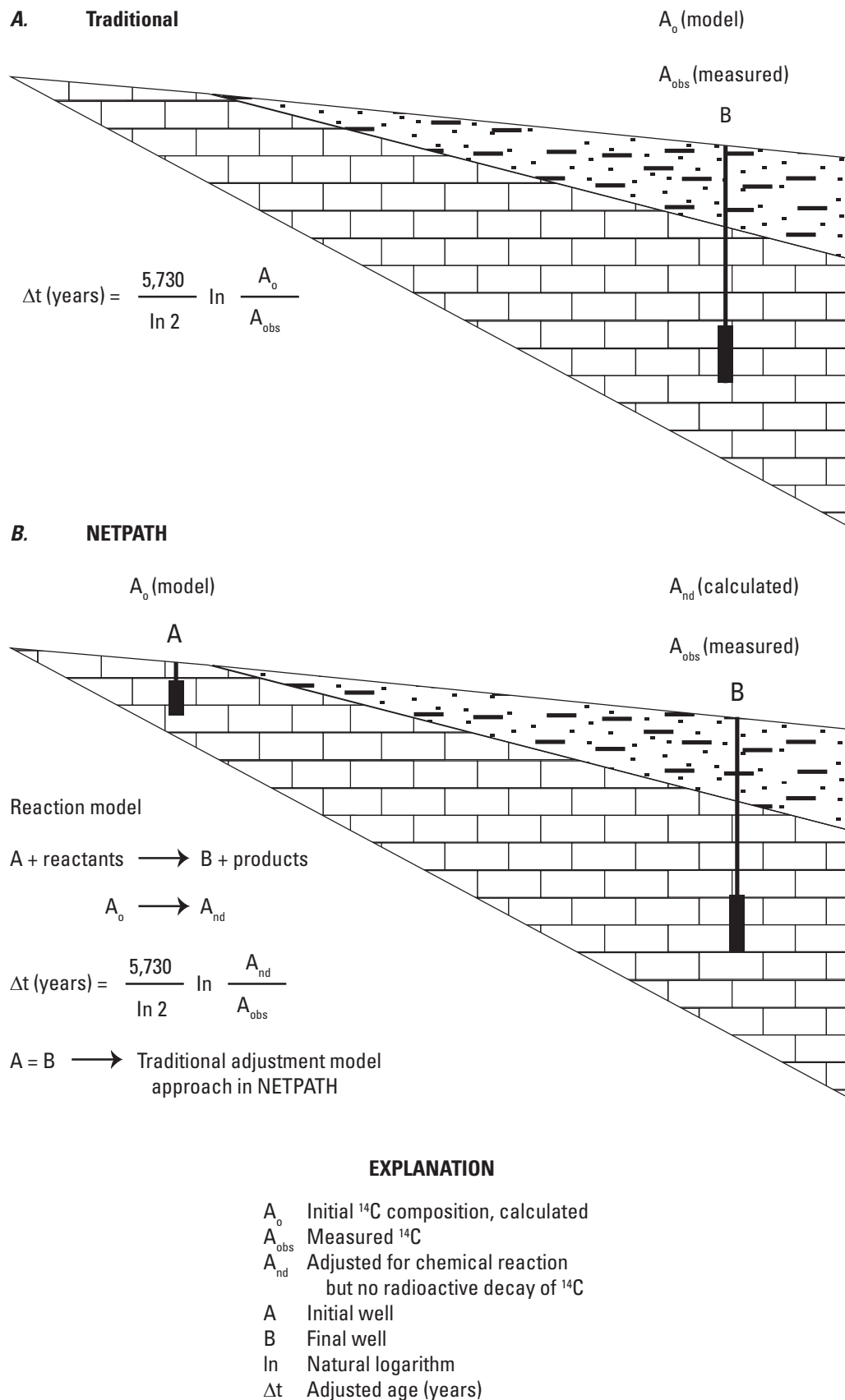


Figure 8. Conceptual approaches to radiocarbon dating of dissolved inorganic carbon (DIC) in groundwater: A. Traditional. B. NETPATH (modified from Plummer and Sprinkle, 2001).

NETPATH (Plummer [and others] 1994) incorporates the modeling approach of Wigley [and others] (1978) and can be used to construct ^{14}C -adjustment models for complex hydrochemical systems that cannot be treated by previous DIC adjustment models. The approach is shown in [figure 8B]. By combining carbon mass-balance equations with Rayleigh distillation equations for all incoming carbon sources and all isotopically fractionating outgoing carbon phases, the initial ^{14}C (A_0) is adjusted for the modeled geochemical reactions [A_{nd} in figure 8B]. NETPATH includes most of the well-known adjustment models that can be applied to the initial water to obtain estimates of A_0 . In radiocarbon dating of DIC in groundwater using NETPATH, the traditional adjustment models are usually applied to the initial water only, where, in the recharge portions of aquifers *** the geochemical reactions are usually relatively simple. In general use, the initial and final waters are defined separately in NETPATH. NETPATH is then used to describe the geochemical reactions that reproduce the chemical and $\delta^{13}\text{C}$ isotopic composition of DIC in the final water. This, in effect, develops a separate adjustment model for each water analysis. The adjustment is applied to the initial ^{14}C to compute the ^{14}C expected in DIC at the final well, as if there were no radioactive decay (A_{nd}) [figure 8B]. The adjusted no-decay ^{14}C activity is then used with the measured ^{14}C activity to compute travel time from the initial to the final point. Further details of radiocarbon dating applications in NETPATH are given in Plummer [and others] (1994).

Plummer and others (1994, p. 25) explained that “NETPATH considers nine options (adjustment models) for definition of A_0 or the initial ^{14}C along the flow path.” Three of the models were considered to represent the conditions that defined the initial ^{14}C ($A_{0\text{TDIC}}$), 1. Ingerson and Pearson (1964), 2. Fontes and Garnier (1979), and 3. Eichinger (1983). The model of Ingerson and Pearson (1964) assumed a carbonate dissolution model to estimate $A_{0\text{TDIC}}$ based on the ^{13}C data for the inorganic carbon system. The model of Fontes and Garnier (1979) used a two-stage evolution of recharge waters that accounts for the dissolution and isotopic exchange of carbonate minerals with CO_2 in the unsaturated zone and isotopic exchange with carbonate rocks in the saturated zone. The Eichinger (1983) model developed an isotope-exchange/mass-balance model for equilibrium isotopic exchange for introduction of soil CO_2 into the water and equilibrium exchange between dissolved inorganic carbon and the carbonate rock.

To simulate geochemical evolution and interpret carbon net mass balances, NETPATH calculated mass transfer

of phases for calcite (CaCO_3), dolomite ($\text{CaMg}(\text{CO}_3)_2$), gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), Ca/Na ion exchange, and CO_2 -gas, mixing between the Chicot and Evangeline aquifer waters, groundwater and isotopic exchange of carbon between dissolved inorganic carbon as bicarbonate and CO_2 gas, and carbon derived by dissolution from solid calcite and dolomite source in the aquifers. Carbon fractionation factors for the inorganic ^{13}C used the approach identified by Mook (1980) and Mook and others (1974). A $\delta^{13}\text{C}$ of 0.0 per mil (‰) was assumed for the carbonate minerals. An initial $\delta^{13}\text{C}$ of -25‰ was used for the soil-gas CO_2 assuming an “open” system where soil gas reservoir supplied CO_2 to groundwater (Clark and Fritz, 1997; Kendall and McDonnell, 1998). The initial ^{14}C activity of 100 pmc was used for the A_0 for the soil-gas CO_2 . Each net reaction was checked for consistency between the observed ^{14}C and the calculated $\delta^{13}\text{C}$ as a way to calibrate the models representing results from each well. The net difference between the observed and calculated $\delta^{13}\text{C}$ was generally less than plus or minus 1‰, although in a few cases it was not possible to constrain the model to this small of a difference between the observed and simulated values. Table 4 shows the initial percent modern carbon (A_0) along with calculated (NETPATH output) and observed (laboratory measured) values for $\delta^{13}\text{C}$ and ^{14}C and the adjusted ages calculated by using NETPATH and the dissolution/precipitation of minerals used in the models along individual flow paths, and the percent mixing for models where mixing was used with composition from more than one initial well to calculate the mass transfer of phases along a flow path. The sensitivity of the models to the assumed $\delta^{13}\text{C}$ for the carbonate minerals was evaluated by using input $\delta^{13}\text{C}$ of -1.0‰ and 1.0‰ for one model from each aquifer to determine the uncertainty of the adjusted ages (table 5). Generally there was very little sensitivity to the carbonate mineral $\delta^{13}\text{C}$ within this limited range of input values.

All three of the models were constrained by calculating $\delta^{13}\text{C}$ close to the observed $\delta^{13}\text{C}$. Calculated reaction used to adjust ^{14}C ages for any well simulated in our modeling efforts represented the overall mass transfer of phases calculated between the initial water and water from a particular final well rather than the mass transfer that would be calculated incrementally between successive wells. Although the wells were along generalized flow paths, the calculated mineral mass transfers were actually independent of flow path (Plummer and Sprinkle, 2001). For sites with adjusted ages that included mixing models involving waters from two separate initial wells, the selection of the second well or water used to mix along a flow path was selected on the basis of an assumption that the water analysis from this site best represented the mixing condition that may be occurring along the flow path. Table 4 provides information on the wells used to adjust for the individual ^{14}C ages along the generalized groundwater flow paths.

Table 4. Summary of adjusted carbon-14 ages and mineral mass transfer in the Chicot, Evangeline, and Jasper Aquifers, Montgomery County, Texas.

[A₀, initial ¹⁴C composition; ¹⁴C, radio-isotope of carbon; ¹³C, stable-isotope of carbon; Ca, calcium; Na, sodium; Ca/Na, ratio of sodium to calcium; CO₂, carbon dioxide; mmol/kg, millimole per kilogram; >, greater than; --, not determined]

Aquifer	Station name	Map identifier (figure 9, table 1)	Wells (by map identifier) or rainwater used to adjust ¹⁴ C ages	A ₀ Initial percent modern carbon calculated ¹	¹⁴ C Percent modern carbon observed	¹⁴ C percent modern carbon calculated	¹³ C (per mil) observed	¹³ C_calc (per mil) calculated	¹⁴ C adjusted ages in years before present ¹
Chicot	TS-60-45-114	25	--	--	101.53	--	--	--	Modern
Chicot	TS-60-45-513	15	25 to 15	88	82.80	96.80	-21.10	-23.20	Modern
Chicot	TS-60-51-811	37	25 to 37	88	66.57	75.47	-16.97	-17.01	900
Chicot	TS-60-51-814	38	25 to 38	88	36.52	66.00	-15.00	-13.80	5,000
Chicot	TS-60-54-805	6	25 to 6	88	93.35	73.04	-17.17	-17.10	Modern
Chicot	TS-60-51-809	36	25 to 36	89	75.52	82.17	-17.70	-18.70	650
Evangeline	TS-60-35-503	11	rainwater ² to 11	98	59.75	61.84	-15.87	-15.46	1,200
Evangeline	TS-60-35-907	32	11 to 32	63	1.02	54.60	-11.80	-12.83	33,000
Evangeline	TS-60-37-909	34	11 to 38 to 34	47	17.72	5.06	-10.87	-9.79	8,000
Evangeline	TS-60-43-511	18	38 to 18	58	28.39	19.97	-7.28	-8.23	900
Evangeline	TS-60-45-716	28	11 to 18 to 28	36	2.54	36.00	-9.88	-9.70	26,000
Evangeline	TS-60-52-199	39	11 to 18 to 39	46	0.29	45.49	-6.89	-8.30	42,000
Evangeline	TS-60-51-599	40	11 to 18 to 40	37	0.75	37.00	-8.07	-7.20	32,000
Evangeline	TS-60-53-516	30	25 to 30	89	86.90	93.00	-21.40	-21.70	Modern
Evangeline	TS-60-55-710	23	11 to 23	63	44.30	57.70	-16.51	-16.10	2,700
Jasper	YU-60-28-802	24	rainwater ² to 24	98	11.67	57.41	-14.87	-12.45	13,000
Jasper	TS-60-36-410	31	24 to 31	59	6.06	10.44	-12.04	-13.40	18,000
Jasper	TS-60-36-812	44	24 to 44	59	0.62	10.80	-12.55	-13.77	37,000
Jasper	TS-60-42-206	43	24 to 43	59	7.88	8.60	-11.30	-11.10	16,000
Jasper	TS-60-35-703	42	24 to 42	59	5.75	9.90	-11.53	-12.70	19,000
Jasper	TS-60-43-514	27	24 to 27	59	2.16	9.69	-11.59	-12.34	27,000
Jasper	YW-59-64-206	17	24 to 17	59	0.03	4.25	-4.68	-5.44	>42,000
Jasper	TS-60-55-313	41	24 to 41	59	0.35	11.67	-13.65	-14.74	42,000

Table 4. Summary of adjusted carbon-14 ages and mineral mass transfer in the Chicot, Evangeline, and Jasper Aquifers, Montgomery County, Texas.—Continued

[A₀, initial ¹⁴C composition; ¹⁴C, radio-isotope of carbon; ¹³C, stable-isotope of carbon; Ca, calcium; Na, sodium; Ca/Na, ratio of sodium to calcium; CO₂, carbon dioxide; mmol/kg, millimole per kilogram; >, greater than; --, not determined]

Aquifer	Station name	Map identifier (figure 9, table 1)	Wells (by map identifier) or rainwater used to adjust ¹⁴ C ages	Initial well 1 percent mixing	Initial well 2 percent mixing	Calculated mass transfer				
						Calcite (mmol/kg) water	Dolomite (mmol/kg) water	Gypsum (mmol/kg) water	Ca/Na exchange (mmol/kg) water	CO ₂ (mmol/kg) water
Chicot	TS-60-45-114	25	--	--	--	--	--	--	--	--
Chicot	TS-60-45-513	15	25 to 15	--	--	1.30	0.12	--	0.50	4.71
Chicot	TS-60-51-811	37	25 to 37	--	--	0.88	0.12	0.74	0.56	--
Chicot	TS-60-51-814	38	25 to 38	--	--	1.29	0.12	--	0.46	-0.87
Chicot	TS-60-54-805	6	25 to 6	--	--	1.27	0.13	--	0.53	0.72
Chicot	TS-60-51-809	36	25 to 36	--	--	0.55	0.11	0.62	0.54	--
Evangeline	TS-60-35-503	11	rainwater ² to 11	--	--	2.11	0.09	0.96	0.68	--
Evangeline	TS-60-35-907	32	11 to 32	--	--	--	0.26	-0.99	0.24	-1.41
Evangeline	TS-60-37-909	34	11 to 38 to 34	85	15	0.09	--	0.79	-0.35	--
Evangeline	TS-60-43-511	18	38 to 18	--	--	2.20	0.51	-1.55	-0.05	--
Evangeline	TS-60-45-716	28	11 to 18 to 28	28	72	--	0.02	0.40	0.82	--
Evangeline	TS-60-52-199	39	11 to 18 to 39	58	42	--	--	-1.07	0.40	-2.48
Evangeline	TS-60-51-599	40	11 to 18 to 40	33	67	-0.40	--	--	0.49	-2.02
Evangeline	TS-60-53-516	30	25 to 30	--	--	--	0.20	2.01	1.79	1.30
Evangeline	TS-60-55-710	23	11 to 23	--	--	-2.64	0.08	1.14	-0.32	--
Jasper	YU-60-28-802	24	rainwater ² to 24	--	--	2.01	0.15	0.11	0.59	-1.46
Jasper	TS-60-36-410	31	24 to 31	--	--	0.46	0.04	-0.27	0.24	--
Jasper	TS-60-36-812	44	24 to 44	--	--	0.16	0.10	-0.17	0.32	--
Jasper	TS-60-42-206	43	24 to 43	--	--	1.52	0.04	-0.81	0.85	--
Jasper	TS-60-35-703	42	24 to 42	--	--	0.77	-0.00	-0.34	0.53	--
Jasper	TS-60-43-514	27	24 to 27	--	--	0.76	0.08	-0.41	0.64	--
Jasper	YW-59-64-206	17	24 to 17	--	--	7.79	-0.11	-3.32	5.73	--
Jasper	TS-60-55-313	41	24 to 41	--	--	-0.12	-0.14	0.69	2.03	--

¹These are averages based on results from Ingerson and Pearson (1964), Fontes and Garnier (1979), and Eichinger (1983.)

²Because an upgradient well was not sampled for modern ¹⁴C, rainwater used in lieu of the upgradient well.

Table 5. Sensitivity analysis for modeled carbon-14 adjusted ages for selected wells within the Chicot, Evangeline, and Jasper aquifers, Montgomery County, Texas.

[A₀, initial ¹⁴C composition; ¹⁴C, radio-isotope of carbon; ¹³C, stable-isotope of carbon; Ca, calcium; Na, sodium; Ca/Na, ratio of sodium to calcium; CO₂, carbon dioxide; mmol/kg, millimole per kilogram; --, not determined]

Aquifer	Station name	Map identifier (table 1)	Wells used to adjust ¹⁴ C ages (map identifier)	Calculated mass transfer				
				A ₀ initial percent modern carbon calculated ¹	¹⁴ C percent modern carbon observed	¹⁴ C percent modern carbon calculated	¹³ C (per mil) observed	¹³ C_calc (per mil) calculated
0.0 per mil carbonate phase								
Chicot	TS-60-45-114	25	15 to 25	88	82.80	96.80	-21.10	-23.20
-1.0 per mil carbonate phase								
Chicot	TS-60-45-114	25	15 to 25	88	82.80	96.70	-21.11	-23.2
1.0 per mil carbonate phase								
Chicot	TS-60-45-114	25	15 to 25	88	82.80	96.77	-21.11	-23.18
0.0 per mil carbonate phase								
Evangeline	TS-60-35-907	32	11 to 32	63	1.02	54.60	-11.80	-12.74
-1.0 per mil carbonate phase								
Evangeline	TS-60-35-907	32	11 to 32	63	1.02	54.6	-11.8	-12.83
1.0 per mil carbonate phase								
Evangeline	TS-60-35-907	32	11 to 32	63	1.02	54.6	-11.8	-12.65
0.0 per mil carbonate phase								
Jasper	TS-60-42-206	43	24 to 43	59	7.88	8.60	-11.30	-11.10
-1.0 per mil carbonate phase								
Jasper	TS-60-42-206	43	24 to 43	57	7.88	8.6	-11.3	-11.23
1.0 per mil carbonate phase								
Jasper	TS-60-42-206	43	24 to 43	61	7.88	8.6	-11.3	-10.7

Table 5. Sensitivity analysis for modeled carbon-14 adjusted ages for selected wells within the Chicot, Evangeline, and Jasper Aquifers, Montgomery County, Texas.—Continued

[A₀, initial ¹⁴C composition; ¹⁴C, radio-isotope of carbon; ¹³C, stable-isotope of carbon; Ca, calcium; Na, sodium; Ca/Na, ratio of sodium to calcium; CO₂, carbon dioxide; mmol/kg, millimole per kilogram; --, not determined]

Aquifer	Station name	Map identifier (table 1)	Calculated mass transfer					
			¹⁴ C adjusted ages in years befor present ¹	Calcite (mmol/kg) water	Dolomite (mmol/kg) water	Gypsum (mmol/kg) water	Ca/Na exchange (mmol/kg) water	CO ₂ (mmol/kg) water
0.0 per mil carbonate phase								
Chicot	TS-60-45-114	25	Modern	1.30	0.12	--	0.50	4.71
-1.0 per mil carbonate phase								
Chicot	TS-60-45-114	25	Modern	0.18	0.06	--	0.05	4.71
1.0 per mil carbonate phase								
Chicot	TS-60-45-114	25	Modern	0.18	0.06	--	0.05	4.71
0.0 per mil carbonate phase								
Evangeline	TS-60-35-907	32	33,000	--	0.26	-0.99	0.24	-1.41
-1.0 per mil carbonate phase								
Evangeline	TS-60-35-907	32	33,000	--	0.26	-0.99	0.24	-1.41
1.0 per mil carbonate phase								
Evangeline	TS-60-35-907	32	33,000	--	0.26	-0.99	0.24	-1.41
0.0 per mil carbonate phase								
Jasper	TS-60-42-206	43	16,000	1.52	0.04	-0.81	0.85	--
-1.0 per mil carbonate phase								
Jasper	TS-60-42-206	43	15,000	1.52	0.04	-0.81	0.85	--
1.0 per mil carbonate phase								
Jasper	TS-60-42-206	43	16,000	1.52	0.04	-0.81	0.85	--

¹These are averages based on results from Ingerson and Pearson (1964), Fontes and Garnier (1979), and Eichinger (1983.)

Environmental Tracer Data and Apparent Groundwater Age

Modern Environmental Tracers

Of the 40 samples collected March–September 2008, 17 were from wells completed in the Chicot aquifer, 13 from wells completed in the Evangeline aquifer, and 7 from wells completed in the Jasper aquifer (table 1). Of the 37 samples collected for modern environmental tracers from wells completed in the Chicot, Evangeline or Jasper aquifer, water from 15 wells was datable by these modern environmental tracer methods (table 6) and were used for calculating recharge estimates presented later in this report. The remaining 25 samples collected in 2008 were not datable because either the concentrations of the modern environmental tracers measured were less than the expected reasonable concentrations within the datable range (apparent age older than 1950s), or the apparent ages were unrealistic when compared to nearby better constrained estimates of apparent groundwater ages, and three wells initially identified as Evangeline aquifer were later determined to be in the Burkeville confining unit. The samples obtained from the seven wells completed in the Jasper aquifer system had detectable concentrations of modern age

tracers, indicating the groundwater was theoretically datable; however, for six of the wells the groundwater was reportedly too old to be datable based on excess ^4He and little to no detectable ^3H in the samples, indicating there may have been a (1) low-level contamination of the equipment or sample, (2) poor well construction, (3) poor well development, or (4) any combination of these factors. Twenty wells from which groundwater samples were not datable by the modern environmental tracer methods in 2008 were resampled in 2011 for ^{14}C .

The hydrogeology of the study area needs to be taken into consideration when evaluating the apparent groundwater ages. There are numerous interbedded silt and clay layers (figs. 4 and 5) within the water-bearing sands of the Chicot and Evangeline aquifers. Multiple sand and clay layers that were relatively thin were identified by using the geophysical techniques described in the “Methods” section (fig. 5). In seven of the logged wells, clay lenses ranging from a few feet to tens of feet thick were identified in the unsaturated zone or near the land surface and might impede the downward movement of water from the surface to the aquifer. The borehole geophysical cross sections made from the few data points collected for this study show that on a local scale, groundwater flow paths, although complex, might have a larger lateral extent than previously discussed by Popkin (1971) and Kasmarek and others (2010). These interbedded clays create localized confinement in the Chicot aquifer which

Table 6. Apparent groundwater age derived by using samples collected during March–September 2008 from wells completed in the Chicot, Evangeline or Jasper aquifer, and the environmental tracer used for apparent age determination, Montgomery County, Texas.

[^4He , helium-4; $^3\text{He}/^3\text{H}$, helium-3/tritium; CFC-12, dichlorofluoromethane; SF_6 , sulfur hexafluoride]

Map identifier (fig. 1).	Station name	Aquifer	Sample date	Sample time	Apparent age (years)	Tracer
1	TS-60-53-719	Chicot	3/12/2008	1415	73	$^3\text{He}/^3\text{H}$
2	TS-60-53-720	Chicot	3/13/2008	1410	27	CFC-12
4	TS-60-45-413	Chicot	3/19/2008	845	62	^4He
5	TS-60-45-414	Chicot	3/19/2008	1215	23	$^3\text{He}/^3\text{H}$
7	TS-60-54-806	Chicot	3/24/2008	1200	71	$^3\text{He}/^3\text{H}$
10	TS-60-54-807	Chicot	3/26/2008	900	32	SF_6
12	TS-60-44-806	Chicot	3/27/2008	1230	48	CFC-12
14	TS-60-26-208	Jasper	4/21/2008	1400	62	CFC-12
16	TS-60-34-301	Evangeline	4/22/2008	1330	88	^4He
19	TS-60-63-110	Chicot	4/24/2008	1530	50	CFC-12
20	TS-60-37-309	Chicot	4/28/2008	1200	44	^4He
21	TS-60-54-702	Chicot	4/30/2008	1030	32	$^3\text{He}/^3\text{H}$
22	TS-60-44-212	Evangeline	7/10/2008	1224	825	^4He
25	TS-60-45-114	Chicot	7/18/2008	1135	35	$^3\text{He}/^3\text{H}$
30	TS-60-53-516	Evangeline	8/18/2008	1530	2,092	^4He

might mean the groundwater is older than the age range that can be determined with the environmental tracers used in this report. The Evangeline aquifer is considered a confined aquifer because of the difference in hydraulic head compared to the overlying Chicot aquifer. Where a confining unit separating the Chicot and Evangeline aquifers is absent, leakage or flow between the two aquifers is possible (Gabrysch and Coplin, 1990; Kasmarek and Strom, 2002); however, even in the absence of a discrete confining unit separating the Chicot and Evangeline aquifers, the Evangeline aquifer is considered confined because of the effects of the many interbedded clays in the Chicot on hydraulic heads (Gabrysch, 1984). The heterogeneity of the aquifer is such that there are reduced vertical flows in the system caused by interbedded clay layers and considerable mixing and dispersion which may make application of the piston-flow assumption problematic in this system, as in many others (Rupert and Plummer, 2009).

Most of the modern environmental tracer data indicate that the groundwater was recharged prior to the 1950s. Water of this age can be difficult to “date” with the modern environmental tracers used for this study in 2008. To date water samples by using $^3\text{He}/^3\text{H}$, the samples generally need to contain at least 2 TU of ^3H . Samples with 1 to 2 TU of ^3H can be dated in favorable conditions, but samples with less than 1 TU are difficult to date even under the most favorable conditions (L. Niel Plummer, U.S. Geological Survey, written commun., 2009). On the basis of these criteria, samples obtained from three wells (TS-60-45-414, TS-60-54-702, and TS-60-45-114) with more than 1 TU of ^3H are datable with the $^3\text{He}/^3\text{H}$ method. Samples obtained from two wells (TS-60-54-806 and TS-60-63-110) with less than 1 TU appear datable based on other tracer data (CFC and or SF_6) (table 7). Water collected from well TS-60-53-719 has less than 1 TU of ^3H determined with the ^3He ingrowth method and is considered datable at 73 years based on its $^3\text{He}/^3\text{H}$ data and on tracer data from nearby well TS-60-53-720 (table 6). Well TS-60-53-720 is located about 15 ft from well TS-60-53-719 and its

top screen is about 35 ft shallower. That well TS-60-53-720 is shallower in depth and intercepts younger water than the deeper well TS-60-53-719 is consistent with the conceptual hydrogeologic model (younger water is shallower than older water). Samples with little to no ^3H indicate premodern water (recharged before the 1950s) and thus would not be datable by either the CFCs or SF_6 method. Samples with no ^3H cannot be dated by using the $^3\text{He}/^3\text{H}$ method. Samples not datable by the $^3\text{He}/^3\text{H}$ method contained ^3H ranging from 0 to 0.83 TU (Oden, 2011).

The ^3H in precipitation was measured in Waco, Tex., from 1953 to about 1985 by the USGS, but there are no recent ^3H precipitation data in the Texas region (International Atomic Energy Agency, 2010). The measured ^3H concentrations in precipitation from Waco were computationally “decayed” for each year from end of ^3H precipitation data collection in Waco to time of sampling (March–September 2008) to project expected concentrations in precipitation. This computed ^3H decay series was compared to ^3H in precipitation data collected in Georgia during 1986–2007 at about the same latitude. On the basis of this comparison, precipitation in Texas (1986–2007) would be expected to contain ^3H ranging from 2 to 5 TU. Assuming the atmospheric background concentration of ^3H (prebomb) was similar or lower than the modern values of about 2 to 5 TU, prebomb water would have a ^3H concentration of about 0.3 TU or less if recovered from the aquifer (Robert L. Michel, U.S. Geological Survey, written commun., 2010).

In samples datable by the CFC, SF_6 , and $^3\text{He}/^3\text{H}$ methods, estimated age dates are generally within 5 years between the different tracers (table 7). The apparent groundwater ages in samples collected from two of five wells completed in the Chicot aquifer with apparent ages determined from more than one environmental tracer were more than 40 years. On the basis of other tracer data, only a minority of samples collected from wells completed in the Chicot or Evangeline aquifers represent groundwater young enough for SF_6 to be detected.

Table 7. Comparison of apparent ages determined from environmental tracers (helium-3/tritium, dichlorofluoromethane, and sulfur hexafluoride) for groundwater samples collected during March–September 2008 from wells completed in the Chicot aquifer in Montgomery County, Texas.

[$^3\text{He}/^3\text{H}$, helium-3/tritium; CFC-12, dichlorodifluoromethane; SF_6 , sulfur hexafluoride; --, not determined]

Map identifier (figs. 1, 11)	Station name	Aquifer	Sample date	Sample time	Apparent $^3\text{He}/^3\text{H}$ age (years)	Apparent CFC-12 age (years)	Apparent SF_6 age (years)
5	TS-60-45-414	Chicot	3/19/2008	1215	23	29	30
7	TS-60-54-806	Chicot	3/24/2008	1200	71	48	--
19	TS-60-63-110	Chicot	4/24/2008	1530	49	50	--
21	TS-60-54-702	Chicot	4/30/2008	1030	32	36	29
25	TS-60-45-114	Chicot	7/18/2008	1135	35	25	31

The detection of SF_6 in all 40 samples obtained from wells sampled in 2008 (Oden, 2011) might indicate a terrigenous, naturally occurring source of SF_6 (Busenberg and Plummer, 2000). An admixture of a small fraction of “young” (less than 60 years old) water at the top of extended well screen intervals is another possible explanation for the detection of SF_6 in all samples. Lastly, because blank samples are not collected and analyzed for any of the tracers, the possibility of slight sample contamination cannot be completely ruled out.

As with SF_6 , the CFC-11 and CFC-12 were detected in all samples and CFC-113 was detected in 33 samples (Oden, 2011). Given the apparent ages of groundwater which were mostly more than about 60 years (recharged prior to 1950), the widespread detection of CFCs was not expected. By using multiple tracers, however, samples from four wells (TS-60-45-414, TS-60-63-110, TS-60-54-702, and TS-60-45-114) completed in the Chicot aquifer yield apparent ages less than about 60 years (table 7), and the CFC-12 compound can be usable for groundwater of this age. The relatively small SF_6 and CFC concentrations measured even in samples of groundwater recharged less than about 60 years ago might be artifacts of well installation and development (Busenberg and Plummer, 2010), poor annular seals (U.S. Environmental Protection Agency, 1994), or a combination of these factors. Additionally, there may be nearby wells with multiple screened intervals in the aquifer(s), allowing for leakage of younger water to the older reservoirs of water and providing a conduit for cross-formational flow. Cross-formational flow or short-circuiting pathways are well known from karst aquifers such as limestones in Florida (Katz and others, 2007) but have also been recently documented in sands and clays of the High Plains (Landon and others, 2008; Landon and others, 2010) where heavy drawdown exists in a region in which wells penetrate and have open intervals to multiple aquifer units. Other possibilities are mixing, dispersion, preferential flow paths, or that the initial assumption of the piston-flow model is overly simplified for these aquifers.

With the lack of datable waters for the study, ^4He was used in cases where other tracers were not viable (appendix 5). Excess ^4He was detected in samples from most wells (Oden, 2011). The helium accumulation rate for the area is an important variable in the ^4He age calculations, and multiple independent samples measured for ^4He concentrations are needed to determine the helium accumulation rate in a regional aquifer (L. Niel Plummer, U.S. Geological Survey, oral commun., 2010). With samples from only five wells datable by multiple modern tracer methods used in this report (table 7), the ^4He accumulation rate could not be reliably estimated for the Chicot and Evangeline aquifers for this study. A helium accumulation rate of 1.9×10^{-10} cubic centimeters at standard temperature and pressure, per gram of water ($\text{cm}^3\text{STP/g}$), which is similar to the rate in a previous study by Busenberg and Plummer (2000). In that study, Busenberg and Plummer (2000) applied the helium accumulation rate measured in the Delmarva Peninsula, a sand aquifer in the North Atlantic Coastal Plain (NACP),

which is of similar composition to the Gulf Coast aquifer system (Trapp and Horn, 1997). A considerable difference, however, is that the NACP lacks both the occasional high levels of uranium enrichment found in the Texas Gulf Coast deposits and the somewhat U-rich volcanic ash layer interbeds (Kier and others, 1977; Cook, 1980). The use of this estimated accumulation rate is reasonable, as a first approximation, but may need to be revisited as more ^4He concentration data and datable waters become available.

In a few cases where multiple wells screened at different depths and aquifers were available in the same location, older waters occurred above younger waters. Such an observation cannot be explained by the piston-flow conceptual model. An age reversal with depth could reflect the effects of aquifer heterogeneity on groundwater flow paths or cross-formation flow through wellbores, which may account for this condition (Katz and others, 2007; Zinn and Konikow, 2007; Landon and others, 2008) as well as occurrence of preferential flow paths documented by Landon and others (2010). A detailed investigation into the occurrence of older waters above younger waters is beyond the scope of this report.

Modeling of Carbon-14 with NETPATH

NETPATH (Plummer and others, 1994) was used to calculate the ^{14}C ages of the groundwater samples, calcite saturation indices of groundwater samples, and mixing of two potential sources of groundwater.

Groundwater geochemical analytical well results for ^{14}C , ^{13}C , bicarbonate, and selected major ions were used in the geochemical model NETPATH to evaluate net flow path reactions to improve estimates for apparent groundwater ages by using model results from Ingerson and Pearson (1964), Fontes and Garnier (1979), and Eichinger (1983).

For 20 wells with samples not datable by modern environmental tracers in 2008, wells were resampled in 2011 for ^{14}C as an attempt to determine the age of the groundwater and estimate the rate of groundwater recharge to those wells. Apparent groundwater ages analyzed from water from selected wells screened into the Chicot, Evangeline, and Jasper aquifers in Montgomery County reflected the influence that thick accretionary wedges of interbedded sand and clay layers have on groundwater movement and residence times. Generally analysis for observed groundwater ^{14}C activity is measured from wells developed into the aquifer by drawing water from different depths within the aquifer. Consequently the observed ^{14}C activity in pmc may have represented a mixture of young and old groundwater withdrawn from unconfined and confined segments within the Chicot and Evangeline aquifers in Montgomery County. Adjusted ^{14}C ages from water from wells developed into the Jasper aquifer were all greater than or equal to 13 thousand (ka) indicating relatively long groundwater residence times and that mixing does not have much effect on these wells.

NETPATH-adjusted groundwater ages identified potential areas where local recharge may be occurring within the Chicot aquifer under water table conditions in contrast to areas where only slight amounts of recharge may be occurring and the groundwater may be under semiconfined conditions (fig. 9). Adjusted groundwater ages for wells (TS-60-45-114, well 25; TS-60-45-513, well 15; and TS-60-54-805, well 6) yielded “modern” water with observed ^{14}C activities of greater than 80 pmc (table 4). The adjusted “modern” age suggested that some recharge may be occurring possibly from the nearby West Fork of the San Jacinto River, other localized sources, or both (fig. 9). Adjusted groundwater ages for wells TS-60-51-811 (well 37), TS-60-51-814 (well 38), and TS-60-51-809 (well 36) yielded slightly older water ages suggesting shallow groundwater may be mixing with deeper older waters. The adjusted age for well TS-60-51-814 is 5 ka years, which is significantly older than apparent ages for wells TS-60-51-811 and TS-60-51-809, 900 and 650 years old, respectively (fig. 9), suggesting there may be a localized interbedded clay layer potentially creating semiconfined conditions near TS-60-51-814 or that pumping may be causing older deeper water to mix with the younger shallow water.

NETPATH-adjusted groundwater ages from wells developed into the Evangeline aquifer does not appear to move along a simple progression in age downgradient; however, localized mixing of water in the Evangeline aquifer with water from the overlying Chicot aquifer or possibly direct recharge from the land surface into the Evangeline aquifer was indicated by the considerable groundwater age variability. The possible effect of preferential flow paths through zones of varying hydraulic conductivity among the interbedded sand and clay layers was indicated. Groundwater from downgradient wells TS-60-53-516 (well 30) and TS-60-55-710 (well 23) yielded adjusted apparent ages of “modern” and 2.7 ka respectively that represented a considerable decrease in apparent age from the upgradient wells TS-60-35-907 (well 32), TS-60-37-909 (well 34), and TS-60-45-716 (well 28) of 33, 8, and 26 ka, respectively. Wells TS-60-53-516 and TS-60-55-710 are located near the West Fork of the San Jacinto River suggesting a relatively short residence time that would be consistent with local recharge and mixing of younger groundwater from the overlying Chicot aquifer. Groundwater from well TS-60-43-511 (well 18) yielded an adjusted age of 900 years before present, decreasing in age from upgradient wells TS-60-35-907 and TS-60-35-503 (well 11), 33 and 1.2 ka, respectively (fig. 9). The decrease in the adjusted age at well site TS-60-43-511 suggested that the aquifer lithology is permeable in this area with recharge entering directly from the land surface or that there is mixing of young water from the overlying Chicot aquifer which may be induced from pumping. Well TS-60-43-511 is located in the general area of the boundary between the unconfined and confined portion of the Evangeline and Chicot aquifers, where mixing with waters from the Chicot aquifer is likely. Modeled ^{13}C values for the observed and calculated values

for TS-60-43-511 were comparable only when Chicot aquifer water from well TS-60-51-814 was used to adjust ^{14}C ages (table 4).

NETPATH-adjusted groundwater ages from wells developed into the Jasper aquifer generally showed a simple progression in age as groundwater moved downgradient along the flow path (fig. 9). The Jasper aquifer is under confined conditions beneath the Burkeville confining unit, prohibiting any mixing from the overlying Evangeline aquifer. The confining unit for the Jasper aquifer is thick, continuous, and expansive in contrast to the Evangeline aquifer where confinement may be poor. Adjusted groundwater ages progressing from 13 to greater than 42 ka indicated that generally the groundwater in the Jasper aquifer is older, deep groundwater compared to the Evangeline aquifer. In addition, the density of producing wells with open screens to multiple zones yielding large volumes of water in the Jasper aquifer was smaller than that in the Evangeline, which is the most used aquifer among these two; therefore, the potential development of preferential flow paths by overstressing the aquifer is somewhat less likely in the Jasper than the Evangeline aquifer.

Estimated Rates of Groundwater Recharge

Recharge is possibly one of the most difficult parameters of groundwater to quantify because it cannot be measured directly and therefore has to be estimated by using multiple methods (Delin and Faltese, 2007). Several methods of estimating recharge, including the use of the concentration of environmental tracers emphasized in the study, are available and each has advantages, disadvantages, and limitations (Scanlon, Healy, and Cook, 2002). Groundwater age distributions with vertical groundwater velocities can provide reasonable estimates of recharge (Solomon and Sudicky, 1991). The interpretation of environmental tracer data can be complicated by multiple factors that affect concentrations along groundwater flow paths, such as degradation, sorption, mixing, and transport through the unsaturated zone (Solomon and Cook, 2000). These factors cannot be readily avoided when planning a sampling program as they are often local in nature and no simple surrogate variable can be used as an indicator that might show where the effects are greatest.

To estimate the groundwater recharge rate for the Chicot, Evangeline, and Jasper aquifers by using the environmental tracers, the specific hydrogeologic properties of the aquifer (eq. 2 and 3) needed to be evaluated as indicated in a conceptual model of idealized flow through an unconsolidated aquifer (fig. 10). Water enters the aquifer (R) and moves along a flow path to a depth (z). If the depth (open interval of the well) and the apparent age of the water from that open interval (t) are known along with other properties, a recharge rate can be estimated. Recharge estimates in the unconfined

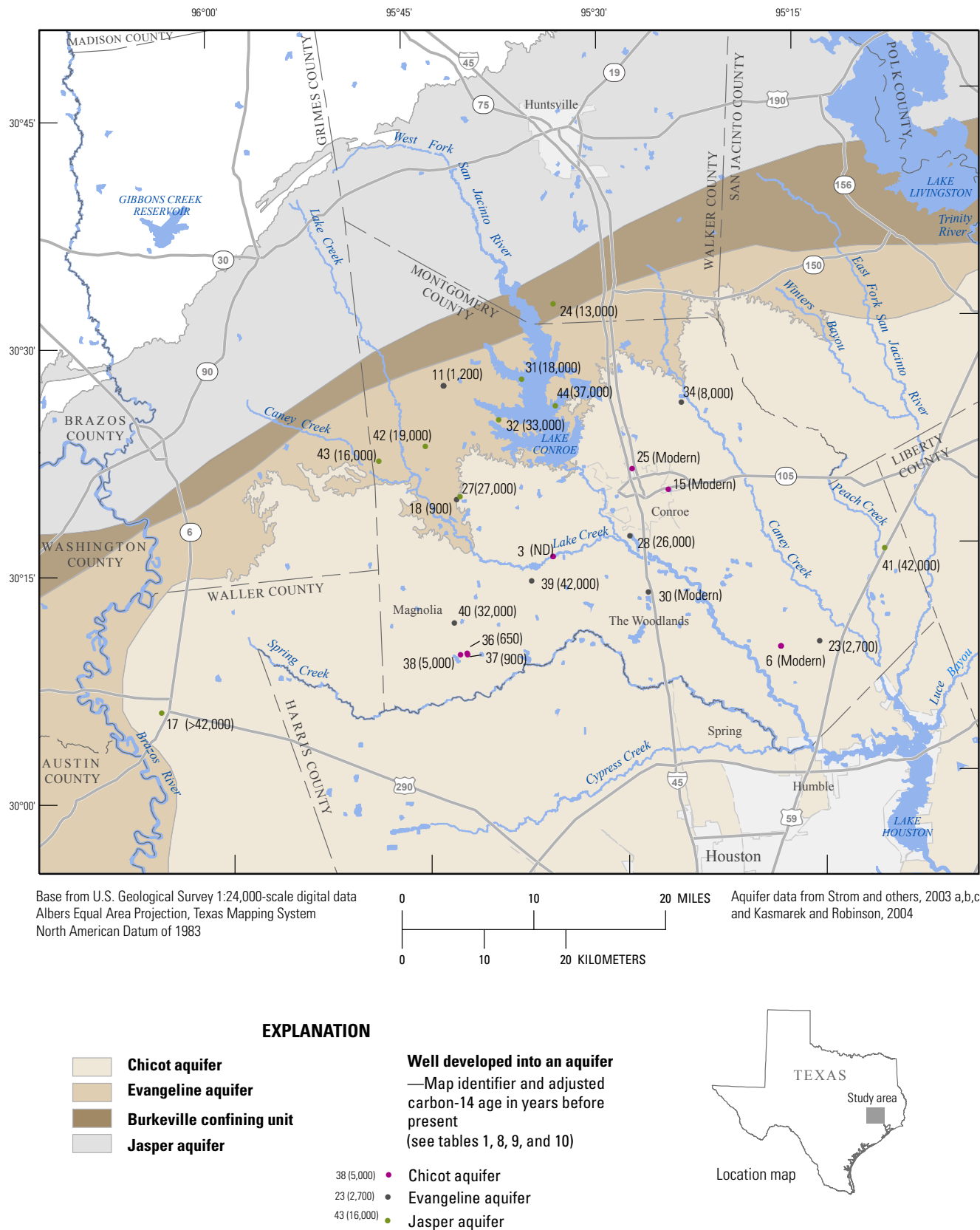
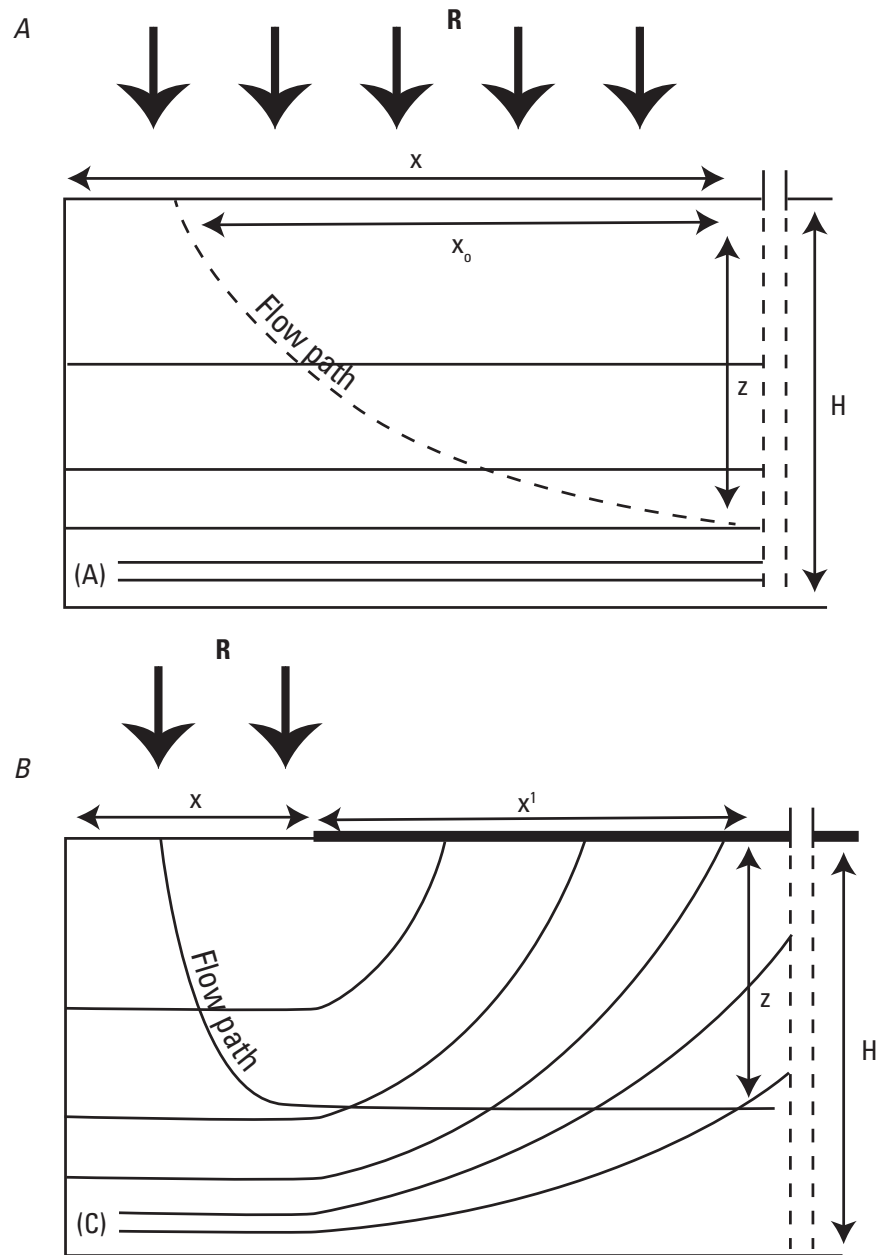


Figure 9. Adjusted carbon-14 ages from wells developed into the Chicot, Evangeline, and Jasper aquifers in Montgomery, Waller, and Walker Counties, Texas.



EXPLANATION

R Recharge;

H Thickness of the unconfined Chicot aquifer or unconfined zone of the Evangeline or Jasper aquifer, in feet (A) or thickness of the confined zone of the Evangeline or Jasper aquifer, in feet (B);

z Depth of sampling point within the aquifer, in feet.

x Width of the aquifer outcrop, in feet.

x_0 Distance from well to beginning of flow path

x' Distance from the well to the outcrop of the aquifer, in feet.

Figure 10. Conceptual model of idealized flow through an unconsolidated aquifer, modified from Cook and Böhlke (2000).

Chicot aquifer and unconfined zone of the Evangeline and Jasper aquifers were determined by using the following equation from Cook and Böhlke (2000):

$$R = \frac{H\varepsilon}{t} \ln \left(\frac{H}{H-z} \right) \quad (2)$$

where:

R is the amount of recharge, in inches per year;

H is the thickness of the unconfined Chicot aquifer or unconfined zone of the Evangeline or Jasper aquifer, in feet;

ε is porosity, in percent;

t is the apparent groundwater age, in years;

\ln is the natural logarithm; and

z is the depth of sampling point within the aquifer, in feet.

In the confined zone of the Evangeline and Jasper aquifer, ages using ^4He accumulation or ^{14}C were used to estimate recharge rates for the wells that were sampled. The following equation (Cook and Böhlke, 2000) was used to estimate recharge (R) in the confined zone of the Evangeline aquifer:

$$R = \frac{z\varepsilon}{t} + \left(\frac{x'H\varepsilon}{tx} \right) \quad (3)$$

where:

H is the thickness of the confined zone of the Evangeline or Jasper aquifer, in feet;

x' is the distance from the well to the outcrop of the aquifer, in feet; and

x is the width of the aquifer outcrop, in feet and other variables were defined for equation 2.

Aquifer Properties for Estimation of Groundwater Recharge Rates

Porosity

Porosity is defined as the percentage of rock or sediments that are void of solid material. Porosity of the unconsolidated sediments is affected by the sediment texture (sand, silt, clay, and gravel), size distribution, and spatial distribution relative to the depositional environments (for example, channel bars, delta forests, and flood plains). Because of the heterogeneity present in the Chicot and Evangeline aquifers in Montgomery County, and the lack of recent empirical

data, a porosity of 23 percent (Noble and others, 1996) was used for the calculation of recharge rates in this report. For the Jasper aquifer, a porosity of 25 percent was used on the basis of information from The University of Texas Bureau of Economic Geology (University of Texas, 2012). It is important to note that porosity is linearly related to calculated recharge rate; consequently, estimated recharge is highly sensitive to estimated porosity.

Aquifer Thickness

At each well, the thicknesses of the unconfined Chicot aquifer, the unconfined zone and confined zone of the Evangeline aquifer, or the unconfined zone and confined zone of the Jasper aquifer at each well were determined by using aquifer altitudes as described in Strom and others (2003 a, b, c). The tops of the Chicot, Evangeline, and Jasper aquifers in the outcrop area were estimated by using land-surface altitudes (NAVD 88). During this process, it was determined on the basis of work done by Strom and others (2003b) that three wells (TS-60-35-503, TS-60-35-504, and TS-60-35-505) assigned the Evangeline aquifer designation in the USGS NWIS GWSI, were more likely screened in the Burkeville confining unit. The uncertainty of the aquifer designation could not be adequately resolved; therefore, these three wells were not considered for recharge estimates of the Evangeline aquifer in this report. Two wells stored in GWSI were coded as Evangeline but based on Strom and others (2003a, b, c) were determined to be in the Chicot (TS-60-37-309) and Jasper (TS-60-35-907) aquifers, respectively, and were treated as being screened in these respective aquifers.

Distance Measurement

In addition to the porosity and thickness of the aquifer, the distance from the well to the outcrop of the aquifer (x') and width of the aquifer outcrop (x) are required to calculate recharge rates in a confined aquifer as described previously (eq. 1 and 2, fig. 10). An approximation of x' was done by measuring along the estimated flow path from the well to the outcrop area. An approximation of x was done by measuring from the edge of the outcrop to the terminus of the aquifer, generally along a straight line northwest to southeast. Approximations of x' and x were made by using geographic information system (GIS) software.

Recharge Estimates for the Unconfined Chicot, Evangeline, and Jasper Aquifers

In the unconfined aquifer system, depth in the aquifer was calculated as the top of the screened interval below land surface datum minus the water level below land surface datum at the time of sampling. Three water levels were not obtained at the time of sampling in 2008 (TS-60-63-110, TS-60-54-702, and TS-60-45-114), so water level was estimated from the regional water-level altitudes in Kasmarek and Houston (2008), and two water levels were not obtained at time of sampling in 2011 (TS-60-51-811 and TS-60-51-814) and were estimated from the regional water-level altitudes in Johnson and others (2011). One well (TS-60-34-301) was outside the mapped area of the regional water-level altitudes determined in 2008; based on water-level measurements by USGS within 4 miles (mi) of the well, water levels generally have varied a few feet, so the previously recorded water level was used (Oden, 2011). The depth in the confined aquifer was considered to be the altitude of the top of the Evangeline or Jasper aquifer minus the altitude of the top of the screened interval.

By using the recharge estimates derived from samples collected from 14 wells completed in the Chicot aquifer for which apparent groundwater ages could be determined, recharge to the Chicot aquifer ranged from 0.2 to 7.2 in./yr (table 8 and fig. 11). Recharge to the unconfined zone of the Evangeline aquifer from 1 well was 0.1 in./yr (table 9 and fig. 12). Recharge to the unconfined zone of the Jasper aquifer from 1 well was 0.5 in./yr (table 10 and fig. 13).

Recharge Estimates for the Confined Zones of the Evangeline and Jasper Aquifers

On the basis of data collected from eight wells, estimated rates of recharge to the confined zone of the Evangeline aquifer ranged from <0.1 to 2.8 in./yr (table 9 and fig. 12). On the basis of data collected from 10 wells, estimated rates of recharge to the confined zone of the Jasper aquifer ranged from <0.1 to 0.1 in./yr (table 10 and fig. 13).

Uncertainty Analysis of the Recharge Rates

The uncertainty of the recharge estimates concerning changes in the input data (aquifer thickness, porosity, age, distance from outcrop, and width of outcrop) were evaluated to assess the effects that changing input variables may have

had on the estimates. The values of the input data were varied within ranges deemed plausible for the Chicot, Evangeline, and Jasper aquifers in Montgomery County. For example, because aquifer thickness values from the literature are unlikely to be off by more than plus or minus 50 ft and porosity likely could range from about 20 to 30 percent for these aquifers, groundwater ages might vary by plus or minus 10 percent.

The wells completed in the Chicot aquifer showed the most variability in the modification of input variables. The calculated recharge rates were most sensitive to changes in age and porosity, whereas they were least sensitive to changes in aquifer thickness. Decreasing porosity to 20 percent and keeping other input variables constant generally decreased the recharge rate at each site, whereas increasing the porosity to 30 percent increased the recharge rate. Using 90 percent of the selected modeled age (younger water) showed an increase in the recharge rate at wells completed in the Chicot aquifer, whereas 110 percent of the age showed a decrease in the recharge rate for wells completed in the Chicot aquifer (fig. 14).

When the same input variables (aquifer thickness, porosity, and groundwater age) were modified, the wells completed in the outcrop area of the Evangeline and Jasper aquifers showed less variability in the recharge rate estimates as compared to the Chicot aquifer, although the same general trends were observed in the variability of recharge rates for the Evangeline and Jasper aquifers (fig. 14).

In the confined parts of the Evangeline and Jasper aquifers, the thickness of the aquifer (adjusted plus or minus \pm 50 ft) showed changes in recharge rates that were generally in the few thousandths of an inch range. Although the same conclusion (few thousandths to few hundredths) tended to hold true for adjusting the well distance to the outcrop (which were varied \pm 1 mi) and width of the outcrop (varied \pm 1 mi), the effect on recharge was generally to a few hundredths. Porosity and age tended to have more effect on the estimated recharge rates for each well; however, the effects were not as pronounced as in the unconfined system. As with the Chicot aquifer, decreasing porosity to 20 percent decreased the estimated recharge rate in the Evangeline and Jasper aquifers, whereas increasing the porosity to 30 percent showed an increase in the estimated recharge rate (figs. 14 and 15). In the confined system, decreasing the age of the water (10 percent for wells less than 10,000 years and decreasing 5,000 years for well greater than 10,000 years) and increasing porosity showed a small increase in the estimated recharge rate (figs. 14 and 15).

Table 8. Apparent groundwater ages and recharge estimates derived by using samples collected during March–September 2008 and April–May 2011 from wells completed in the Chicot aquifer in Montgomery County, Texas.

[in./yr, inches per year; ^4He , helium-4; $^3\text{He}/^3\text{H}$, helium-3/tritium; CFC-12, dichlorofluoromethane; SF_6 , sulfur hexafluoride; ^{14}C , carbon-14; ND, not determined; NA, not applicable]

Map identifier (figs. 1, 11)	Station name	Sample date	Sample time	Recharge (in./yr)	Apparent age (years)	Tracer
1	TS-60-53-719	3/12/2008	1415	3.7	73	$^3\text{He}/^3\text{H}$
2	TS-60-53-720	3/13/2008	1410	4.8	27	CFC-12
3	¹ TS-60-44-805	3/17/2008	1300	ND	ND	NA
4	TS-60-45-413	3/19/2008	845	3.8	62	^4He
5	TS-60-45-414	3/19/2008	1215	2.3	23	$^3\text{He}/^3\text{H}$
6	² TS-60-54-805	3/21/2008	1315	ND	ND	NA
7	TS-60-54-806	3/24/2008	1200	2.7	71	$^3\text{He}/^3\text{H}$
10	TS-60-54-807	3/26/2008	900	2.1	32	SF_6
12	TS-60-44-806	3/27/2008	1230	1.0	48	CFC-12
15	² TS-60-45-513	4/22/2008	930	ND	ND	NA
19	TS-60-63-110	4/24/2008	1530	2.4	50	CFC-12
20	TS-60-37-309	4/28/2008	1200	1.9	44	^4He
21	TS-60-54-702	4/30/2008	1030	3.4	32	$^3\text{He}/^3\text{H}$
25	TS-60-45-114	7/18/2008	1135	7.2	35	$^3\text{He}/^3\text{H}$
36	TS-60-51-809	4/18/2011	1025	0.9	650	^{14}C
37	TS-60-51-811	4/18/2011	1100	0.4	900	^{14}C
38	TS-60-51-814	4/18/2011	920	0.2	5,000	^{14}C

¹Poor well construction, well not datable.

²Well not datable, too old for modern tracer, not old enough for ^{14}C .

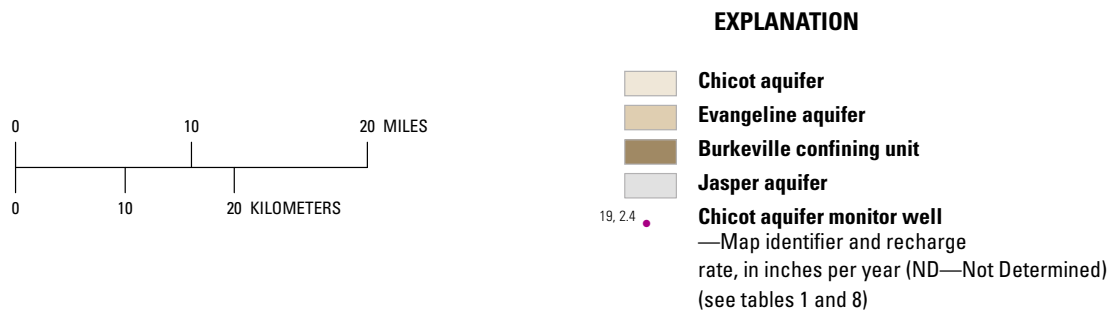
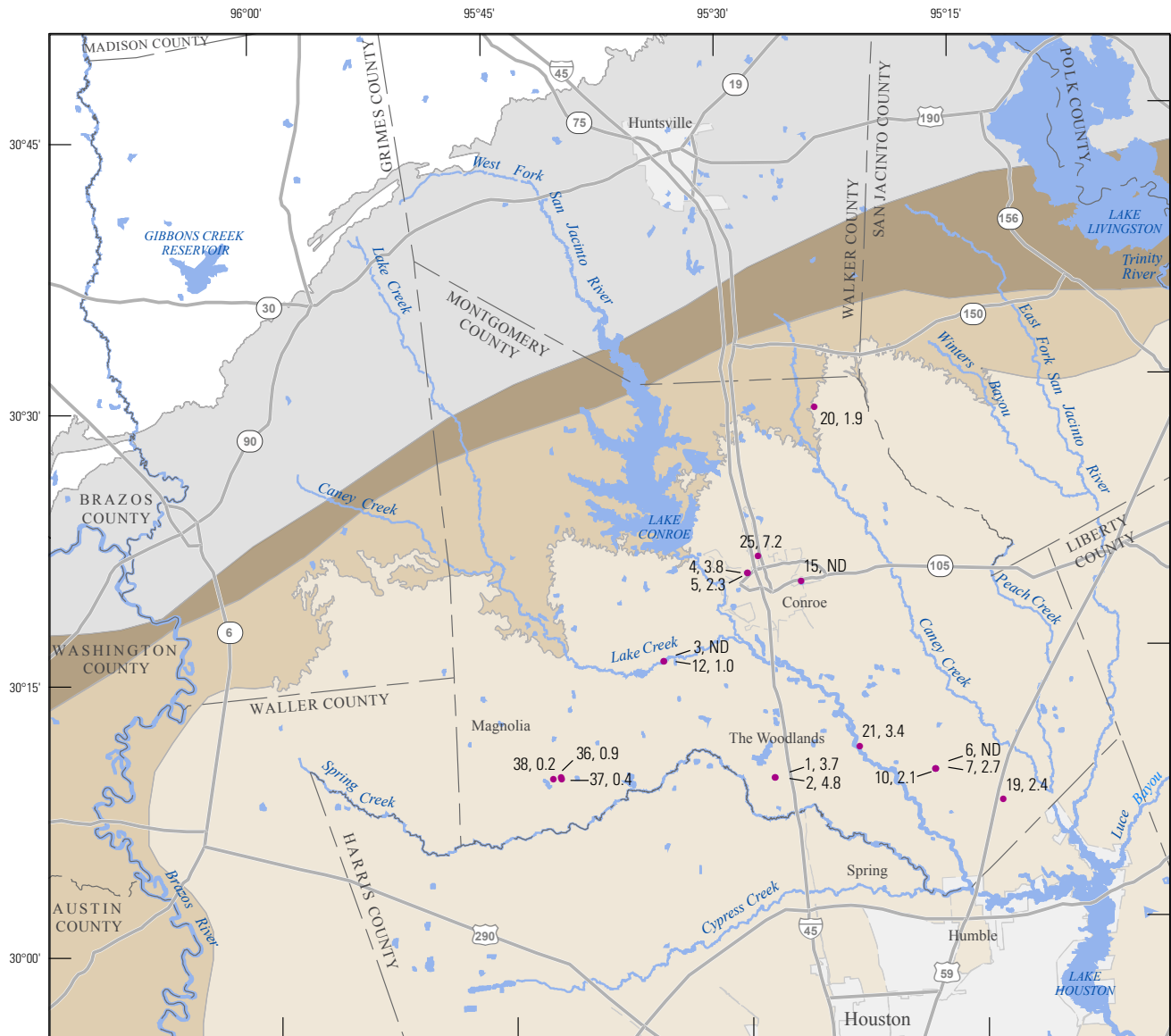
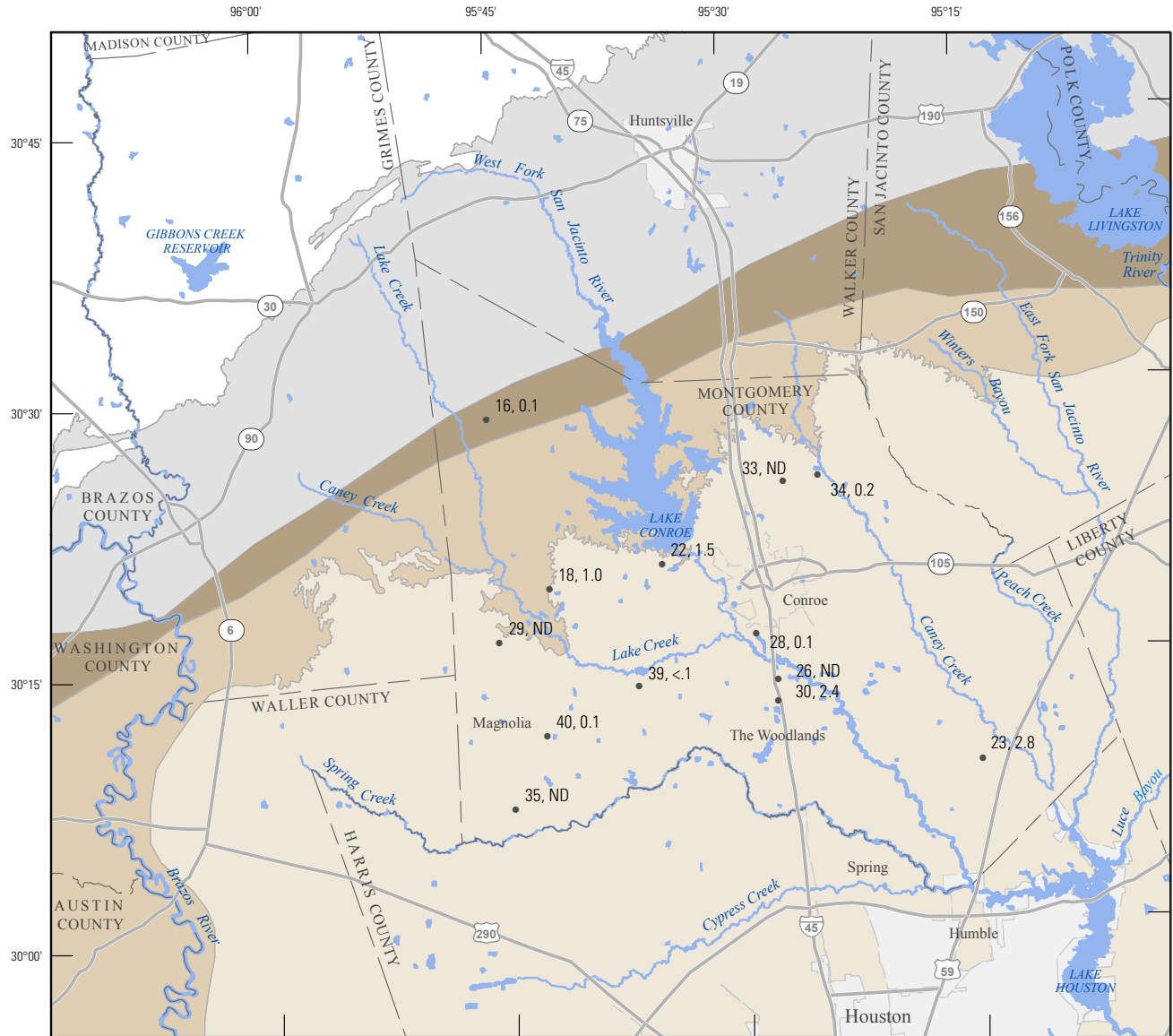


Figure 11. Recharge estimates at wells completed in the Chicot aquifer in Montgomery County, Texas, during March–September 2008 and April–May 2011.

Table 9. Apparent groundwater ages and recharge estimates derived by using samples collected during March–September 2008 and April–May 2011 from wells completed in the Evangeline aquifer in Montgomery County, Texas.[in./yr, inches per year; CFC-12, dichlorofluoromethane; ⁴He, helium-4; ¹⁴C, carbon-14; ND, not determined; NA, not applicable; <, less than]

Map identifier (figs. 1, 12)	Station name	Sample date	Sample time	Recharge (in./yr)	Apparent age (years)	Tracer	Well unconfined or confined
16	TS-60-34-301	4/22/2008	1330	0.1	52	CFC-12	Unconfined
18	TS-60-43-511	4/20/2011	1140	1.0	900	¹⁴ C	Confined
22	TS-60-44-212	7/10/2008	1224	1.5	825	⁴ He	Confined
23	TS-60-55-710	5/3/2011	1640	2.8	2,700	¹⁴ C	Confined
26	¹ TS-60-53-210	7/21/2008	935	ND	ND	NA	Confined
28	TS-60-45-716	4/26/2011	1200	0.1	26,000	¹⁴ C	Confined
29	² TS-60-42-902	8/1/2008	1400	ND	ND	NA	Confined
30	TS-60-53-516	8/18/2008	1530	2.4	2,092	⁴ He	Confined
33	² TS-60-37-806	9/3/2008	1245	ND	ND	NA	Confined
34	TS-60-37-909	4/25/2011	1100	0.2	8,000	¹⁴ C	Confined
35	² TS-60-59-102	9/4/2008	915	ND	ND	NA	Confined
39	³ TS-60-52-199	4/21/2011	1125	<0.1	42,000	¹⁴ C	Confined
40	³ TS-60-51-599	4/21/2011	945	0.1	32,000	¹⁴ C	Confined

¹Well sampling point reconfigured by owner, unable to resample in 2011.²Unable to obtain permission to resample in 2011.³Final State well number assignment pending Texas Water Development Board.



Base from U.S. Geological Survey 1:24,000-scale digital data
Albers Equal Area Projection, Texas Mapping System
North American Datum of 1983

Aquifer data from Strom and others, 2003 a, b, c,
and Kasmarek and Robinson, 2004

EXPLANATION

- Chicot aquifer
- Evangeline aquifer
- Burkeville confining unit
- Jasper aquifer
- Evangeline aquifer monitor well
—Map identifier and recharge
rate, in inches per year (ND—Not Determined)
(see tables 1 and 9)



Figure 12. Recharge estimates at wells completed in the Evangeline aquifer in Montgomery County, Texas, during March–September 2008 and April–May 2011.

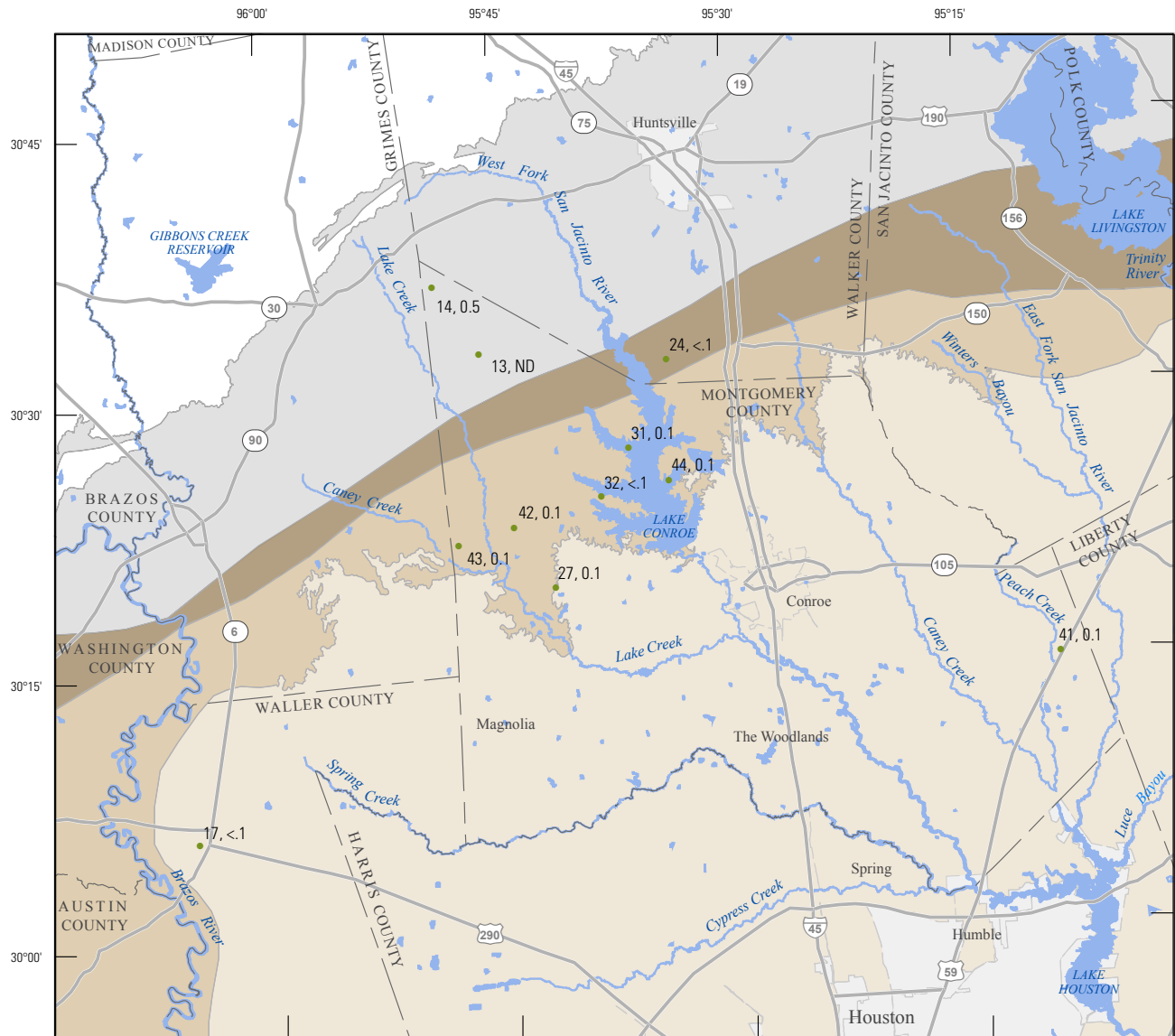
38 Estimated Rates of Groundwater Recharge to the Chicot, Evangeline, and Jasper Aquifers in Texas, 2008 and 2011

Table 10. Apparent groundwater ages and recharge estimates derived by using samples collected during March–September 2008 and April–May 2011 from wells completed in the Jasper aquifer in Montgomery, Walker, and Waller County, Texas.

[in./yr, inches per year; <, less than; >, greater than; CFC-12, dichlorofluoromethane; ¹⁴C, carbon-14; ND, not determined; NA, not applicable]

Map identifier (figs. 1, 13)	Station name	Sample date	Sample time	Recharge (in./yr)	Apparent age (years)	Tracer	Well unconfined or confined
13	¹ TS-60-26-901	4/21/2008	1030	ND	ND	NA	Unconfined
14	TS-60-26-208	4/21/2008	1400	0.5	62	CFC-12	Unconfined
17	YW-59-64-206	4/27/2011	1100	<0.1	>42,000	¹⁴ C	Confined
24	YU-60-28-802	5/9/2011	1310	<0.1	13,000	¹⁴ C	Confined
27	TS-60-43-514	4/20/2011	1030	0.1	27,000	¹⁴ C	Confined
31	TS-60-36-410	4/15/2011	1000	0.1	18,000	¹⁴ C	Confined
32	TS-60-35-907	4/28/2011	1050	<.1	33,000	¹⁴ C	Confined
41	TS-60-55-313	5/11/2011	912	0.1	42,000	¹⁴ C	Confined
42	TS-60-35-703	5/12/2011	925	0.1	19,000	¹⁴ C	Confined
43	TS-60-42-206	5/12/2011	1040	0.1	16,000	¹⁴ C	Confined
44	TS-60-36-812	5/13/2011	940	0.1	37,000	¹⁴ C	Confined

¹Unable to obtain permission to resample in 2011



Base from U.S. Geological Survey 1:24,000-scale digital data
 Albers Equal Area Projection, Texas Mapping System
 North American Datum of 1983

Aquifer data from Strom and others, 2003 a, b, c
 and Kasmarek and Robinson, 2004

EXPLANATION

- Chicot aquifer
- Evangeline aquifer
- Burkeville confining unit
- Jasper aquifer

Jasper aquifer monitor well
 —Map identifier and recharge
 rate, in inches per year (ND—Not Determined)
 (see tables 1 and 10)

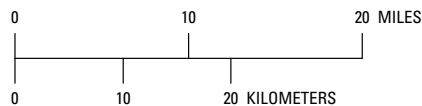


Figure 13. Recharge estimates at wells completed in the Jasper aquifer in Montgomery, Walker, and Waller County, Texas, during March–September 2008 and April–May 2011.

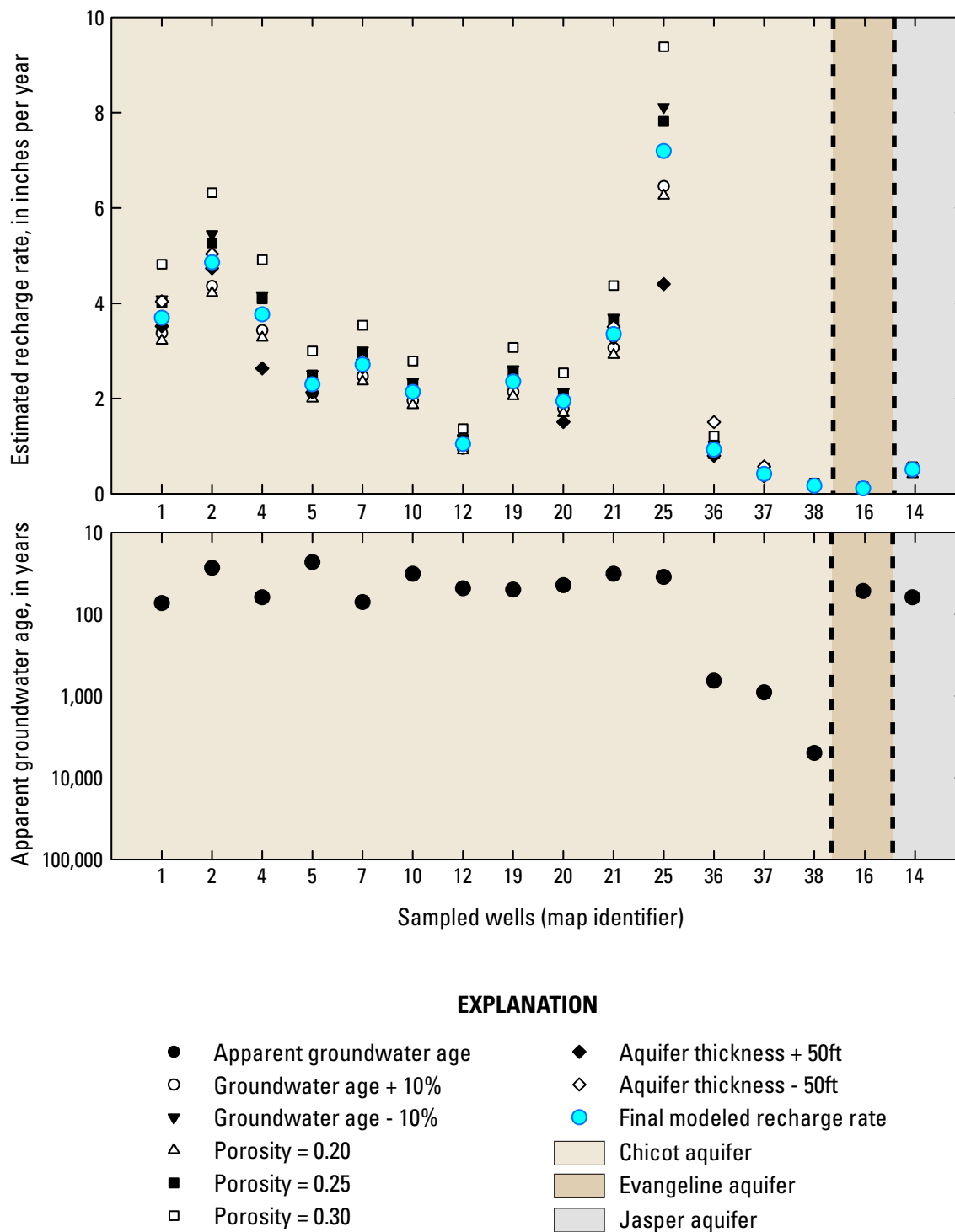
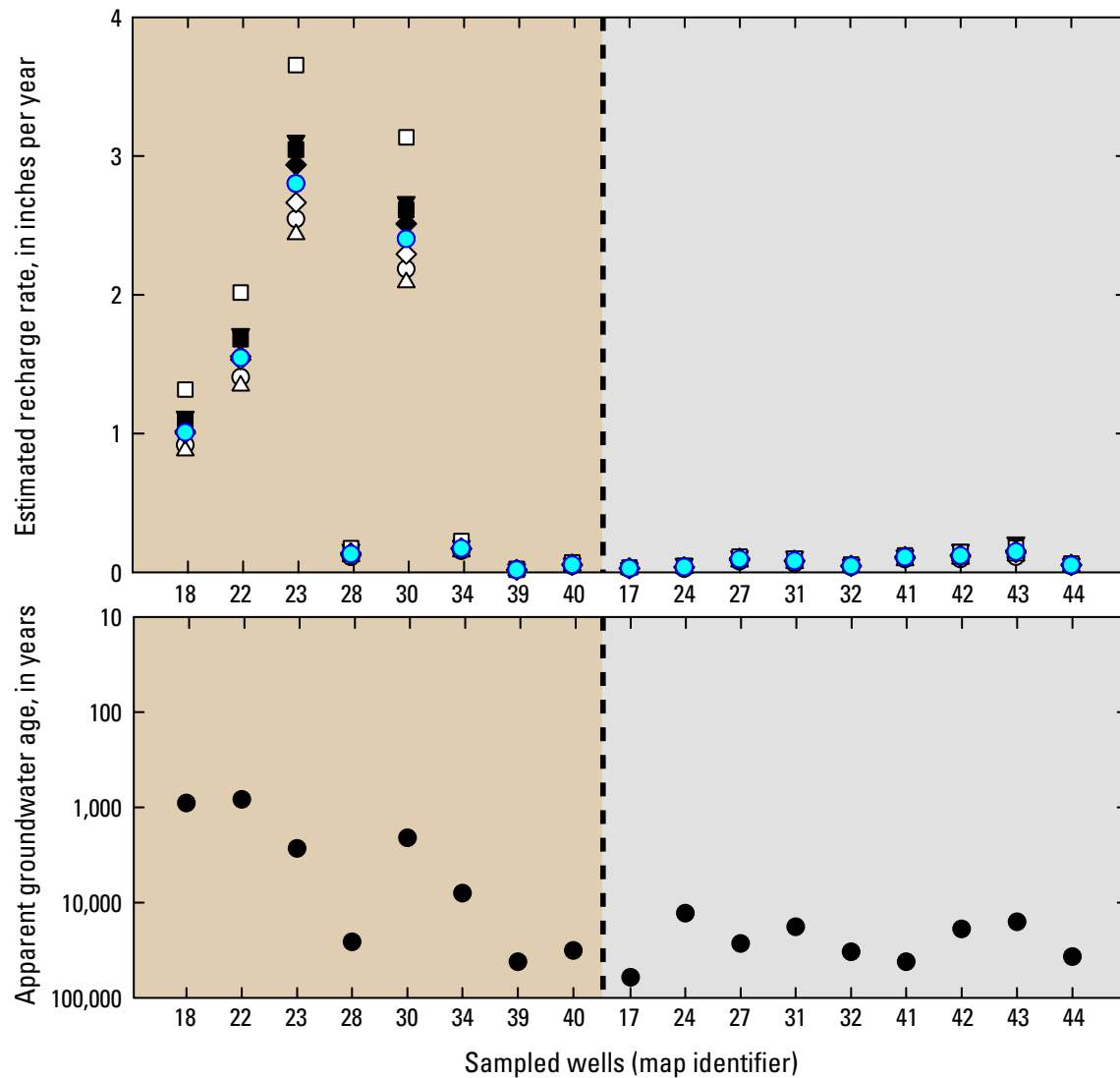


Figure 14. Uncertainty analysis of recharge rates for unconfined wells screened in the Chicot, Evangeline, and Jasper aquifers.



EXPLANATION

- Apparent groundwater age
- Groundwater age + 10% or 5,000 years for ages > 10,000 years
- ▼ Groundwater age - 10% or 5,000 years for ages > 10,000 years
- △ Porosity = 0.20
- Porosity = 0.25
- Porosity = 0.30
- ◆ Aquifer thickness + 50ft
- ◇ Aquifer thickness - 50ft
- Final modeled recharge rate
- Evangeline aquifer
- Jasper aquifer

Figure 15. Uncertainty analysis of recharge rates for confined wells screened in the Evangeline and Jasper aquifers.

Limitations of Estimating Recharge Rates

Estimation of groundwater ages and recharge rates requires assumptions of the hydrogeologic properties of the aquifer system, resulting in uncertainty in these apparent-age and recharge estimates. Despite the complexity of the aquifer system in Montgomery County, the estimates of groundwater ages and recharge rates are appropriate for use as a general guide in hydrologic investigations. For example, these estimates can be used for further investigation into the availability of the groundwater resources in Montgomery County and can be used as input parameters in groundwater-flow models in the area. Recharge estimates from this study are within the range of expected recharge values estimated by other methods within and near the study area (tables 11 and 12). The following limitations of these results should be considered:

1. The hydrogeology in the study area is highly variable on a regional scale and may exhibit localized groundwater flow paths contrary to the regional flow pattern. Localized variations in sand thickness and spatial continuity might allow for preferential flow paths within the aquifer and decrease the apparent age of the water, consequently increasing the calculated recharge rate. If the apparent decrease in age is simply a result of diverted flow or recharge from the surface or somewhere else in a focused manner to the well point, then the focused flow is capturing additional recharge, but the overall recharge to the aquifer may not experience an actual increase on the regional scale. Understanding the localized flow paths and preferential flow paths is thus important.
2. Piston flow in each of the aquifers is assumed for the conceptual model of this system (fig. 10). This assumption may over simplify the flow system in areas within the study area where hydrologic connection with overlying aquifers is prevalent.
3. The calculation of recharge for confined and unconfined aquifers requires an estimation of the porosity. Although the assumed final average porosity value along the flow path used to calculate the recharge rates presented within this report is within the range of expected porosity for this aquifer material, localized variation in sand and clay percentages and in sand grain size could affect the apparent age of the water. A decrease in porosity estimation will lower the estimated recharge rate, whereas an increase in porosity estimation will raise the estimated recharge rate.
4. Concentrations of the modern environmental tracer were often at or near analytical detection limits, and such low concentrations can result in relatively large age-estimate errors.
5. The possibility exists for the mixing of waters of different composition and age through vertical connection or along preferential pathways. Mixing of groundwater may occur over long flow paths as well as long screened intervals in some of the wells used for this study. Dispersion may also affect environmental tracer concentrations given the heterogeneity of the aquifers.
6. The estimated recharge rates calculated for this study are specific to each well location, and any individual well estimate should not be extrapolated or inferred as a countywide average. Local variations in the hydrogeology and surficial conditions can affect the recharge rate at a local scale.
7. The interpretation of environmental tracer data can be complicated as tracers move along individual groundwater flow paths. The complications resulting from additional independent variables can affect the tracer concentrations such as degassing, contamination, dispersion, sorption, transport through thick unsaturated zones, and aquifer-water interactions, including input of excess ^4He .

Table 11. Recharge methods and estimates of annual recharge rates previously determined (Nolan and others, 2007, table A2) for four wells completed in the Chicot aquifer in Montgomery County, Texas.

[in./yr, inches per year; --, not determined]

Station identifier	Sample identifier	Aquifer	Darcian-pedotransfer method (in./yr)	Chloride tracer in unsaturated zone (in./yr)	Chloride tracer in saturated zone (in./yr)
300825095274801	MW14	Chicot	4.80	0.24	0.04
301008095302901	MW13	Chicot	--	56.22	0.24
301220095305501	MW15	Chicot	2.87	0.51	0.43
301716095400501	REF03	Chicot	0.04	1.85	2.13

Table 12. Comparison of recharge rates determined in Montgomery County during March–September 2008 and April–May 2011 by using environmental age tracers with recharge rates from previous studies that used various methods in the Gulf Coast aquifer system in Montgomery County and adjacent counties in Texas.[in./yr, inches per year; <, less than; ⁴He, helium-4; ³He/³H, helium-3/tritium; CFC-12, dichlorodifluoromethane; SF₆, sulfur hexafluoride; ¹⁴C, carbon-14; ³H, tritium; Cl, chloride]

Sample collection dates	Counties	Recharge rate (in./yr)	Method
March–September 2008 April–May 2011	Montgomery	<0.1–7.2	Environmental age tracers (³ He/ ³ H, CFC-12, SF ₆ , ⁴ He and ¹⁴ C)

Previous studies	Counties	Recharge rate (in./yr)	Method
Popkin (1971)	Montgomery	1.7	Transmission capacity
Ryder (1988)	Montgomery	0–2	Groundwater model
Williamson and others (1990)	Montgomery	0.00–0.66	Groundwater model - Predevelopment conditions
		0.66–3.00	Groundwater model - 90 percent 1980 pumpage
Noble and others (1996)	Harris, Montgomery, and Walker	0.0–6.0	³ H interface method
Nolan and others (2007)	Harris and Montgomery	0.04–2.13	Cl tracer in saturated zone
Scanlon and others (2011)	Montgomery	0.8–4.8	Hydrograph analysis and chloride mass balance

Summary

Montgomery County is in the northern part of the Houston, Texas, metropolitan area, the fourth most populous metropolitan area in the United States. A good understanding of the rate of recharge is important to water managers to help them ensure the amount of groundwater withdrawn from the Gulf Coast aquifer system in Montgomery County is sustainable. Accordingly, the USGS, in cooperation with the Lone Star Groundwater Conservation District, estimated rates of groundwater recharge in 2008 and 2011 to the Chicot, Evangeline, and Jasper aquifers at selected wells using a combination of different environmental tracers in Montgomery County.

Groundwater is withdrawn from the Gulf Coast aquifer system, which comprises the Chicot, Evangeline, and Jasper aquifers; Burkeville confining unit; and the underlying Catahoula confining system. The individual sand and clay sequences of the aquifers composing the Gulf Coast aquifer system are not laterally or vertically continuous on a regional scale; however, on a local scale, individual sand and clay lenses can extend over several miles.

In total, 36 sample sites representing 44 existing groundwater wells in or near Montgomery County were selected for sampling. Groundwater-quality samples were collected once from each of 40 wells March–September 2008 and analyzed for chlorofluorocarbons (CFCs), sulfur hexafluoride (SF_6), tritium (^3H), helium-3/tritium ($^3\text{He}/^3\text{H}$), helium-4 (^4He), and dissolved gases (DG). Groundwater-quality samples were collected once from each of 24 wells April–May 2011 and analyzed for major ions and carbon-14 (^{14}C), and a subset of wells were analyzed for ^4He and DG.

Modern environmental tracers CFCs, SF_6 , ^3H , and $^3\text{He}/^3\text{H}$ were used to estimate apparent ages of modern groundwater, which was defined for this report as water that was recharged and isolated from the atmosphere between 1950 and 2008. The radioactive isotope of hydrogen (^3H) was used to identify recent groundwater recharge or groundwater mixtures that contained some recent water. The environmental tracer ^{14}C was used to estimate apparent ages of groundwater more than about 1,000 years before present.

Most DG samples contained little excess air (0.9 to 5.8 cubic centimeters). The small amount of excess air within the samples was consistent with diffuse rather than focused recharge. Diffuse recharge occurs over a large area as water from precipitation infiltrates and percolates through the unsaturated zone to the water table. Focused recharge, which can occur rapidly, resulting in larger quantities of excess air being trapped in aquifer pores and dissolving under recharge conditions, occurs when recharge is focused at a preferential pathway or location.

The median recharge temperature of all sites was 15.7 °C. Field water temperatures measured at the time of sampling were typically higher than the recharge temperature determined by using DG, with a median difference of 8.0 °C, indicating that groundwater at the

time of sampling probably recharged at lower temperatures than current groundwater temperatures and most likely is premodern. Other factors affecting the estimated recharge temperature of the groundwater included the likelihood that most recharge in the region might occur in winter and early spring, which are the coolest times of the year.

Groundwater ages, or apparent age, were determined by assuming piston-flow. For the piston-flow conceptual model, the constituent concentration was assumed not to be altered by mixing or dispersion from the point of entry to the measurement point in the aquifer. Most of the modern environmental tracer data indicated that the water at each of these wells was recharged prior to the 1950s, limiting the usefulness of CFCs, SF_6 , and ^3H concentrations as tracers. Additionally, low-level concentrations of CFCs and SF_6 , as noted in several wells, may have been an artifact of well installation, well development, or poor annular seals for the well. Additionally, there may be nearby wells with multiple screened intervals in the aquifer(s), allowing for leakage of younger water to the older reservoirs of water, providing a conduit for cross-formational flow and biasing the resulting apparent age. In many cases, no modern tracer was usable at a well for the purpose of estimating an apparent age and was subsequently resampled for ^{14}C as a tracer for older groundwater.

Estimation of groundwater ages and recharge rates requires assumptions of the hydrogeologic properties of the aquifer system, resulting in uncertainty in these estimates. Porosity, a component in the calculation of recharge rate in the unconfined and confined zones of an aquifer, was estimated as 23 percent for the Chicot and Evangeline aquifers, whereas 25 percent was used for the Jasper aquifer. By using the recharge estimates derived from samples collected from 14 wells completed in the Chicot aquifer for which apparent groundwater ages could be determined, recharge to the Chicot aquifer ranged from 0.2 to 7.2 inches per year (in./yr). Based on data from one well, recharge to the unconfined zone of the Evangeline aquifer (outcrop) was 0.1 in./yr. Based on data from eight wells, estimated rates of recharge to the confined zone of the Evangeline aquifer ranged from <0.1 to 2.8 in./yr. On the basis of data from one well, recharge to the unconfined zone of the Jasper aquifer (outcrop) was 0.5 in./yr. Based on data from nine wells, estimated rates of recharge to the confined zone of the Jasper aquifer ranged from <0.1 to 0.1 in./yr.

There is an appropriate use for these data, and there are limitations in their applicability for several reasons. Estimation of groundwater ages and recharge rates requires assumptions of the hydrogeologic properties of the aquifer system, resulting in uncertainty in these estimates. Despite the complexity of the aquifer system in Montgomery County, the estimates of groundwater ages and recharge rates are appropriate for use as a general guide in hydrologic investigations regarding the availability of the groundwater resources in the Montgomery County area. The hydrogeology in the study area is highly variable on the

regional scale and may exhibit localized groundwater flow paths contrary to the regional flow pattern, which may allow for preferential flow paths within the aquifer and decrease the apparent age of the water, consequently increasing the recharge rate. For a conceptual model of this system, piston flow in the aquifer is assumed, which in the case of the Evangeline aquifer may be inaccurate at the local scale because of the direct hydrologic connection between the Evangeline aquifer with the overlying Chicot aquifer, and the possibility of mixing of the two waters. The calculation of recharge for both confined and unconfined aquifers requires an assumption of porosity, which was assumed to be uniform countywide. The estimated recharge rates calculated for this study are specific to each well location and should not be extrapolated or inferred as a countywide average. Local variations in the hydrogeology and surficial conditions can affect recharge rates at a local scale because localized variation in sand and clay percentages and in sand grain size could affect the apparent age of the water.

Other limitations include the fact that concentrations of the environmental tracer were often at or near analytical detection limits, and at such low concentrations, the analytical imprecision is relatively large and thus can result in relatively large age-estimate errors. Furthermore, because there were relatively few wells available for sampling, sample collection could not exclude wells with long well screens, and mixing of groundwater might have been enhanced by long open intervals and deep wells; in addition, dispersion might affect environmental tracer concentrations given the heterogeneity of the aquifers.

References

- American Public Health Association, American Water Works Association, and Water Environment Federation, 1998, Standard methods for the examination of water and wastewater (20th edition), 1998: Washington, D.C., p. 3-37 to 3-43.
- Baker, E.T., Jr., 1979, Stratigraphic and hydrogeologic framework of part of the coastal plain of Texas: Texas Department of Water Resources Report 236, 43 p.
- Baker, E.T., Jr., 1986, Hydrology of the Jasper aquifer in the southeast Texas coastal plain: Texas Department of Water Resources Report 295, 64 p.
- Busenberg, Eurybiades, and Plummer, L.N., 1992, Use of chlorofluorocarbons (CCl₃F and CCl₂F₂) as hydrologic tracers and age-dating tools—The alluvium and terrace system of Central Oklahoma: Water Resources Research, v. 28, no. 9, p. 2257–2283.
- Busenberg, Eurybiades, and Plummer, L.N., 1997, Use of sulfur hexafluoride as a dating tool and as a tracer of igneous and volcanic fluids in ground water: Abstract of Geological Society of America, 1997 Annual Meeting, GSA Abstracts with Programs, v. 29, no. 6, p. A-78.
- Busenberg, Eurybiades, and Plummer, L.N., 2000, Dating young ground water with sulfur hexafluoride: Natural and anthropogenic sources of sulfur hexafluoride: Water Resources Research, v. 36, no. 10, p. 3011–3030.
- Busenberg, Eurybiades, and Plummer, L.N., 2010, A rapid method for the measurement of sulfur hexafluoride (SF₆), trifluoromethyl sulfur pentafluoride (SF₅CF₃), and Halon 1211 (CF₂ClBr) in hydrologic tracer studies: Geochemistry, Geophysics, and Geosystems, v. 11, Q11001, doi:10.1029/2010GC003312
- Busenberg, Eurybiades, Plummer, L.N., and Bartholomay, R.C., 2001, Estimated age and source of the young fraction of ground water at the Idaho National Engineering and Environmental Laboratory: U.S. Geological Survey Water-Resources Investigations Report 01–4265, 144 p.
- Busenberg, Eurybiades, Weeks, E.P., Plummer, L.N., and Bartholomay, R.C., 1993, Age dating groundwater by use of chlorofluorocarbons (CCl₃F and CCl₂F₂) and distribution of chlorofluorocarbons in the unsaturated zone, Snake River Plain aquifer, Idaho National Engineering Laboratory, Idaho: U.S. Geological Survey Water-Resources Investigations Report 93–4054, 47 p.
- Carr, J.E., Meyer, W.R., Sandeen, W.M., and McLane, I.R., 1985, Digital models for simulation of ground-water hydrology of the Chicot and Evangeline aquifers along the Gulf Coast of Texas: Texas Department of Water Resources Report 289, 101 p.
- Chowdhury, A.H. and Turco, M.J., 2006, Geology of the Gulf Coast aquifer, Texas, chap. 2 in Mace R.E., Davidson, S.C., Angle, E.S., and Mullican, W.F., III, eds., Aquifers of the Gulf Coast of Texas: Texas Water Development Board Report 365, p. 23–50.
- Clark, I.D., and Fritz, P., 1997, Environmental isotopes in hydrogeology: New York, Lewis Publishers, 328 p.
- Clarke, W.B., Jenkins, W.J., and Top, Z., 1976, Determination of tritium by mass spectrometric measurements of ³He: International Journal of Applied Radiation and Isotopes, v. 27, no. 9, p. 515–522.
- Cook, L.M., 1980, The uranium district of the Texas gulf coastal plain, in Gessel, T.F., and Lowder, W.M., eds., Natural Radiation Environment III: U.S. Department of Energy, Washington, D.C., p. 1602–1922.

- Cook, P.G., and Böhlke, J.K., 2000, Determining timescales for groundwater flow and solute transport, chap 1. of P.G. Cook and A.L. Herczeg, eds., *Environmental tracers in subsurface hydrology*: Boston, Mass., Kluwer Academic Press, p. 1-30.
- Delin, G.N., and Falteisek, J.D., 2007, Ground-water recharge in Minnesota: U.S. Geological Survey Fact Sheet 2007-3002, 6 p.
- Eichinger, L., 1983, A contribution to the interpretation of ^{14}C groundwater ages considering the example of a partially confined sandstone aquifer: *Radiocarbon*, v. 25, p. 347–356.
- Ekwurzel, Brenda, Schlosser, Peter, Smethie, W.M., Jr., Plummer, L.N., Busenberg, Eurybiades, Michel, R.L., Weppernig, Ralf, and Stute, Martin, 1994, Dating of shallow groundwater—Comparison of the transient tracers $^3\text{H}/^4\text{He}$, chlorofluorocarbons, and ^{85}Kr : *Water Resources Research*, v. 30, no. 6, p. 1693–1708.
- Fishman, M.J., ed., 1993, *Methods of analysis by the U.S. Geological Survey National Water Quality Laboratory—Determination of inorganic and organic constituents in water and fluvial sediments*: U.S. Geological Survey Open-File Report 93-125, 217 p.
- Fishman, M.J., and Friedman, L.C., 1989, *Methods for determination of inorganic substances in water and fluvial sediments*: U.S. Geological Survey Techniques of Water-Resources Investigations, book 5, chap. A1, 545 p.
- Fontes, Jean-Charles, and Garnier, Jean-Marie, 1979, Determination of the initial ^{14}C activity of the total dissolved carbon—A review of the existing models and a new approach: *Water Resources Research*, v. 15, p. 399–413.
- Gabrysch, R.K., 1984, Case history no. 9.12, The Houston-Galveston region, Texas, USA, in J.F. Poland, ed., *Guidebook to studies of land subsidence due to groundwater withdrawal*: UNESCO Studies and Reports in Hydrology 20, p. 252-262.
- Gabrysch, R.K. and Coplin, L.S., 1990, Land-surface subsidence resulting from ground-water withdrawals in the Houston–Galveston region, Texas through 1987: Harris–Galveston Coastal Subsidence District Report of Investigations 90-01, 53 p.
- Hem, J.D., 1985, *Study and interpretation of the chemical characteristics of natural water* (third edition): U.S. Geological Survey Water-Supply Paper 2254, 263 p.
- Houston–Galveston Area Council, 2006, *Houston–Galveston Area Council 2035 Regional Growth Forecast*: Houston, Texas, Houston-Galveston Area Council, 20 p.
- Hunt, A.G., Lambert, R.B., and Fahlquist, Lynne, 2010, Sources of groundwater based on helium analyses in and near the freshwater/saline-water transition zone of the San Antonio segment of the Edwards aquifer, south-central Texas, 2002–03: U.S. Geological Survey Scientific Investigations Report 2010–5030, 16 p.
- Ingerson, E., and Pearson, Jr., F.J., 1964, Estimation of age and rate of motion of groundwater by the ^{14}C -method: Maruzen, Tokyo, *Proceedings of the Sugawara Festival on Recent Researches in the Fields of Atmosphere, Hydrosphere, and Nuclear Geochemistry*, p. 263–283.
- International Atomic Energy Agency (IAEA), 2006, *Use of chlorofluorocarbons in hydrology—A guidebook*: Vienna, Austria, International Atomic Energy Agency, 277 p., accessed May 27, 2010, at http://www-pub.iaea.org/MTCD/publications/PDF/Pub1238_web.pdf.
- International Atomic Energy Agency (IAEA), 2010, *Water Isotope System for Data Analysis, Visualization and Electronic Retrieval (WISER)*: Accessed September 14, 2011, at http://www-naweb.iaea.org/napc/ih/IHS_resources_isohis.html.
- Johnson, M.R., Ramage, J.K., and Kasmarek, M.C., 2011, Water-level altitudes 2011 and water-level changes in the Chicot, Evangeline, and Jasper aquifers and compaction 1973–2010 in the Chicot and Evangeline aquifers, Houston–Galveston region, Texas: U.S. Geological Survey Scientific Investigations Map 3174, 17 p., 16 sheets.
- Kasmarek, M.C., and Houston, N.A., 2008, Water-level altitudes 2008 and water-level changes in the Chicot, Evangeline, and Jasper aquifers and compaction 1973–2007 in the Chicot and Evangeline aquifers, Houston–Galveston region, Texas: U.S. Geological Survey Scientific Investigations Map 3031, 4 p., 17 sheets.
- Kasmarek, M.C., Johnson, M.R., and Ramage, J.K., 2010, Water-level altitudes 2010 and water-level changes in the Chicot, Evangeline, and Jasper aquifers and compaction 1973–2009 in the Chicot and Evangeline aquifers, Houston–Galveston region, Texas: U.S. Geological Survey Scientific Investigations Map 3138, 17 p., 16 sheets, 1 appendix.
- Kasmarek, M.C., and Robinson, J.L., 2004, *Hydrogeology and simulation of ground-water flow and land-surface subsidence in the northern part of the Gulf Coast aquifer system, Texas*: U.S. Geological Survey Scientific Investigations Report 2004-5102, 111 p.
- Kasmarek, M.C., and Strom, E.W., 2002, *Hydrogeology and simulation of ground-water flow and land-surface subsidence in the Chicot and Evangeline aquifers, Houston area, Texas*: U.S. Geological Survey Water-Resources Investigation Report 02-4022, 61 p.

- Katz, B.G., Crandall, C.A., Metz, P.A., McBride, W.S., and Berndt, M.P., 2007, Chemical characteristics, water sources and pathways, and age distribution of ground water in the contributing recharge area of a public-supply well near Tampa, Florida, 2002-05: U.S. Geological Survey Scientific Investigations Report 2007-5139, 85 p.
- Kendall, C., and McDonnell, J.J., eds., 1998, Isotope tracers in catchment hydrology: Amsterdam, Netherlands, Elsevier Science B.V., p. 577-602.
- Keys, W.S., 1990, Borehole geophysics applied to ground-water investigations: U.S. Geological Survey Techniques of Water-Resources Investigations, book 2, chap. E-2, 149 p.
- Keys, W.S., 1997, A practical guide to borehole geophysics in environmental investigations: Boca Raton, Florida, CRC Press/Lewis Publishers, 176 p.
- Kier, R.S., Garner, L.E. and Brown, L.F., 1977, Land resources of Texas: University of Texas at Austin, Bureau of Economic Geology, 42 p.
- Landon, M. K., Clark, B.R., McMahon, P.B., McGuire, V.L., and Turco, M.J., 2008, Hydrogeology, chemical characteristics, and transport processes in the zone of contribution of a public-supply well in York, Nebraska: U.S. Geological Survey Scientific Investigations Report 2008-5050, 149 p.
- Landon, M.K., Jurgens, B.C., Katz, B.G., Eberts, S.M., Burow, K.R., and Crandall, C.A., 2010, Depth-dependent sampling to identify short-circuit pathways to public-supply wells in multiple aquifer settings in the United States: Hydrogeology Journal, v. 18, no. 3, p. 577-593.
- Lone Star Groundwater Conservation District, 2008, Lone Star Groundwater Conservation District rules and bylaws: Accessed September 13, 2011, at http://www.lonestargcd.org/pdf/Re_adpotedMgmtPlan101408.pdf.
- Lucas L.L., and Unterweger, M.P., 2000, Comprehensive review and critical evaluation of the half-life of tritium: Journal of Research of the National Institute of Standards and Technology, v. 105, no. 4, p. 541-549.
- Maiss, M., and Brenninkmeijer, C.A.M., 1998, Atmospheric SF₆—Trends, sources, and prospects: Environmental Science Technology, no. 32, p. 3077-3086.
- Mook, W.G., 1972, On the reconstruction of the initial ¹⁴C content of groundwater from the chemical and isotopic composition, in Proceedings of the 8th International Conference on Radiocarbon Dating, v. 1: Wellington, Royal Society of New Zealand, p. 342-352.
- Mook, W.G., 1980, The dissolution-exchange model for dating of groundwater with ¹⁴C, in Fritz, P. and Fontes, J.-C., eds., Handbook of environmental isotopes geochemistry, v. 1: Amsterdam, Netherlands, Elsevier, p. 50-74.
- Mook, W.G., Bommerson, J.C., and Staverman, W.H., 1974, Carbon isotope fractionation between dissolved bicarbonate and gaseous carbon dioxide: Earth and Planetary Science Letters, v. 22, p. 169-176.
- National Climatic Data Center, 2010, Climate at a glance—Annual precipitation, Houston, Texas, 1947-2008: Accessed July 19, 2010, at <http://www.ncdc.noaa.gov/oa/climate/research/cag3/v1.html>.
- National Oceanic and Atmospheric Administration, 2010, Houston, extremes, normals and annual summaries: Accessed June 14, 2010 at http://www.srh.noaa.gov/hgx/?n=climate_iah_normals_summary.
- Nimmo, J.R., Deason, J.A., Izbicki, J.A., and Martin, P., 2002, Evaluation of unsaturated zone water fluxes in heterogeneous alluvium at a Mojave Basin site: Water Resources Research, v. 38, no. 10, p. 33-1 to 33-13.
- Noble, J.E., Bush, P.W., Kasmarek, M.C., and Barbie, D.L., 1996, Estimated depth to the water table and estimated rate of recharge in outcrops of the Chicot and Evangeline aquifers near Houston, Texas: U.S. Geological Survey Water-Resources Investigation Report 96-4018, 19 p.
- Nolan, B.T., Healy, R.W., Taber, P.E., Perkins, K., Hitt, K.J., and Wolock, D.M., 2007, Factors influencing ground-water recharge in the eastern United States: Journal of Hydrology, no. 332, p. 187-205.
- Oden, T.D. 2011, Groundwater environmental tracer data collected from the Chicot, Evangeline, and Jasper aquifers in Montgomery and adjacent counties, Texas, 2008: U.S. Geological Survey Data Series 580, 37 p.
- Östlund, H.G., and Werner, E., 1962, Electrolytic enrichment of tritium and deuterium for natural tritium measurements—Tritium in the physical and biological sciences: Vienna, Austria, International Atomic Energy Agency, v. 1, p. 96-104.
- Plummer, L.N., and Busenberg, Eurybiades, 2000, Chlorofluorocarbons, in Cook, P.G., and Herczeg, A.L., eds., Environmental tracers in subsurface hydrology: Boston, Mass., Kluwer Academic Press, chap. 15, p. 441-478.
- Plummer, L.N., Busenberg, Eurybiades, and Cook, P.G., 2006, Principles of chlorofluorocarbon dating, in Use of chlorofluorocarbons in hydrology—A guidebook: Vienna, International Atomic Energy Agency, p. 17-29, accessed April 19, 2011, at http://www-pub.iaea.org/MTCD/publications/PDF/Pub1238_web.pdf#page=30.
- Plummer, L.N., Busenberg, Eurybiades, and Widman, P.K., 2004, Applications of dissolved N₂ and Ar in groundwater: Geological Society of America, Abstracts with Programs, v. 36, no. 5, p. 468.

- Plummer, L.N., and Friedman, L.C., 1999, Tracing and dating young ground water: U.S. Geological Survey Fact Sheet FS-134-99, 4 p.
- Plummer, L.N., Michel, R.L., Thurman, E.M., and Glynn, P.D., 1993, Environmental tracers for age-dating young ground water; *in* W.M. Alley, ed., Regional ground-water quality, chap. 11: New York, Van Nostrand Reinhold, p. 255-294.
- Plummer, L.N., Parkhurst, D.L., Thorstenson, D.C., 1983, Development of reaction models for ground-water systems: *Geochim Cosmochim Acta*, v. 47, p. 665-686.
- Plummer, L.N., Prestemon, E.C., Parkhurst, D.L., 1991, An interactive code (NETPATH) for modeling NET geochemical reactions along a flow PATH: U.S. Geological Survey Water-Resources Investigations Report 91-4078, 227 p.
- Plummer, L.N., Prestemon, E.C., Parkhurst, D.L., 1994, An interactive code (NETPATH) for modeling NET geochemical reactions along a flow PATH, ver. 2.0: U.S. Geological Survey Water-Resources Investigations Report 94-4169, 130 p.
- Plummer, L.N., and Sprinkle, C.L., 2001, Radiocarbon dating of dissolved inorganic carbon in groundwater from confined parts of the Floridian aquifer, Florida, USA: *Hydrogeology Journal*, v. 9, p. 127-150.
- Popkin, B.P., 1971, Groundwater resources of Montgomery County, Texas: Texas Water Development Board Report 136, 143 p.
- Poreda, R.J., Cerling, T.E., and Solomon, D.K., 1988, Tritium and helium isotopes as hydrologic tracers in a shallow unconfined aquifer: *Journal of Hydrology*, v. 103, p. 1-9.
- Rounds, S.A., 2006, Alkalinity and acid neutralizing capacity, ver. 3.0: U.S. Geological Survey Techniques of Water-Resources Investigations, book 9, chap. A6., sec. 6.6, accessed April 6, 2011, at <http://pubs.water.usgs.gov/twri9A6/>.
- Rupert, M.G., and Plummer, L.N., 2009, Groundwater quality, age, and probability of contamination, Eagle River watershed valley-fill aquifer, north-central Colorado, 2006-2007: U.S. Geological Survey Scientific Investigations Report 2009-5082, 59 p.
- Ryder, P.D., 1988, Hydrogeology and predevelopment flow in the Texas Gulf Coast aquifer systems: U.S. Geological Survey Water-Resources Investigations Report 87-4248, 109 p.
- Ryder, P.D., 1996, Ground water atlas of the United States—Segment 4, Oklahoma and Texas: U.S. Geological Survey Hydrologic Atlas 730-E, accessed June 15, 2010, at http://pubs.usgs.gov/ha/ha730/ch_e/index.html.
- Scanlon, B.R., Dutton, A.R., and Sophocleous, M.A., 2002, Groundwater recharge in Texas: University of Texas at Austin, Bureau of Economic Geology, final contract report, variously paginated.
- Scanlon, B.R., Healy, R.W., and Cook, P.G., 2002, Choosing appropriate techniques for quantifying groundwater recharge: *Hydrogeology Journal*, v. 10, p. 18-39.
- Scanlon, B.R., Reedy, R.C., Strassberg, Gil, Huang, Yun, and Senay, Gabriel, 2011, Estimation of groundwater recharge to the Gulf Coast aquifer in Texas, USA: University of Texas at Austin, Bureau of Economic Geology, final contract report, variously paginated.
- Schlosser, Peter, Stute, Martin, Dörr, H., Sonntag, Christian, and Münnich, K.O., 1988, Tritium/³He dating of shallow groundwater: *Earth and Planetary Science Letters*, v. 89, p. 353-362.
- Schlosser, P., Stute, M., Sonntag, C., and Münnich, K.O., 1989, Tritogenic ³He in shallow groundwater: *Earth and Planetary Science Letters*, v. 94, p. 245-256.
- Solomon, D.K., 2000, ⁴He in groundwater, chap 14 *of* Cook, P.G., and Herczeg, A.L., eds., Environmental tracers in subsurface hydrology: Boston, Mass., Kluwer Academic Press, p. 425-439.
- Solomon, D.K., and Cook, P.G., 2000, ³H and ³He, chap 13 *of* Cook, P.G., and Herczeg, A.L., eds., Environmental tracers in subsurface hydrology: Boston, Mass., Kluwer Academic Press, p. 397-424.
- Solomon, D.K., Hunt, A., and Poreda, R.J., 1996, Source of radiogenic helium 4 in shallow aquifers—Implications for dating young groundwater: *Water Resources Research*, v. 32, no. 6, p. 1805-1813.
- Solomon, D.K., and Sudicky, E.A., 1991, Tritium and helium-3 isotope ratios for direct estimation of spatial variations in groundwater recharge: *Water Resources Research*, v. 27, p. 2309-2319.
- Strom, E.W., Houston, N.A., and Garcia, A.C., 2003a, Selected hydrogeologic datasets for the Chicot aquifer, Texas: U.S. Geological Survey Open-File Report 2003-297, 1 CD-ROM.
- Strom, E.W., Houston, N.A. and Garcia, A.C., 2003b, Selected hydrogeologic datasets for the Evangeline aquifer, Texas: U.S. Geological Survey Open-File Report 2003-298, 1 CD-ROM.
- Strom, E.W., Houston, N.A. and Garcia, A.C., 2003c, Selected hydrogeologic datasets for the Jasper aquifer, Texas: U.S. Geological Survey Open-File Report 2003-299, 1 CD-ROM.

- Szabo, Zoltan, Rice, D.E., Plummer, L.N., Busenberg, Eurybiades, Drenkard, S., and Schlosser, P., 1996, Age-dating of shallow groundwater with chlorofluorocarbons, tritium/helium 3, and flow path analysis, southern New Jersey coastal plain: *Water Resources Research*, v. 32, no. 4, p. 1023-1038.
- Szabo, Zoltan, Keller, E.A., and Defawe, R.M., 2006, Pore-Water quality in the clay-silt confining units of the lower Miocene Kirkwood Formation and hypothetical effects on water quality of the Atlantic City 800-Foot Sand, northeastern Cape May County, New Jersey, 2001: U.S. Geological Survey Scientific Investigations Report 2006-5134, 37 p.
- Tamers, M.A., 1975, Validity of radiocarbon dates on groundwater: *Surveys in Geophysics*, v. 2, p. 217-239.
- Thatcher, L.L., Janzer, V.J., and Edwards, K.W., 1977, Methods for determination of radioactive substances in water and fluvial sediments: U.S. Geological Survey Techniques of Water-Resources Investigations, book 5, chap. A5, 95 p.
- Trapp, Jr., H., and Horn, M.A., 1997, Ground water atlas of the United States—Segment 11, Delaware, Maryland, New Jersey, North Carolina, Pennsylvania, Virginia, and West Virginia: U.S. Geological Survey Hydrologic Atlas 730-L: Accessed June 14, 2010 at http://pubs.usgs.gov/ha/ha730/ch_1/index.html.
- University of Texas, 2012, Bureau of Economic Geology—Jasper interval, east Texas Gulf Coast: Accessed November 27, 2012, at <http://www.beg.utexas.edu/enviro/qtlty/co2seq/co2data/0jasper.htm>.
- U.S. Census Bureau, 2011a, The 2011 statistical abstract—The national data book: Accessed May 3, 2011, at <http://www.census.gov/compendia/statab/cats/population.html>.
- U.S. Census Bureau, 2011b, 2010 census results: Accessed May 3, 2011, at <http://2010.census.gov/2010census/data/index.php>.
- U.S. Department of Agriculture (USDA), 1972, Soil survey of Montgomery County, Texas, 1959-1965: Accessed January 31, 2013, at <http://soildatamart.nrcs.usda.gov/Manuscripts/TX339/0/Montgomery.pdf>.
- U.S. Department of Agriculture, Natural Resources Conservation Service, 2006, Digital general soil map of U.S.—Tabular digital data and vector digital data, vector digital data, Fort Worth, Tex.: Accessed January 31, 2013, at <http://soildatamart.nrcs.usda.gov/Survey.aspx?State=TX>.
- U.S. Environmental Protection Agency, 1994, Design, operation, and closure of municipal solid waste landfills: Office of Research and Development, accessed August 16, 2011 at <http://nepis.epa.gov>.
- U.S. Geological Survey, variously dated, National field manual for the collection of water-quality data: U.S. Geological Survey Techniques of Water-Resources Investigations, book 9, chaps. A1–A9, accessed May 27, 2010, at <http://pubs.water.usgs.gov/twri9A>.
- U.S. Geological Survey, 2009a, The Reston Chlorofluorocarbon Laboratory: Accessed May 27, 2010, at <http://water.usgs.gov/lab/>.
- U.S. Geological Survey, 2009b, The Reston Chlorofluorocarbon Laboratory air curve: Accessed September, 14, 2011, at http://water.usgs.gov/lab/software/air_curve/.
- U.S. Geological Survey, 2011a, The Reston Chlorofluorocarbon Laboratory—Why measure dissolved helium in ground water: accessed April 19, 2011, at <http://water.usgs.gov/lab/dissolved-gas/lab/helium.html>.
- U.S. Geological Survey, 2011b, The Reston chlorofluorocarbon laboratory—Why collect samples for N₂, Ar, CH₄, O₂, CO₂: Accessed June 13, 2011, at http://water.usgs.gov/lab/dissolved-gas/lab/about_gas.html.
- Wigley, T.M.L., Plummer, L.N., and Pearson, Jr., F.J., 1978, Mass transfer and carbon isotope evolution in natural water systems: *Geochim Cosmochim Acta*, v. 42, p. 1117-1139.
- Williamson, A.K., Grubb, H.F. and Weiss, J.S., 1990, Ground-water flow in the Gulf Coast Aquifer Systems, south central United States—A preliminary analysis: U.S. Geological Survey Water-Resources Investigations Report 89-4071, 124 p.
- Woods Hole Oceanographic Institution, 2011, NOSAMS, National Ocean Sciences Accelerator Mass Spectrometry Facility—The Sample Preparation Laboratory: Accessed June 25, 2012, at <http://www.whoi.edu/page/live.do?pid=43315>.
- Zinn, B.A., and Konikow, L.F., 2007, Effects of intraborehole flow on groundwater age distribution: *Hydrogeology Journal*, v. 15, no. 4, p. 633-643.

ISBN 978-1 4113 3590-5

