National Water-Quality Assessment Program

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Scientific Investigations Report 2009–5091

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Foreword

The U.S. Geological Survey (USGS) is committed to providing the Nation with reliable scientific information that helps to enhance and protect the overall quality of life and that facilitates effective management of water, biological, energy, and mineral resources (http://www.usgs.gov/). Information on the Nation's water resources is critical to ensuring long-term availability of water that is safe for drinking and recreation and is suitable for industry, irrigation, and fish and wildlife. Population growth and increasing demands for water make the availability of that water, measured in terms of quantity and quality, even more essential to the long-term sustainability of our communities and ecosystems.

The USGS implemented the National Water-Quality Assessment (NAWQA) Program in 1991 to support national, regional, State, and local information needs and decisions related to water-quality management and policy (http://water.usgs.gov/nawqa). The NAWQA Program is designed to answer: What is the quality of our Nation's streams and ground water? How are conditions changing over time? How do natural features and human activities affect the quality of streams and ground water, and where are those effects most pronounced? By combining information on water chemistry, physical characteristics, stream habitat, and aquatic life, the NAWQA Program aims to provide science-based insights for current and emerging water issues and priorities. From 1991 to 2001, the NAWQA Program completed interdisciplinary assessments and established a baseline understanding of water-quality conditions in 51 of the Nation's river basins and aquifers, referred to as Study Units (http://water.usgs.gov/nawqa/studyu.html).

In the second decade of the Program (2001–2012), a major focus is on regional assessments of water-quality conditions and trends. These regional assessments are based on major river basins and principal aquifers, which encompass larger regions of the country than the Study Units. Regional assessments extend the findings in the Study Units by filling critical gaps in characterizing the quality of surface water and ground water, and by determining water-quality status and trends at sites that have been consistently monitored for more than a decade. In addition, the regional assessments continue to build an understanding of how natural features and human activities affect water quality. Many of the regional assessments employ modeling and other scientific tools, developed on the basis of data collected at individual sites, to help extend knowledge of water quality to unmonitored, yet comparable areas within the regions. The models thereby enhance the value of our existing data and our understanding of the hydrologic system. In addition, the models are useful in evaluating various resource-management scenarios and in predicting how our actions, such as reducing or managing nonpoint and point sources of contamination, land conversion, and altering flow and (or) pumping regimes, are likely to affect water conditions within a region.

Other activities planned during the second decade include continuing national syntheses of information on pesticides, volatile organic compounds (VOCs), nutrients, trace elements, and aquatic ecology; and continuing national topical studies on the fate of agricultural chemicals, effects of urbanization on stream ecosystems, bioaccumulation of mercury in stream ecosystems, effects of nutrient enrichment on stream ecosystems, and transport of contaminants to public-supply wells.

The USGS aims to disseminate credible, timely, and relevant science information to address practical and effective water-resource management and strategies that protect and restore water quality. We hope this NAWQA publication will provide you with insights and information to meet your needs, and will foster increased citizen awareness and involvement in the protection and restoration of our Nation's waters.

The USGS recognizes that a national assessment by a single program cannot address all water-resource issues of interest. External coordination at all levels is critical for cost-effective management, regulation, and conservation of our Nation's water resources. The NAWQA Program, therefore, depends on advice and information from other agencies—Federal, State, regional, interstate, Tribal, and local—as well as nongovernmental organizations, industry, academia, and other stakeholder groups. Your assistance and suggestions are greatly appreciated.

Matthew C. Larsen
Associate Director for Water

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Conversion Factors

Inch/Pound to SI

Multiply	By	To obtain
	Length	
inch (in.)	25.4	millimeter (mm)
foot (ft)	0.3048	meter (m)
mile (mi)	1.609	kilometer (km)
	Area	
acre	0.004047	square kilometer (km^2)
square foot (ft^2)	0.09290	square meter (m^2)
square mile (mi^2)	2.590	square kilometer (km^2)
	Volume	
gallon (gal)	0.003785	cubic meter (m^3)
million gallons (Mgal)	3,785	cubic meter (m^3)
cubic foot (ft^3)	0.02832	cubic meter (m^3)
	Flow rate	
inch per year (in/yr)	25.4	millimeter per year (mm/yr)
foot per second (ft/s)	0.3048	meter per second (m/s)
foot per day (ft/d)	0.3048	meter per day (m/d)
cubic foot per second (ft^3/s)	0.02832	cubic meter per second (m^3/s)
cubic foot per day (ft^3/d)	0.02832	cubic meter per day (m^3/d)
gallon per minute (gal/min)	0.06309	liter per second (L/s)
gallon per day (gal/d)	0.003785	cubic meter per day (m^3/d)
million gallons per day (Mgal/d)	0.04381	cubic meter per second (m^3/s)
	Radioactivity	
picocurie per liter (pCi/L)	0.037	becquerel per liter (Bq/L)
	Application rate	
pounds per acre per year [(lb/acre)/yr]	1.121	kilograms per hectare per year [(kg/ha)/yr]

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

$$°F = (1.8 \times °C) + 32$$

Vertical coordinate information is referenced to the National Geodetic Vertical Datum of 1929 (NGVD of 1929).

Horizontal coordinate information is referenced to the North American Datum of 1927 (NAD27).

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

Specific conductance is given in microsiemens per centimeter at 25 degrees Celsius (µS/cm at 25 °C).

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

Abbreviations and Acronyms

CWA	Clean Water Act
DO	dissolved oxygen
GIS	Geographic Information System
HA	health advisory
HBSL	health-based screening level
MCL	maximum contaminant level
MEK	methyl ethyl ketone
MMM	multimedia mitigation
MRVA	Mississippi River Valley alluvial aquifer
MTBE	methyl tert-butyl ether
NAWQA	National Water-Quality Assessment Program
NWQL	National Water Quality Laboratory
PVC	polyvinyl chloride
QC	quality control
RL	reporting limit
SDWA	Safe Drinking Water Act
SMCL	secondary maximum contaminant level
TDS	total dissolved solids
TU	tritium unit
USEPA	U.S. Environmental Protection Agency
USGS	U.S. Geological Survey
UST	underground storage tank
VOC	volatile organic compound

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Abstract

The Mississippi embayment-Texas coastal uplands aquifer system is an important source of drinking water, providing about 724 million gallons per day to about 8.9 million people in Texas, Louisiana, Mississippi, Arkansas, Missouri, Tennessee, Kentucky, Illinois, and Alabama. The Mississippi River Valley alluvial aquifer ranks third in the Nation for total withdrawals of which more than 98 percent is used for irrigation. From 1994 through 2004, water-quality samples were collected from 169 domestic, monitoring, irrigation, and public-supply wells in the Mississippi embayment-Texas coastal uplands aquifer system and the Mississippi River Valley alluvial aquifer in various land-use settings and of varying well capacities as part of the U.S. Geological Survey's National Water-Quality Assessment Program. Groundwater samples were analyzed for physical properties and about 200 water-quality constituents, including total dissolved solids, major inorganic ions, trace elements, radon, nutrients, dissolved organic carbon, pesticides, pesticide degradates, and volatile organic compounds.

The occurrence of nutrients and pesticides differed among four groups of the 114 shallow wells (less than or equal to 200 feet deep) in the study area. Tritium concentrations in samples from the Holocene alluvium, Pleistocene valley trains, and shallow Tertiary wells indicated a smaller component of recent groundwater than samples from the Pleistocene terrace deposits. Although the amount of agricultural land overlying the Mississippi River Valley alluvial aquifer was considerably greater than areas overlying parts of the shallow Tertiary and Pleistocene terrace deposits wells, nitrate was rarely detected and the number of pesticides detected was lower than other shallow wells. Nearly all samples from the Holocene alluvium and Pleistocene valley trains were anoxic, and the reducing conditions in these aquifers likely result in denitrification of nitrate. In contrast, most samples from the Pleistocene terrace deposits in Memphis, Tennessee, were oxic, and the maximum nitrate concentration measured was 6.2 milligrams per liter. Additionally, soils overlying the Holocene alluvium and Pleistocene valley trains, generally in areas near the wells, had lower infiltration rates and higher percentages of clay than soils overlying the shallow Tertiary and Pleistocene terrace deposits wells. Differences in these soil properties were associated with differences in the occurrence of pesticides. Pesticides were most commonly detected in samples from wells in the Pleistocene terrace deposits, which generally had the highest infiltration rates and lowest clay content.

Median dissolved phosphorus concentrations were 0.07, 0.11, and 0.65 milligram per liter in samples from the shallow Tertiary, Pleistocene valley trains, and Holocene alluvium, respectively. The widespread occurrence of dissolved phosphorus at concentrations greater than 0.02 milligram per liter suggests either a natural source in the soils or aquifer sediments, or nonpoint sources such as fertilizer and animal waste or a combination of natural and human sources. Although phosphorus concentrations in samples from the Holocene alluvium were weakly correlated to concentrations of several inorganic constituents, elevated concentrations of phosphorus could not be attributed to a specific source. Phosphorus concentrations generally were highest where samples indicated anoxic and reducing conditions in the aquifers. Elevated dissolved phosphorus concentrations in base-flow samples from two streams in the study area suggest that transport of phosphorus with groundwater is a potential source contributing to high yields of phosphorus in the lower Mississippi River basin.

Water from 55 deep wells (greater than 200 feet deep) completed in regional aquifers of Tertiary age represent a sample of the principal aquifers used for drinking-water supply in the study area. The wells were screened in both confined and unconfined parts of these aquifers, and tritium samples collected from 11 wells did not indicate a significant component of recent water. The quality of the water generally was good, and concentrations of most inorganic constituents were less than water-quality criteria for drinking water. Relatively few pesticides or volatile organic compounds were detected. Secondary drinking-water standards were exceeded

for iron, manganese, and total dissolved solids in a total of 20, 17, and 10 wells, respectively. Fluoride was detected in one sample at a concentration greater than its secondary maximum contaminant level. Radon activities were greater than 300 picocuries per liter in samples from 10 wells screened in the middle Wilcox aquifer in northwestern Louisiana. While not a drinking-water concern, elevated phosphorus concentrations also were measured in the drinking-water supply aquifers. A relation between phosphorus concentrations and dissolved solids and fluoride suggests a geologic source of phosphorus in these deep wells.

Groundwater withdrawals from these regional aquifers have lowered water levels, which increases the potential of movement of shallow groundwater to deep aquifers. Water-level data for a few wells in the Pleistocene terrace deposits in the Memphis area suggest a hydraulic connection between this shallow aquifer and the deeper middle Claiborne aquifer, locally named the Memphis aquifer, that is used for public supply. Additionally, pesticides and volatile organic compounds were detected in samples from wells screened in shallow and deeper portions of the middle Claiborne aquifer, further illustrating the potential vulnerability of this source of drinking water.

Introduction

Groundwater is one of the Nation's most important resources and is the source of drinking water for about 50 percent of the population, or about 130 million U.S. residents (U.S. Geological Survey, 1999). In 1991, the U.S. Geological Survey began full implementation of the National Water-Quality Assessment (NAWQA) Program to describe the status and trends in the quality of the Nation's surface water and groundwater resources and to determine the natural and human-related factors that affect water quality (Hirsch and others, 1988; Gilliom and others, 1995). More than 50 major river basins or aquifer systems were identified for investigation as part of the first decade (1991–2001) of sampling for the NAWQA Program. Together, these basins and aquifer systems include water resources available to more than 60 percent of the Nation's population and encompass about one-half of the land area in the conterminous United States. Knowledge of the quality of the Nation's surface-water and groundwater resources is important for the protection of human and aquatic health and for the management of land and water resources and the conservation and regulation of those resources.

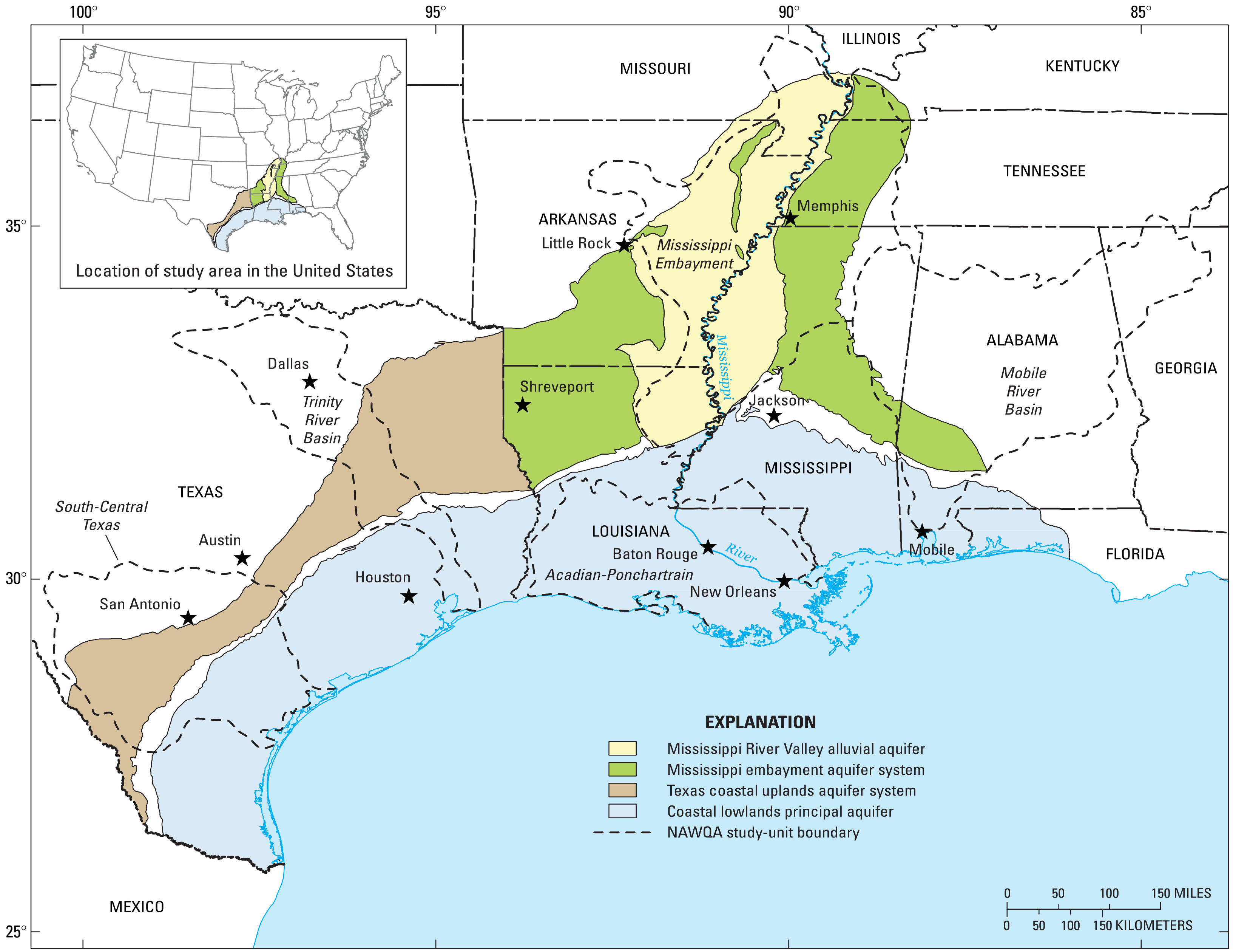
A major focus for groundwater studies in the NAWQA Program during the second decade (2002–2012) of sampling is for regional- and national-scale assessments of groundwater status and trends in 19 of 62 principal aquifers identified by the U.S. Geological Survey Office of Groundwater (U.S. Geological Survey, 2003). A principal aquifer is a regionally extensive aquifer or aquifer system that has the potential of or currently is being used as a primary source of drinking water. Three quarters of the estimated withdrawals for drinking-water supply in 1990 came from the 19 principal aquifers.

The Mississippi embayment and Texas coastal uplands regional aquifers (fig. 1) were selected as principal aquifers for additional study in the NAWQA Program. Water-quality data collected by three NAWQA study units, the Acadian-Ponchartrain, Mississippi embayment, and Trinity River Basin study units, in the Tertiary aquifers are included in this report. Water-quality data collected from the Mississippi River Valley alluvial (MRVA) aquifer and the Pleistocene terrace deposits near Memphis, TN, also are included in this report because locally both aquifers are hydraulically connected with the underlying Tertiary aquifers.

In general, the NAWQA Program focuses on compounds with well-established analytical methods for constituents such as pesticides, nutrients, volatile organic compounds (VOCs), and trace elements that have been or are currently being used in agricultural and urban areas across the Nation. Analytes are measured at very low concentrations, many of them 10 to 100 times lower than Federal or State standards and health advisories. Detection of compounds does not necessarily translate to risks to humans, but detection of compounds at low concentrations can be useful for evaluating groundwater trends and for identifying and assessing movement of contaminants. Detections are compared to human-health benchmarks to determine if a potential health concern exists and whether additional monitoring may be warranted.

This report describes the quality of shallow (less than or equal to 200 feet [ft]) water in parts of the Mississippi embayment-Texas coastal uplands aquifer system and the MRVA aquifer. The occurrence of nutrients, selected pesticides, and VOCs in shallow groundwater from wells in two subunits of the MRVA aquifer, Pleistocene terrace deposits, and shallow parts of three aquifers in sediments of Tertiary age is characterized with respect to differences in hydrogeology, groundwater geochemistry and residence time, selected properties of the overlying soils, and land use. This report also compares the quality of the water in deeper parts of the aquifer systems to shallow groundwater quality because in much of the study area, groundwater gradients are such that water from shallow aquifers can move to deeper units that are used as drinking-water sources.

Data included in this report were collected as part of the NAWQA Program from 1994 to 2004. Samples were analyzed for major and trace inorganic constituents, nutrients, VOCs, and pesticides, and a subset of wells were sampled for tritium analysis. Inorganic constituents and tritium data were used to characterize groundwater geochemistry and residence time in the aquifer to aid in the interpretation of occurrence of nutrients, VOCs, and pesticides. Data were collected from 114 shallow wells and 55 deep wells that are used primarily for drinking water, either domestic or public supply. The shallow well dataset includes several different well types, but largely consists of domestic, irrigation, and monitoring wells.



Base map modified from
U.S. Geological Survey
digital data, 1:250,000

Figure 1. Locations of National Water-Quality Assessment (NAWQA) Program study units, the Mississippi embayment-Texas coastal uplands aquifer system, and the Mississippi River Valley alluvial aquifer, south-central United States (Miller, 1990; Trapp and Horn, 1997).

Description of Study Area

The study area covers approximately 197,000 square miles and includes parts of Alabama, Arkansas, Illinois, Kentucky, Louisiana, Mississippi, Missouri, Tennessee, and Texas (fig. 1) and includes three principal aquifers or aquifer systems: the Mississippi embayment aquifer system, the Texas coastal uplands aquifer system, and the Mississippi River Valley alluvial aquifer (MRVA). Geologic units of Tertiary age in the Mississippi embayment and Texas coastal uplands aquifer systems are stratigraphically equivalent and, in this report, these aquifer systems are referred to collectively as the Tertiary aquifers. A large regional aquifer, the MRVA, overlies most of the central part of the Mississippi embayment and Texas coastal uplands aquifer systems (fig. 1). The MRVA is about 70 to 120 miles wide and covers approximately 33,000 square miles in parts of Arkansas, Louisiana, Mississippi, and Tennessee. Locally, shallow aquifers composed of sediments of Pleistocene and Holocene age overlie the regional aquifers. For example, in the Memphis area, terrace deposits of Pleistocene age contain a shallow water-table aquifer that overlies and in most locations is separated by a confining unit from the Tertiary aquifers. Hydrogeologic units of Cretaceous age crop out in a small area of Alabama, and, because no wells were sampled in these units, these aquifers are not discussed in this report.

Hydrogeology

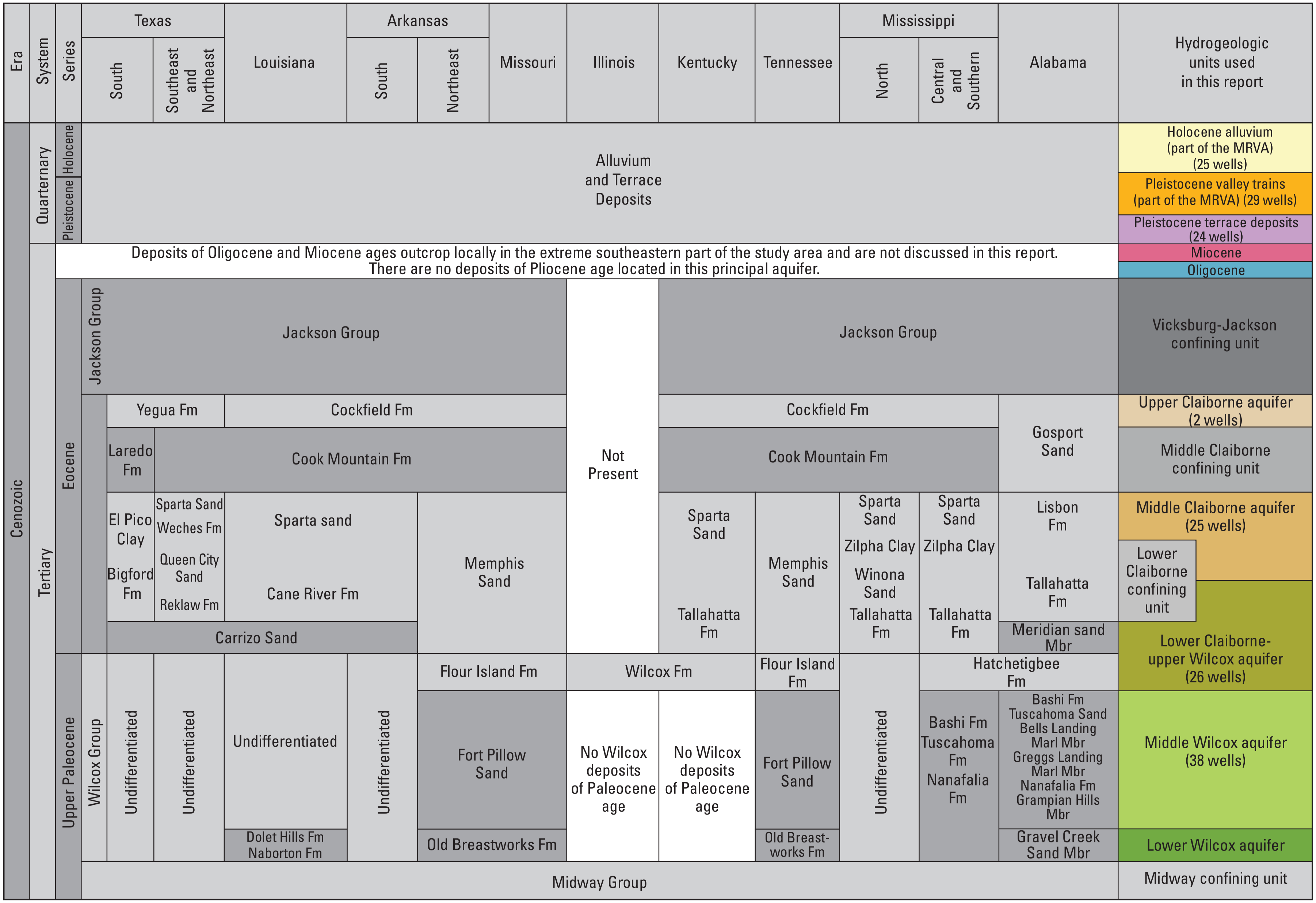
Hydrogeologic units of Tertiary age consist of predominantly unconsolidated to semiconsolidated sand, silt, and clay and underlie the entire study area (fig. 1). In the western part of the study area, these units dip coastward (southward) beneath the coastal lowlands aquifer system and range in thickness from a feathered edge to more than 6,000 ft (Renken, 1998). In the eastern part of the study area, the Tertiary units are thickest near the Mississippi River, which approximates the axis of the Mississippi embayment, a trough-like structure in which these sediments were deposited. The units thin to the west and east, upgradient from the center of the Mississippi embayment.

The Tertiary aquifers consist of several regional aquifers and confining units, which have been described in detail by Lloyd and Lyke (1995), Ryder (1996), and Renken (1998). The regional aquifers consist of one or more local aquifers, the names of which may vary between States and, in some cases, within a State (fig. 2). The regional aquifers sampled as part of this study include the upper and middle Claiborne aquifer, the lower Claiborne-upper Wilcox aquifer, and the middle Wilcox aquifer (figs. 2 and 3). The lower Wilcox aquifer underlies the middle Wilcox aquifer; however, this unit was not sampled for this study. The aquifers in the regional aquifer system are bounded at the top by the Vicksburg-Jackson confining unit and at the bottom by the Midway confining unit throughout most of the study area (Hosman and Weiss, 1991). Regional confining units that separate some of the aquifers throughout the study area are the middle Claiborne and lower Claiborne confining units (figs. 2 and 3). In Texas, Louisiana, Mississippi, and southern Arkansas, clays in the lower Claiborne serve as a regional confining unit that is not present in Tennessee, Missouri, and northeastern Arkansas.

Groundwater generally moves from outcrop areas, which are the primary source of recharge for these aquifers, downdip to areas of discharge. In the outcrop areas, groundwater is unconfined, and generally, the aquifers are confined downgradient from the recharge areas. In the southern part of the study area, groundwater generally moves southward from outcrop bands downdip to the deeper parts of the system. In the northern part of the study area, groundwater flow direction is generally eastward and westward toward the axis of the Mississippi embayment. Groundwater discharge is to pumping wells, incised rivers and streams, and as upward leakage to shallower aquifers (Lloyd and Lyke, 1995). In the area of the Sabine uplift along the Texas and Louisiana State line, groundwater flow paths differ from the regional flow paths; groundwater flow is generally radial, away from the center of the uplift. Additionally, faulting in the northern half of the Sabine uplift has further affected local groundwater flow (Rapp, 1996).

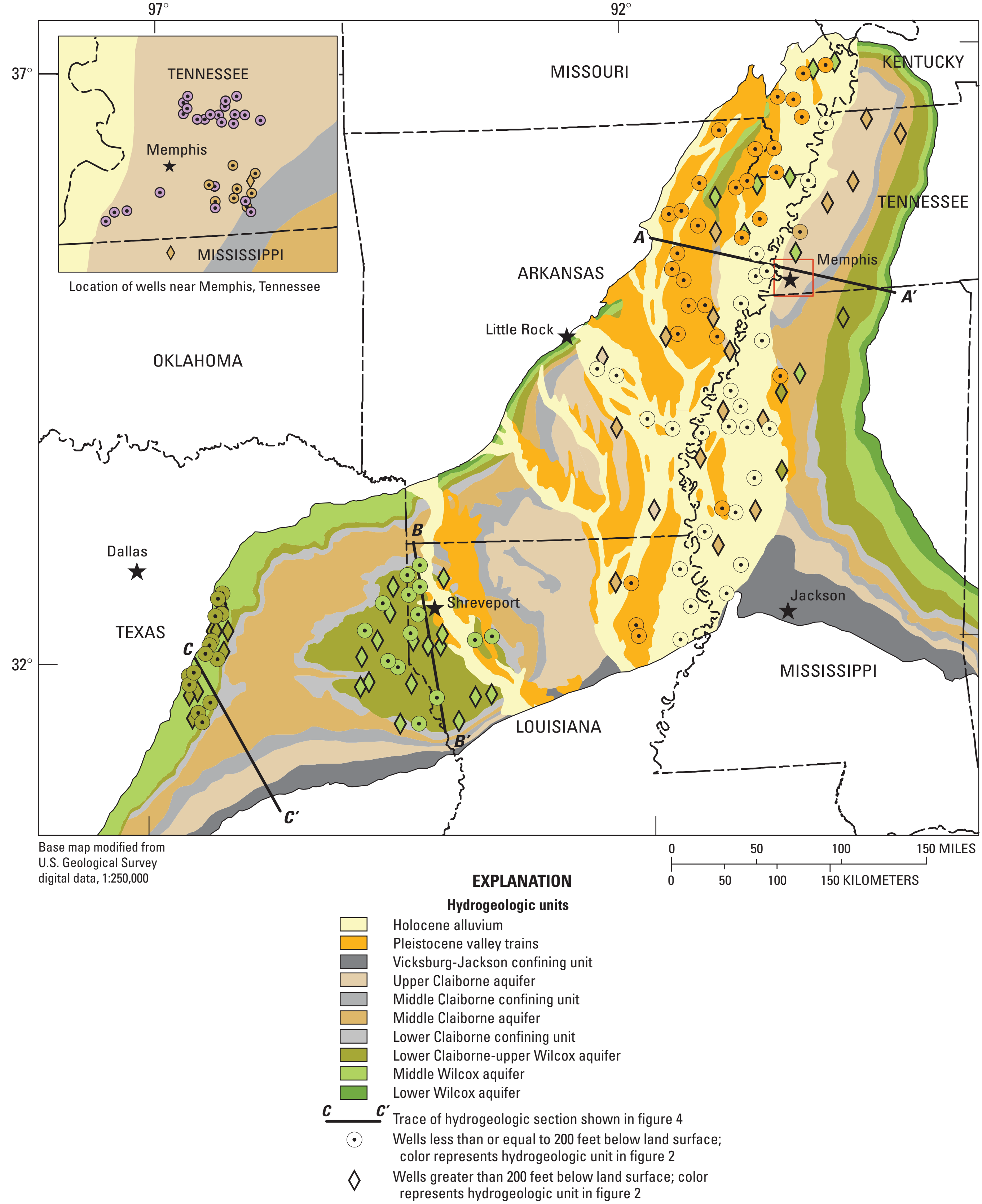
The hydrogeologic units of Quaternary age are largely alluvial deposits of unconsolidated sand and gravel, silt, and clay (fig. 1). The largest deposit of Quaternary age in the study area is the Mississippi River alluvium, which includes the MRVA aquifer. The MRVA aquifer consists of a braided sequence of gravel and coarse sand and overlies the Tertiary aquifers in the east-central part of the study area. Thickness of the MRVA aquifer ranges from 25 to 150 ft and is more than 75 ft in most locations. The MRVA aquifer is divided into two subunits based on different lithologic characteristics: the Pleistocene valley trains and Holocene alluvium. As a result of different depositional environments, the Pleistocene valley trains generally contain coarser sediments than the Holocene alluvium. Both units have a surficial layer of silt and clay; however, the clay layer overlying the Holocene alluvium is thicker. These fine-grained sediments are an upper confining unit for much of the MRVA aquifer (Renken, 1998).

The sources of recharge for the MRVA aquifer include infiltration of precipitation through the overlying confining unit, downward movement of water from streams that incise the aquifer (the Mississippi River and smaller tributaries), and locally, upward flow from underlying aquifers. The contribution to recharge to the MRVA aquifer from these sources has changed over time as a result of withdrawals from both the MRVA and the underlying Tertiary aquifers. Prior to development, water levels (hydraulic head) in the Tertiary aquifers generally were higher than those in the MRVA aquifer (Arthur, 2001). In areas where withdrawal from the Tertiary aquifers has lowered groundwater levels and a hydraulic connection exists, groundwater may move downward from the MRVA to the Tertiary aquifers. Conversely, where these aquifers are connected and heads are lower in the MRVA aquifer, water



Era	System	Series		Texas		Louisiana	Arkansas		Missouri	Illinois	Kentucky	Tennessee	Mississippi		Alabama	Hydrogeologic units used in this report
				South	Southeast and Northeast		South	Northeast					North	Central and Southern		
Cenozoic	Quaternary	Holocene	Alluvium and Terrace Deposits													Holocene alluvium (part of the MRVA) (25 wells)
		Pleistocene														Pleistocene valley trains (part of the MRVA) (29 wells)
																Pleistocene terrace deposits (24 wells)
	Tertiary	Deposits of Oligocene and Miocene ages outcrop locally in the extreme southeastern part of the study area and are not discussed in this report. There are no deposits of Pliocene age located in this principal aquifer.														Miocene
																Oligocene
		Eocene	Jackson Group	Jackson Group						Not Present	Jackson Group					Vicksburg-Jackson confining unit
				Yegua Fm	Cockfield Fm						Cockfield Fm				Gosport Sand	Upper Claiborne aquifer (2 wells)
				Laredo Fm	Cook Mountain Fm						Cook Mountain Fm					Middle Claiborne confining unit
				El Pico Clay	Sparta Sand Weches Fm	Sparta sand		Memphis Sand			Sparta Sand	Memphis Sand	Sparta Sand	Sparta Sand	Lisbon Fm	Middle Claiborne aquifer (25 wells)
				Bigford Fm	Queen City Sand Reklaw Fm	Cane River Fm							Zilpha Clay Winona Sand	Zilpha Clay	Tallahatta Fm	Lower Claiborne confining unit
				Carrizo Sand							Tallahatta Fm		Tallahatta Fm	Tallahatta Fm	Meridian sand Mbr	Lower Claiborne-upper Wilcox aquifer (26 wells)
		Upper Paleocene	Wilcox Group	Undifferentiated	Undifferentiated	Undifferentiated	Undifferentiated	Flour Island Fm		Wilcox Fm		Flour Island Fm	Undifferentiated	Hatchetigbee Fm		
								Fort Pillow Sand		No Wilcox deposits of Paleocene age	No Wilcox deposits of Paleocene age	Fort Pillow Sand		Bashi Fm Tuscahoma Fm Nanafalia Fm	Bashi Fm Tuscahoma Sand Bells Landing Marl Mbr Greggs Landing Marl Mbr Nanafalia Fm Grampian Hills Mbr	Middle Wilcox aquifer (38 wells)
						Dolet Hills Fm Naborton Fm		Old Breastworks Fm				Old Breast-works Fm			Gravel Creek Sand Mbr	Lower Wilcox aquifer
			Midway Group													Midway confining unit

Figure 2. Stratigraphic column of the Mississippi embayment-Texas coastal uplands aquifer system (modified from Hosman and Weiss, 1991; Ryder, 1996; Warwick and others, 1997; Renken, 1998; MRVA, Mississippi River Valley alluvial aquifer; Fm, formation; Mbr, member).



Base map modified from
U.S. Geological Survey
digital data, 1:250,000

Figure 3. Hydrogeologic units and locations of wells sampled from 1994 to 2004 in the Mississippi embayment-Texas coastal uplands aquifer system and Mississippi River Valley alluvial aquifer.

may move from the Tertiary aquifers into the MRVA aquifer. In addition to movement into deeper aquifers, groundwater discharge from the MRVA is to wells, streams, and rivers. The general direction of groundwater flow in the MRVA aquifer is southward, down the Mississippi River valley, and locally, toward cones of depression created by large volumes of water being pumped from wells screened in the aquifer (Renken, 1998).

The Pleistocene terrace deposits aquifer is a shallow water-table aquifer that overlies the Tertiary aquifers in parts of western Tennessee. The terrace deposits are predominantly sand and gravel of Pleistocene age, and equivalent deposits are present in much of the study area and locally are shallow water-table aquifers. In the Memphis area, this unit generally is between 10 and 100 ft thick and consists of sand and gravel. Locally, the lower part of the Pleistocene terrace deposits is cemented with iron oxide to form ferruginous sandstone. Throughout much of the Memphis area, the middle Claiborne confining unit separates this shallow water-table aquifer from the underlying middle Claiborne aquifer. Recharge to the Pleistocene terrace deposits aquifer is predominantly from the infiltration of precipitation and locally from losing reaches of streams where the streambed intersects the aquifer. Groundwater moves from recharge areas to either streams or seeps and, where the lower confining unit is thin or absent, to the underlying Tertiary aquifers (Parks, 1990).

Groundwater Networks

From 1994 through 2004, a total of six groundwater network studies were completed in the Tertiary aquifers, MRVA, and Pleistocene terrace deposits (table 1). Samples were collected from existing wells in five of these networks (Tertiary aquifers and MRVA) to characterize the occurrence and distribution of natural and anthropogenic constituents in major aquifers, many of which are used as sources of drinking

Table 1. Regional aquifers and hydrogeologic units sampled in the Mississippi embayment-Texas coastal uplands aquifer system and Mississippi River Valley alluvial aquifer.

[LSD, land-surface datum; N, number of wells; median values are in parentheses; N/A, not applicable]

Aquifer system	Regional aquifer sampled	Primary well types	Well depth, in feet	Water level, in feet below LSD	Source
Mississippi River Valley alluvial aquifer	Holocene alluvium N=25	Irrigation	60 – 200 (100)	8 – 46.8 (24)	Gonthier, 2003
Mississippi River Valley alluvial aquifer	Pleistocene valley trains N=29	Irrigation and public supply	25 – 180 (110)	6 – 95 (20)	Gonthier, 2003
Mississippi embayment	Upper Claiborne aquifer Middle Claiborne aquifer Lower Claiborne-upper Wilcox aquifer Middle Wilcox aquifer N=30	Public supply	208 – 1,466 (675)	13.5 – 242 (55)[a]	Gonthier, 2000
Mississippi embayment and Texas coastal uplands	Middle Wilcox aquifer N=30	Domestic	65 – 330 (210)	6.5 – 130.6 (48.2)	N/A
Texas coastal uplands	Lower Claiborne-upper Wilcox aquifer N=23	Domestic and public supply	21 – 490 (160)	6.1 – 130.6 (28.9)[b]	Reutter and Dunn, 2000
Water-table aquifer Mississippi embayment	Pleistocene terrace deposits Middle Claiborne aquifer N=32	Monitoring	33 – 109 (67)	8.3 – 73.1 (25.2)	Gonthier, 2002

[a] Values and median are based on 19 of 30 wells. [b] Values and median are based on 14 of 23 wells.

water. In the Tertiary aquifers, the predominant sampled well types were domestic and public-supply wells. In the MRVA networks, irrigation wells were the principal well type; however, 10 public-supply wells sampled were completed in the Pleistocene valley trains. The well capacities varied considerably for these networks, with domestic wells having the lowest yields, typically less than 100 gallons per minute (gal/min) and public-supply and irrigation wells producing as much as 2,000 to 5,000 gal/min. Samples from a sixth network were collected from 2-inch observation wells screened in the Pleistocene terrace deposits and upper part of the middle Claiborne aquifer to characterize the quality of shallow groundwater in an urban setting. Of the 32 wells in the network, 22 were completed in the Pleistocene terrace deposits, 8 were completed in the middle Claiborne aquifer, and 2 wells were completed in more recent alluvium in the flood plain of a stream in the Memphis, TN, area. The two wells completed in the local alluvium were included with the wells in the terrace deposits because of the well type and location, which did not correspond to wells completed in the MRVA. The monitoring wells generally produced less than 1 gal/min.

Generalized hydrogeologic sections through parts of the study area show the approximate locations of wells sampled in the aquifers (fig. 4). Most of the wells completed in the lower Claiborne-upper Wilcox and middle Wilcox in Texas and Louisiana were sampled in areas without an overlying regional confining unit, and conditions can range from confined to unconfined in these aquifers depending on local geology; whereas, most wells in the upper Claiborne and middle Claiborne in Tennessee, Arkansas, Mississippi, and Missouri were below regional confining units and represented confined parts of these aquifers. The Pleistocene terrace deposits in the Memphis area represent a water-table aquifer and generally are unconfined, but locally, the overlying loess deposits create semiconfined to confined conditions. Three networks sampled a single regional aquifer or hydrogeologic unit, and three networks sampled wells completed in two or more aquifers (table 1). In this report, wells are grouped based on the aquifer in which they are completed and by depth: shallow (less than or equal to 200 ft deep) and deep (greater than 200 ft deep). Wells greater than 200 ft deep generally are representative of water that is used for drinking-water purposes and are classified as Tertiary drinking-water aquifers in this report.

Water Use

About 1,327 million gallons per day (Mgal/d) of water were withdrawn from the Tertiary aquifers for public supply, irrigation, and self-supplied industrial uses in 2000 (Maupin and Barber, 2005). Groundwater withdrawals of 9,290 Mgal/d from the MRVA aquifer accounted for about 12 percent of the total groundwater withdrawals in the Nation and placed the MRVA aquifer as third largest in withdrawals from the 66 principal aquifers across the Nation (Maupin and Barber, 2005). Most of the water withdrawn from the Tertiary aquifers was used for public supply, whereas most of the water withdrawn from the MRVA was used for irrigation.

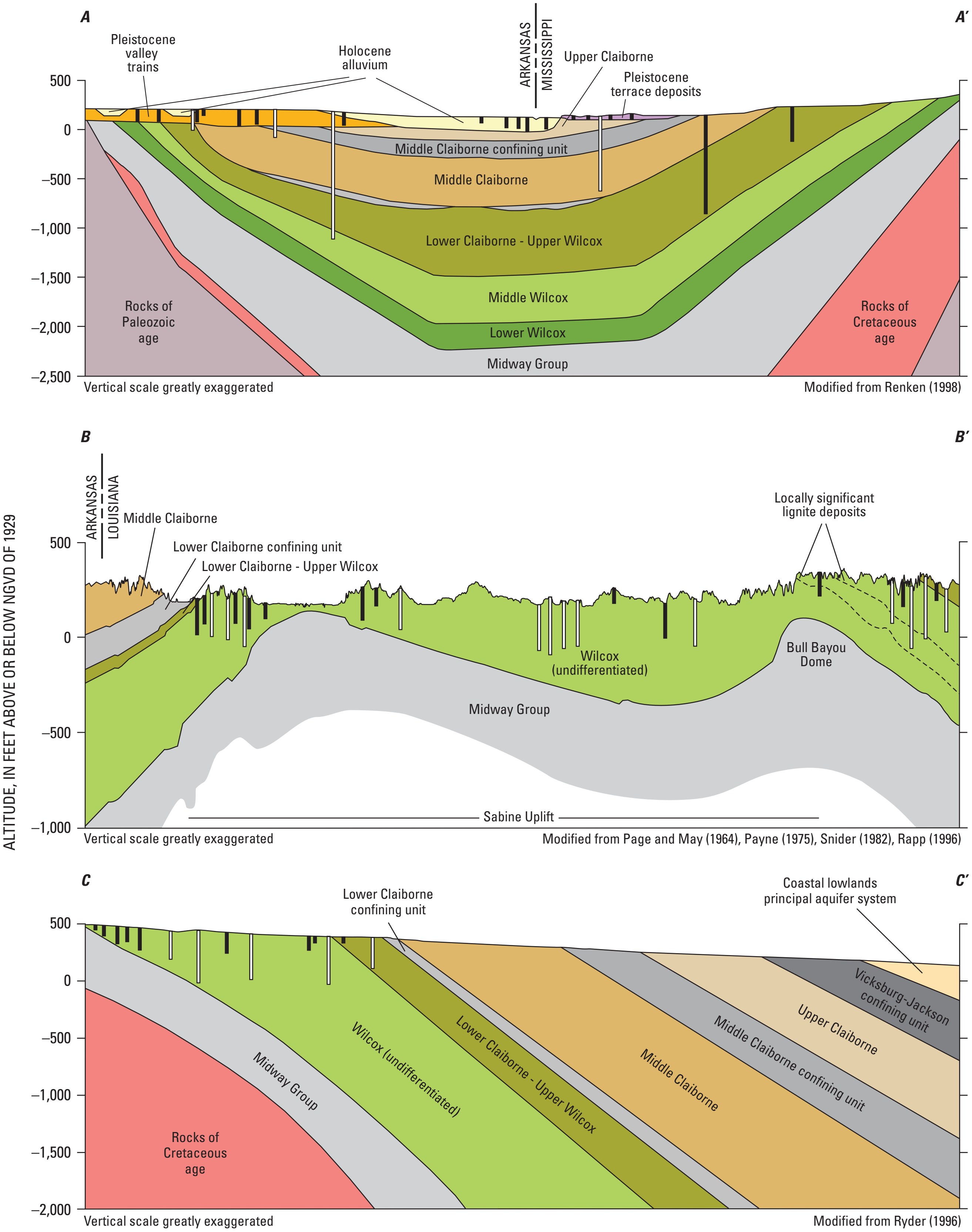
Groundwater represents the primary source of drinking water for most of the population in the study area. In 2000, the total groundwater withdrawals for public supply in the study area were about 794 Mgal/d (Maupin and Barber, 2005). About 90 percent (724 Mgal/d) of these withdrawals were from the Tertiary aquifers. Some of the largest withdrawals in the Tertiary aquifers are from the middle Claiborne and lower Claiborne-upper Wilcox aquifers. Specifically, large withdrawals for public supply occur in western Tennessee, particularly the Memphis area, and parts of northwestern Mississippi, north-central Louisiana, and southern and eastern Arkansas (fig. 5*A*). In rural areas, both Tertiary aquifers and alluvial aquifers are used for domestic supply. Domestic supply use is relatively evenly distributed throughout the study area, and withdrawals are relatively small (about 80 Mgal/d) compared to public-supply use.

In 2000, about 9,533 Mgal/d were withdrawn from the Tertiary aquifers and MRVA aquifer for irrigation (Maupin and Barber, 2005). In contrast to public-supply use, about 96 percent (9,150 Mgal/d) of the irrigation withdrawals were from the MRVA aquifer, most of which was in Arkansas and Missouri and counties and parishes that lie along the Mississippi River in Mississippi and Louisiana (fig. 5*B*).

Withdrawals of groundwater from both the Tertiary aquifers and the MRVA aquifer have lowered water levels in these regional aquifers, particularly near pumping centers (Criner and Parks, 1976; Edds and Fitzpatrick, 1984; Renken, 1998). Prior to these withdrawals, groundwater levels in parts of the Tertiary aquifers were higher than in the overlying MRVA aquifer, and groundwater moved upward into the MRVA. Locally, areas of high chloride concentration and elevated dissolved solids concentrations in the MRVA aquifer in parts of Arkansas, Louisiana, and Mississippi have been interpreted to be the result of movement into the MRVA of more mineralized groundwater from deep aquifers as leakage through the lower confining unit, along faults, or through abandoned oil and gas wells (Morris and Bush, 1986). Large groundwater withdrawals from the middle Claiborne aquifer in the Memphis area, northern Louisiana, and southern Arkansas have lowered groundwater levels as much as 100 ft and induced downward leakage from the MRVA to the Tertiary aquifers (Renken, 1998) throughout the study area.

Land Use

Agriculture accounts for 41 percent of the land use in the study area with much of the use occurring in areas along the Mississippi River (fig. 6). Sixty percent of the area overlying the MRVA is agricultural land used mostly to cultivate soybeans, cotton, corn, and rice (Coupe, 2000). These row crops may require large amounts of pesticides to control grasses, broadleaf weeds, and insects; however, the intensity of pesticide use differs. Propanil, a herbicide used to control weeds



Vertical scale greatly exaggerated

Modified from Renken (1998)

Vertical scale greatly exaggerated

Modified from Page and May (1964), Payne (1975), Snider (1982), Rapp (1996)

Vertical scale greatly exaggerated

Modified from Ryder (1996)

Figure 4. Idealized hydrogeologic sections of the study area: (A–A′) west to east in Arkansas and Mississippi; (B–B′) north to south in Arkansas and Louisiana; and (C–C′) north to south in southwestern Texas. Wells projected onto section represent generalized National Water-Quality Assessment Program sampling zones (black, less than or equal to 200 feet below land surface; white, greater than 200 feet below land surface); key aquifers and formations are identified in parentheses. The lines of sections are shown in figure 3.

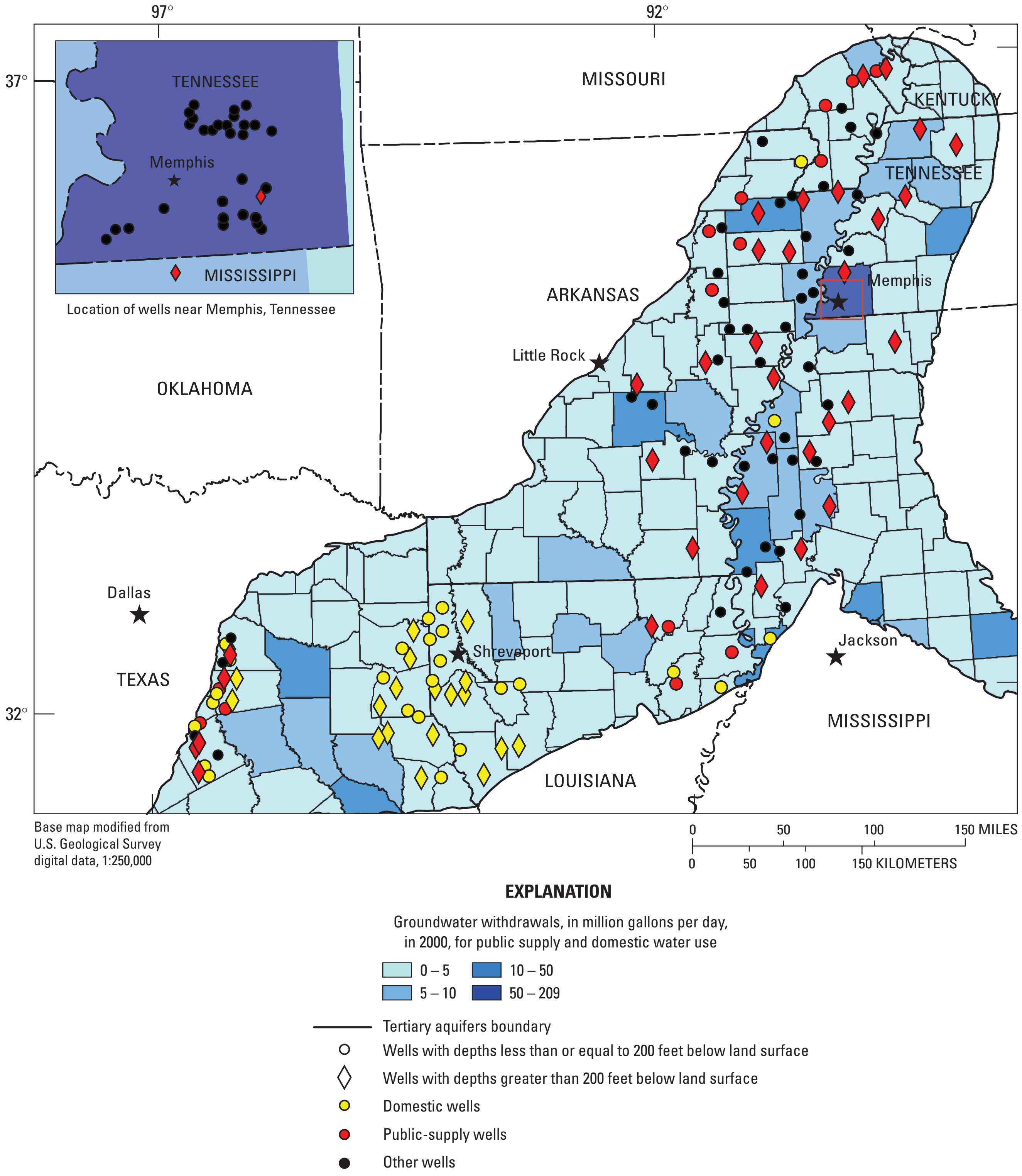
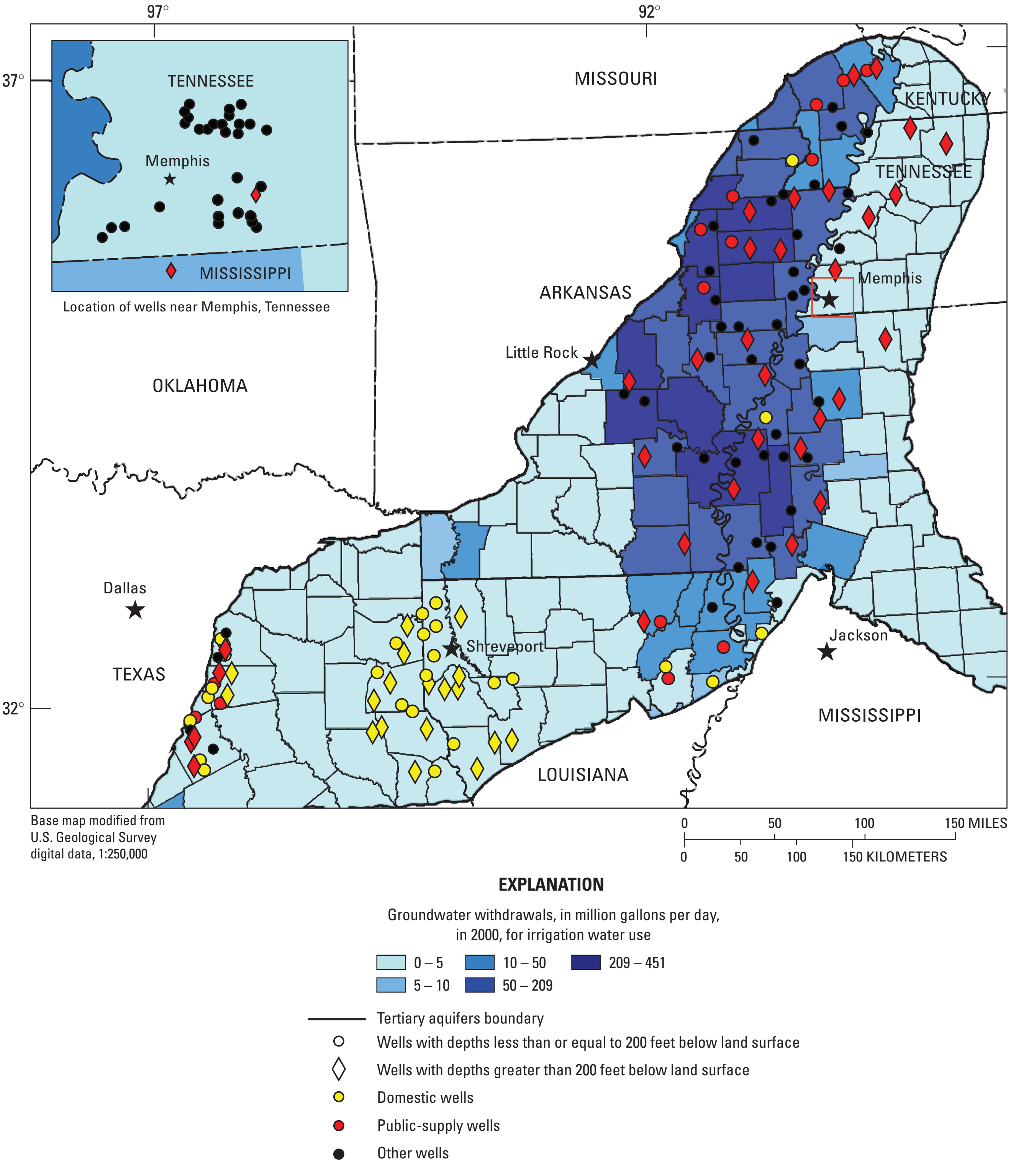


Figure 5*A*. Total groundwater withdrawals for public supply and domestic use by county from the Mississippi embayment-Texas coastal uplands aquifer system and Mississippi River Valley alluvial aquifer, south-central United States, 2000.



Base map modified from
U.S. Geological Survey
digital data, 1:250,000

Figure 5*B*. Total groundwater withdrawals for irrigation use by county from the Mississippi embayment-Texas coastal uplands aquifer system and Mississippi River Valley alluvial aquifer, south-central United States, 2000.

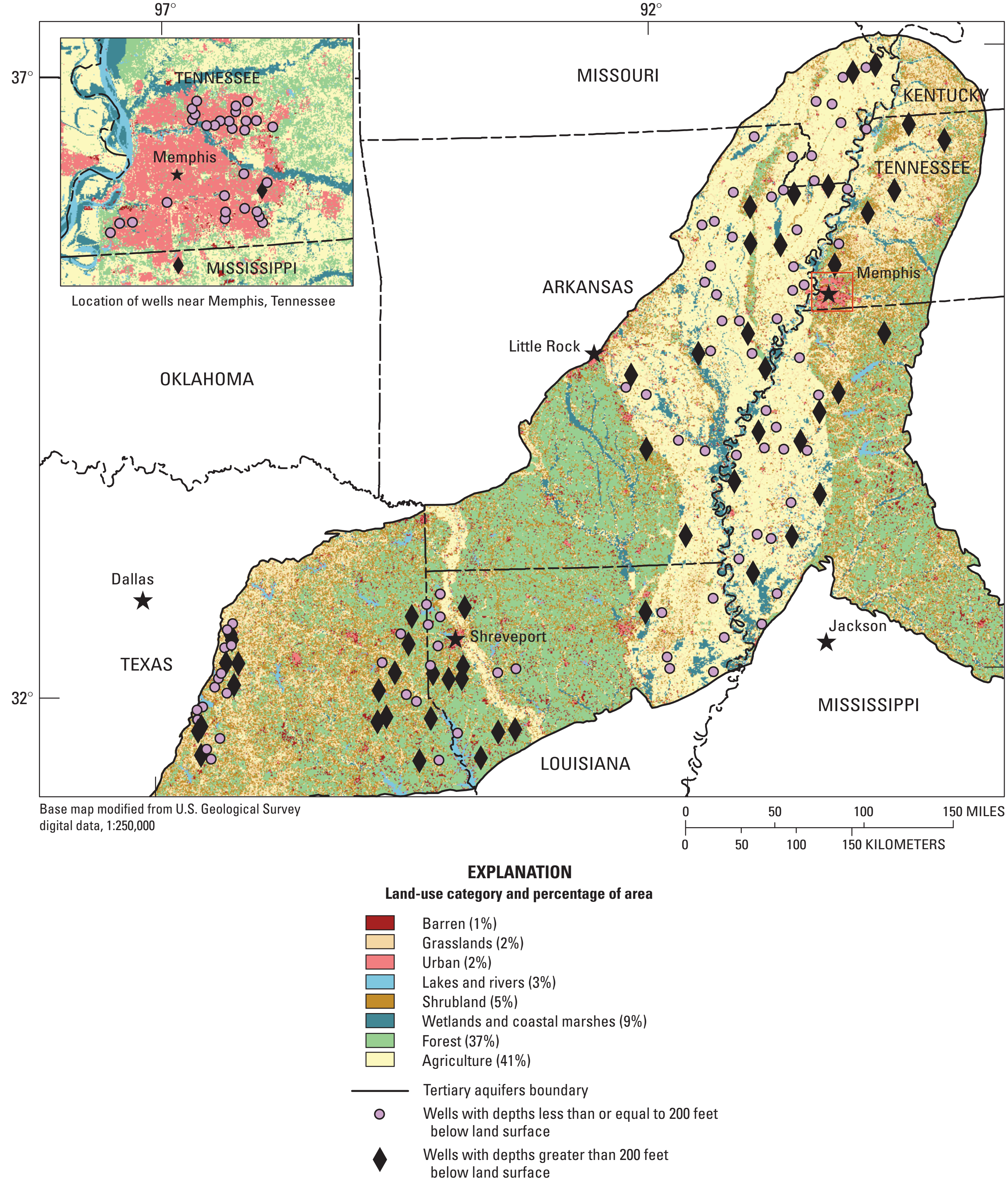


Figure 6. Land use and location of wells sampled in the Mississippi embayment-Texas coastal uplands aquifer system and Mississippi River Valley alluvial aquifer, south-central United States (land-use data from Vogelmann and others, 1998a, 1998b).

for rice cultivation, was the most heavily applied (more than 6,000,000 pounds) pesticide in the study area; however, its use was largely in rice-growing areas overlying the MRVA aquifer. In contrast, a lower total amount of the herbicide glyphosate was used, but it was applied over a much broader area than propanil (table 2). Other herbicides with relatively large amounts of use and intensity of use include atrazine, molinate, and fluometuron—herbicides used primarily on corn, rice, and cotton, respectively. Malathion, methyl parathion, and aldicarb are the only insecticides included in the 25 most heavily used pesticides in the study area. Malathion and methyl parathion are used predominantly on cotton but may have use on other crops, and aldicarb is incorporated in the soil with cotton seeds at planting to control nematodes.

Forests cover large parts of northern Louisiana, east Texas, south-central Arkansas, and east-central Mississippi, totaling about 37 percent of the study area (fig. 6). Forested land represents about 60 percent of the land use in the outcrop areas of the Tertiary aquifers. In contrast, about 20 percent of the area overlying the MRVA aquifer is forest.

Urban areas account for about 2 percent of the land use in the study area (fig. 6). In 2000, the total population of parishes or counties within or partially within the study area boundary was about 8,900,000 (U.S. Census Bureau, 2002). The largest metropolitan area is Memphis, TN, with a population of about 650,000 in 2000. Other major urban areas are Shreveport, Louisiana (population about 200,000); Bryan-College Station, Texas (population about 134,000); Tyler,

Table 2. Application rates for agricultural pesticides in the Mississippi embayment-Texas coastal uplands aquifer system and Mississippi River Valley alluvial aquifer, 1997.

[H, herbicide; I, insecticide; MSMA, monosodium methanearsonate]

Pesticide	Amount applied, in thousands of pounds	Acres applied, in thousands of acres	Amount applied per acre, in pounds	Type	Principal crop or use
Propanil	6,000	1,800	3.3	H	rice
Glyphosate	4,800	20,400	0.24	H	soybeans and corn
Metolachlor	3,100	14,200	0.22	H	soybean, peanuts, cotton
Atrazine	3,000	2,700	1.1	H	corn
Methyl parathion	2,900	10,100	0.29	I	rice, cotton (mites)
2,4-D	2,900	38,100	0.08	H	pasture, corn, soybean, rice, cotton
Pendimethalin	2,800	14,500	0.19	H	soybean, cotton, rice, corn
Trifluralin	2,400	11,900	0.20	H	soybean, cotton
Malathion	2,300	8,700	0.26	I	general use on cotton and rice; boll weevil control
Fluometuron	2,200	3,500	0.63	H	cotton
Sodium chlorate[a]	2,100	9,600	0.22	H	defoliant on cotton and soybean
Ethephon[a]	1,800	3,500	0.51	H	cotton, rice
MSMA[a]	1,800	3,500	0.51	H	cotton
Tribuphos	1,700	3,500	0.49	H	defoliant used for cotton crops
Cyanazine	1,500	4,700	0.32	H	corn, cotton
Molinate	1,400	1,800	0.78	H	rice
Bentazon	900	10,200	0.09	H	soybean, corn, rice
Paraquat[a]	780	13,800	0.06	H	non-selective defoliant for total vegetation control
Norflurazon	710	3,500	0.20	H	cotton
Aldicarb	700	3,500	0.20	I	roundworms, aphids, spider mites (cotton)
Alachlor	680	4,500	0.15	H	rice, cotton, corn, soybean
Acifluorfen	640	9,800	0.07	H	soybeans, rice
Thiobencarb	640	1,800	0.36	H	rice
Acetochlor	580	2,000	0.29	H	corn
Prometryn	520	3,500	0.15	H	cotton

[a] Pesticide not analyzed in this study.

Texas (population about 84,000); Monroe-West Monroe, Louisiana (population about 66,000); and Lufkin-Nacogdoches, Texas (population about 63,000).

Methods

Data Compilation and Quality-Control Data

From 1994 through 2004, water samples were collected from 169 wells and were analyzed for 5 physical properties, total dissolved solids, major and trace inorganic constituents, nutrients, radon, dissolved organic carbon, 75 pesticides, 7 pesticide degradates, and as many as 84 volatile organic compounds (VOCs). A subset of the 169 wells sampled included the analysis of tritium: 90 wells 200 ft deep or less and 11 wells greater than 200 ft deep were sampled. This report focuses on major and trace inorganic constituents, tritium, selected nutrients, pesticides, and VOCs.

During the period of sample collection, some changes in analytical methods occurred, such as the addition or removal of constituents in an analytical method or, for some analytical methods, changes in the laboratory minimum reporting levels. For example, samples collected before 1998 were analyzed for both dissolved phosphorus and orthophosphate and after 1998 only for orthophosphate. In this report, data for orthophosphate for the network without dissolved phosphorus analyses were included with the dissolved phosphorus data for the remaining networks. The analytical method for VOCs had a minimum laboratory reporting level of 0.2 microgram per liter (µg/L) for most compounds analyzed prior to 1996 (Moran and others, 2006). Samples collected subsequently were analyzed with lower detection and reporting levels; however, in this report, detection frequencies of VOCs are reported at a common assessment level of 0.2 µg/L. Detection frequencies determined with and without an assessment level are summarized in Appendix 1.

Concentrations of many pesticides and VOCs were estimated (“E”) by the USGS National Water Quality Laboratory (NWQL). Childress and others (1999) documented several reasons that justify an “E” code: (1) the concentration was greater than or equal to the long-term method detection level but less than the laboratory reporting limit; (2) the concentration was greater than or equal to the long-term method detection level but less than the lowest calibration standard; (3) the result was extrapolated above the calibration curve; (4) data quantification was not performed according to method-specific criteria; (5) performance of the analyte did not meet acceptable method-specific criteria; (6) deviation from the standard operating procedure was required; (7) some moderate losses occurred in sample preparation but were not quantifiable; and (8) moderate matrix interference conditions occurred. Values coded with a remark code of “E” were treated as detections in this report.

Quality-control (QC) data were collected to ensure that sample-collection, sample-processing, and laboratory-analysis procedures did not introduce bias into results and to determine the variability associated with collection and analysis of samples. QC samples collected included field-equipment blanks, replicate samples, and field-spiked samples. Replicate environmental samples were collected to assess the effects of sample collection and laboratory analysis on measurement variability. The spike samples were environmental samples to which known concentrations of the analytes of interest were added to determine the accuracy and precision of organic analyses, the stability of analytes during typical holding times, and whether characteristics of the environmental sample might interfere with the analysis. Previous reports (Gonthier, 2000, 2002, and 2003; Reutter and Dunn, 2000; Roland W. Tollett, U.S. Geological Survey, written commun., 2005) summarizing results for specific networks included in this report indicated that recoveries were within expected ranges (60 to 140 percent) and that the results were reproducible.

Field-equipment blank samples were collected to verify that decontamination procedures were sufficient and that collection and analysis procedures did not contaminate the samples. Several compounds that were present in one field blank also were detected in a water sample collected on the same day and in a sample collected the previous day. Results for these compounds in the samples and field blanks were interpreted to represent contamination of the sampling equipment or during sample shipment, and results for these compounds were removed from the dataset. Ten VOC compounds were detected in 10 percent or more of the field blanks (table 3). Field blanks collected prior to 1997 may have had detection of a few compounds because of their presence in the organic-free water used for blanks (Halde and others, 1998). Organic-free water used after July 1997 was purged by the laboratory supplier with nitrogen gas to remove any low-level VOCs that might be present in the blank water. Many of the detections were in field blanks collected using the unpurged blank water; however, toluene, 1,2,4-trimethylbenzene, and methyl ethyl ketone (MEK) were detected in field blanks that used nitrogen-purged blank water. Additionally, many of the detections in field blanks were less than the 0.2 µg/L assessment level used in this report, and the potential bias from sample contamination was considered to be low. Methyl ethyl ketone was detected in two field blanks and eight samples at concentrations between 0.5 and 1.6 µg/L. The similar range in concentration in blanks and environmental samples, lack of other VOC or pesticide detections, and no detections of MEK in subsequent samples (2002 and 2005) from one of these wells suggested MEK results were affected by sample contamination, and these data were not included in this report.

Malathion was the only pesticide detected in a field blank, but several agricultural pesticides were detected in a groundwater sample collected in 1997 in an urban area. One of the pesticides detected was acetochlor, which was introduced for use in 1994 primarily as a herbicide for corn. Tritium was

Table 3. Volatile organic compounds detected in more than 10 percent of field blanks.

[µg/L, microgram per liter; E, estimated]

Compound	Laboratory reporting level, in µg/L	Number of blanks (N)	Detection frequency in blanks, in percent	Maximum concentration, in µg/L
1,2,4-Trimethylbenzene	0.05	15	26.7	6.8
Acetone	5.0	13	38.5	19.1
Carbon disulfide	0.05	13	15.4	E 0.027
Chlorobenzene	0.05	15	13.3	E 0.009
Dichloromethane	0.05	15	26.7	0.70
Methyl ethyl ketone	5.0	13	23.1	1.6
Tetrahydrofuran	8.79	13	15.4	E 0.7
Toluene	0.05	15	33.3	0.18
Trichlorofluoromethane	0.05	15	13.3	0.20
Trichloromethane	0.05	15	40.0	0.30

not detected in this sample, suggesting that most of the water was older than the early 1950s. These results combined with results for a second sample collected during 2006 without detections of acetochlor and several other agricultural pesticides suggest that the data for the original sample may have been switched with a surface-water sample from another area, either physically in the laboratory or electronically with data entry. The data for 1997 for this sample were not included in the dataset; however, the resample from 2006 was used.

Ancillary Data

The occurrence of many of the constituents analyzed is related to the presence of a source in the contributing area of a well, the physical and chemical properties of the constituent, and environmental factors such as soil properties in the contributing area of a well. Contributing areas for wells, however, are rarely delineated. An approach used by the NAWQA Program to relate occurrence of compounds to environmental factors, particularly for shallow observation wells, has been to characterize land use and other data, such as soil properties, within a buffer area with a 1,640-ft radius around each well. This approach for characterizing potential sources of contaminants and factors that may affect their movement likely is less applicable for deep or high-capacity wells, because the contributing (recharge) areas could be very different from the 1,640 ft around the well.

Ancillary data used in this report for buffer areas around wells include land use, soil properties, nitrogen loading, and pesticide use. Land use was estimated using a 30-meter (98-ft) resolution digital dataset based on the 1992 National Land Cover Data (Vogelmann and others, 1998a, 1998b) with selected classifications from the USGS aerial photograph-based Land Use Land Cover Data of the mid-1970s to mid-1980s. A 1,640-ft radius circular buffer was delineated around each site, and the fraction of the total buffer represented by each land-use category was calculated (U.S. Geological Survey, 2008). Soil organic matter, average clay content, and soil hydrologic group data were compiled for buffer areas from State Soil Geographic Data (U.S. Department of Agriculture, 1995).

Nitrogen input data for well buffers were prepared (Kerie J. Hitt, U.S. Geological Survey, written commun., 2005) from county-level estimates of nutrient inputs (Ruddy and others, 2006). Fertilizer and manure inputs for each buffer area were based on the amount of agricultural land from the Enhanced National Land Use Data 1992 and fertilizer and manure application rates (Nakagaki and others, 2007). Nitrogen from atmospheric deposition was assumed to be independent of land use. A weighted average for the buffer area for nitrogen from fertilizer, manure, and atmospheric deposition was calculated for each well for each year of compilation (1987 through 2001), and data were used from the year that corresponded to the year the well was sampled.

County-wide agricultural pesticide use data were used to create a use estimate in the buffer area for 1992 and 1997 (Majewski, 1997). Use estimates for more than 200 compounds were derived by applying county areal weights of agricultural land use in the buffer area and prorating county pesticide use to determine the estimate of chemical use in the buffer, in kilograms, geoprocessed at the 30-meter resolution (Majewski, 1997). For wells sampled in 1994, the 1992 data were used, but for all other wells, the 1997 data were used to interpret water-quality data.

Water-Quality Standards and Human Health Benchmarks

In 1972, Congress passed the Clean Water Act (CWA) to better assess water-quality issues primarily in surface water (U.S. Environmental Protection Agency, 2003). Because the CWA did not directly address groundwater or water-quantity issues, the Safe Drinking Water Act (SDWA) was passed in 1974 to regulate the Nation's public drinking-water supply and its sources: rivers, lakes, reservoirs, springs, and groundwater wells. The SDWA gives the U.S. Environmental Protection Agency (USEPA) the authority to set drinking-water standards in the form of primary (MCLs) and secondary maximum contaminant levels (SMCLs). Primary drinking-water regulations are legally enforceable on finished water (both surface water and groundwater) used for public drinking-water supplies, and the secondary regulations are non-enforceable guidelines that relate mainly to cosmetic and aesthetic effects (U.S. Environmental Protection Agency, 2006).

For those compounds with Federal drinking-water standards, concentrations in samples from Tertiary aquifer wells were compared to USEPA MCLs, SMCLs, or health advisories (HAs) listed in Appendix 2 (U.S. Environmental Protection Agency, 2004). Some concentrations of unregulated compounds were compared to health-based screening levels (HBSLs), which were developed by the USGS in collaboration with the USEPA, New Jersey Department of Environmental Protection, and the Oregon Health & Science University (Appendix 2). Although HBSLs are non-enforceable regulatory standards, they are concentrations of contaminants in water that may be of potential human-health concern. The HBSLs are based on health effects alone and have been calculated for unregulated contaminants analyzed by the NAWQA Program. Screening levels were developed using standard USEPA Office of Water methodologies and the most current, USEPA peer-reviewed, publicly available human-health toxicity information. The HBSLs are regularly reviewed and, as needed, revised to incorporate the most recent toxicity information and research findings (Toccalino and others, 2003).

Quality of Shallow Groundwater in the Mississippi Embayment-Texas Coastal Uplands and Mississippi River Valley Alluvial Aquifer Systems

Because of the large range in depths (21 to 1,466 ft) of the wells sampled in this study, a subset of 114 wells less than or equal to 200 ft deep was selected to characterize the occurrence of many of the constituents analyzed. This depth was used to subset the data because it included the greatest depth of wells completed in the MRVA; it included the majority of the wells in the dataset, and many of the constituents analyzed have sources related to human activities at land surface. In this report, shallow is used to describe wells and samples collected from wells 200 ft deep or shallower. Four groups of shallow wells were defined: (1) shallow Tertiary aquifer wells, (2) wells completed in the Holocene alluvium and (3) Pleistocene valley trains of the MRVA, and (4) wells completed in the Pleistocene terrace deposits (the shallow water-table aquifer in the Memphis, TN, area). Of the 36 wells in the shallow Tertiary group, 8 were completed in the middle Claiborne, 14 in the lower Claiborne-upper Wilcox, and 14 in the middle Wilcox aquifers.

Inorganic Constituents and Physical Properties

Concentrations of major inorganic constituents and total dissolved solids typically reflect the composition of the aquifer material and the length of time that groundwater is in contact with the aquifer. The composition of groundwater often changes with residence time and along regional flow paths. In addition to changes along flow paths, regional differences in inorganic water quality in both the Tertiary aquifers and the MRVA have been delineated (Pettijohn, 1996). In the updip and northern parts of the Tertiary aquifers, groundwater is predominantly a calcium or sodium bicarbonate type with dissolved solids concentrations less than 1,000 milligrams per liter (mg/L). Total dissolved solids concentrations generally increase in downdip areas and in the southern part of the study area where chloride becomes the dominant anion and sodium concentrations increase (Pettijohn, 1996). Some of the changes in water quality in downgradient areas are a result of groundwater evolution along regional flow paths, but upward leakage from deeper aquifers also may affect water quality in these aquifers (Pettijohn, 1996).

Groundwater in the two subunits of the MRVA aquifer generally is more mineralized than groundwater in the Pleistocene terrace deposits and shallow Tertiary wells. The median dissolved solids concentrations for samples from the Holocene alluvium and Pleistocene valley trains were about 350 and 325 mg/L, respectively (fig. 7). The dominant ions in these aquifers were calcium, magnesium, and bicarbonate. The dissolved solids concentrations for samples from the Pleistocene terrace deposits and Tertiary wells were somewhat lower (170 and 200 mg/L, respectively); however, the shallow Tertiary wells had the greatest variability of all four shallow well groups (fig. 7). The large variability for dissolved solids, bicarbonate, sodium, and chloride concentrations observed in the Tertiary wells may be a result of wells being completed in three different Tertiary aquifers, as well as the wide geographic distribution of wells. In general, samples from Tertiary wells screened in the middle Wilcox aquifer in the southern part of the study area (located in Louisiana and Texas) had higher dissolved solids concentrations than other parts of the Tertiary aquifers.

Most of the shallow wells were sampled for tritium, which can be used as a qualitative indicator of groundwater age or residence time. The presence of tritium in groundwater indicates that a component of the water includes recent recharge; that is, recharge after the initial atmospheric tritium bomb peak in 1953. The absence of tritium in a sample indicates that most of the water was recharged prior to 1953 (fig. 8) or that the contribution of recent recharge represents a small fraction of the sample.

Of the 90 samples from shallow wells analyzed for tritium, 73 percent had tritium concentrations greater than 1 tritium unit (TU) indicating a component of recent recharge; however, tritium concentrations were less than 1 TU in samples from at least one well from each group (fig. 8*A*). Based on decay-corrected concentrations for precipitation in the study area (Michel, 1989), samples with tritium concentrations between 3 and 10 TUs likely indicate a large component of recharge to wells after about 1975 (fig. 8*B*). Using this range in concentration as a qualitative indicator of average groundwater residence time, groundwater from the Pleistocene terrace deposits generally has the largest component of recent

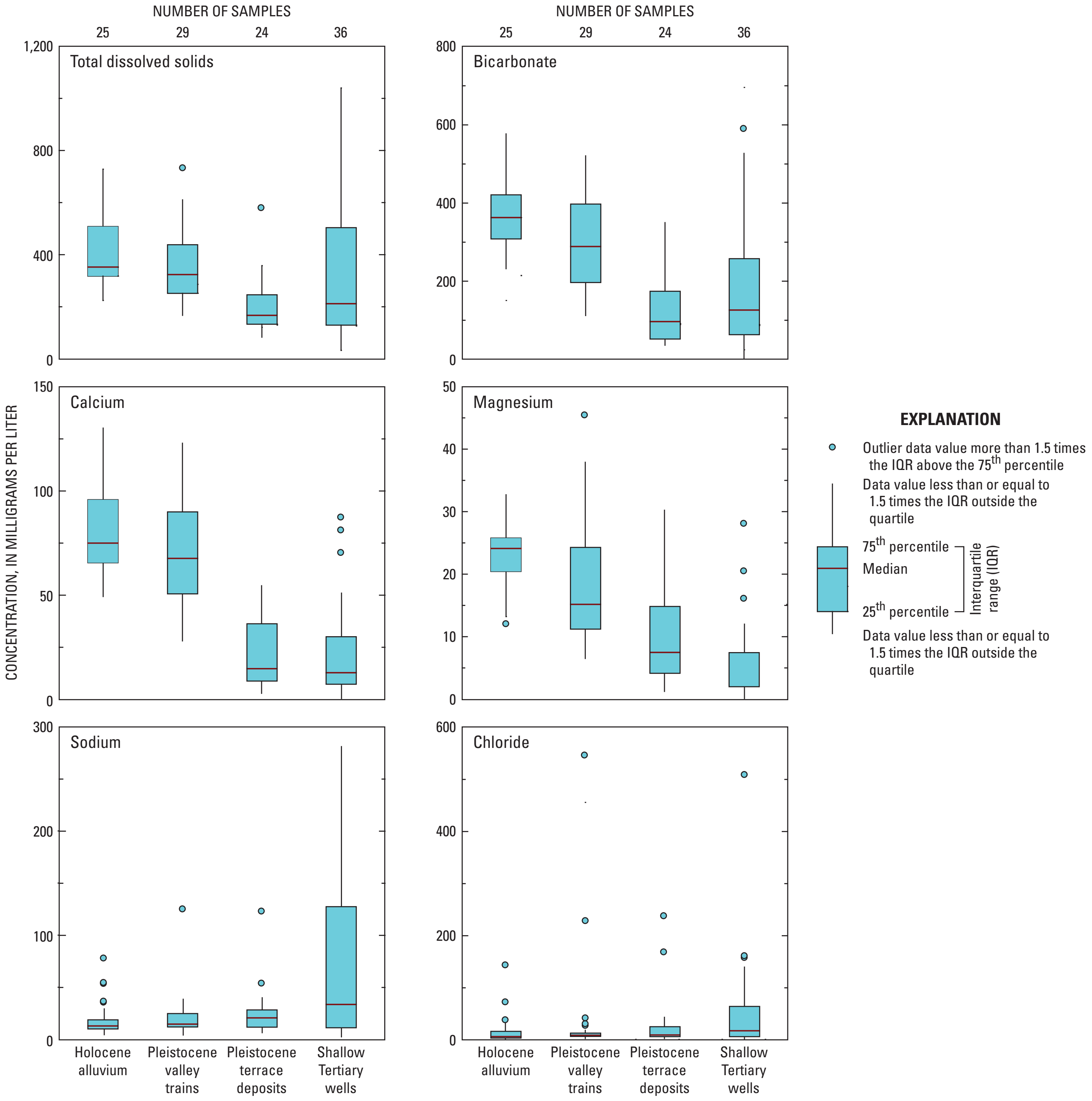


Figure 7. Concentrations of major inorganic constituents in samples from four shallow well groups in the Mississippi embayment-Texas coastal uplands aquifer system and Mississippi River Valley alluvial aquifer.

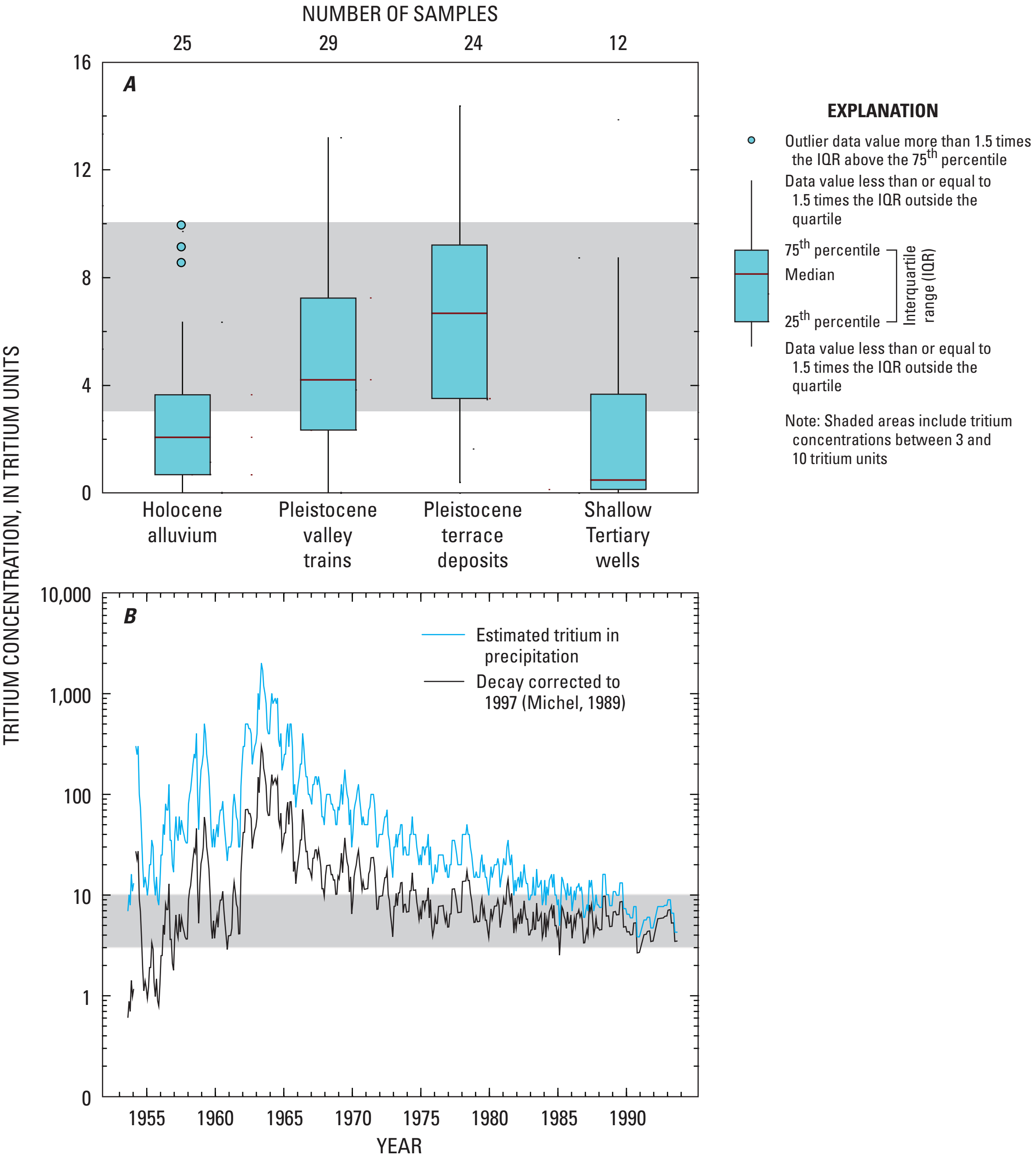


Figure 8. *(A)* Tritium concentrations in samples from four shallow well groups in the Mississippi embayment-Texas coastal uplands aquifer system and Mississippi River Valley alluvial aquifer and *(B)* decay-corrected tritium concentrations in precipitation.

recharge in samples among the four shallow groups with more than half of the groundwater in the wells having an apparent age less than about 20 years. Tritium concentrations were substantially higher in the Pleistocene valley trains than in the Holocene alluvium (Gonthier, 2003), suggesting younger water in this aquifer than in the Holocene alluvium (fig. 8*A*). Water samples from 10 of the 25 wells in the Holocene alluvium had tritium concentrations less than 1 TU. Median concentrations of both the Holocene alluvium and shallow Tertiary wells were less than 3 TUs, indicating a relatively small component of recharge in the last 30 years. Eight of the 12 samples from the shallow Tertiary wells completed in the middle Claiborne and middle Wilcox aquifers had tritium concentrations less than 1 TU, indicating little to no recent recharge to these wells. The four samples containing tritium in the Tertiary group also were from wells completed in the middle Claiborne and middle Wilcox aquifers. In contrast, median tritium concentrations greater than 3 TU suggest that most of the samples from wells completed in the Pleistocene valley trains and Pleistocene terrace deposits typically included a substantial amount of water younger than 30 years.

Tritium concentrations were inversely related to the concentration of some inorganic constituents in two of the shallow aquifers (fig. 9). In samples from both the Pleistocene valley trains and shallow Tertiary wells, total dissolved solids concentrations were highest when tritium concentrations were low, which likely reflects an increase in the concentration of inorganic constituents in groundwater as the residence time increases in these aquifers. This relation did not exist for wells completed in the Holocene alluvium and Pleistocene terrace deposits. The lack of a relation between the inorganic water quality and apparent groundwater age in these aquifers may reflect greater heterogeneity of the sediments that make up these aquifers, or samples may represent more complex mixtures of groundwater with varying residence times.

In addition to water-rock interactions along a groundwater flow path, microbial activity, primarily microbial respiration, also affects groundwater geochemistry. Concentrations of dissolved oxygen, nitrate, manganese, iron, and sulfate are affected by the oxidation-reduction (redox) conditions in the aquifer. Dissolved oxygen (DO) that enters an aquifer with recharge plays an important role in redox conditions by influencing the solubility of redox-sensitive constituents. As water moves along a flow path, DO can be consumed by subsurface microorganisms that use available organic carbon in the aquifer matrix or in groundwater. Generally, DO values less than 0.5 mg/L in groundwater indicate anoxic or reducing conditions in an aquifer (McMahon and Chapelle, 2008). As DO is consumed in an aquifer, redox conditions typically progress sequentially from an oxygen-reducing environment (oxic) to nitrate-, manganese-, iron-, sulfate-reducing conditions (anoxic), and finally to methanogenic conditions under which organic carbon is reduced to form methane (Chapelle, 1993) given the presence of each of these electron acceptors in the aquifer. The presence or absence of DO, nitrate, iron, manganese, and sulfate in groundwater can be used to characterize the redox conditions in the aquifer (fig. 10).

Dissolved-oxygen concentrations varied considerably among the four aquifers, ranging from predominantly oxic to anoxic conditions (fig. 10). Groundwater in the Pleistocene terrace deposits generally is oxic (DO > 0.5 mg/L) with a

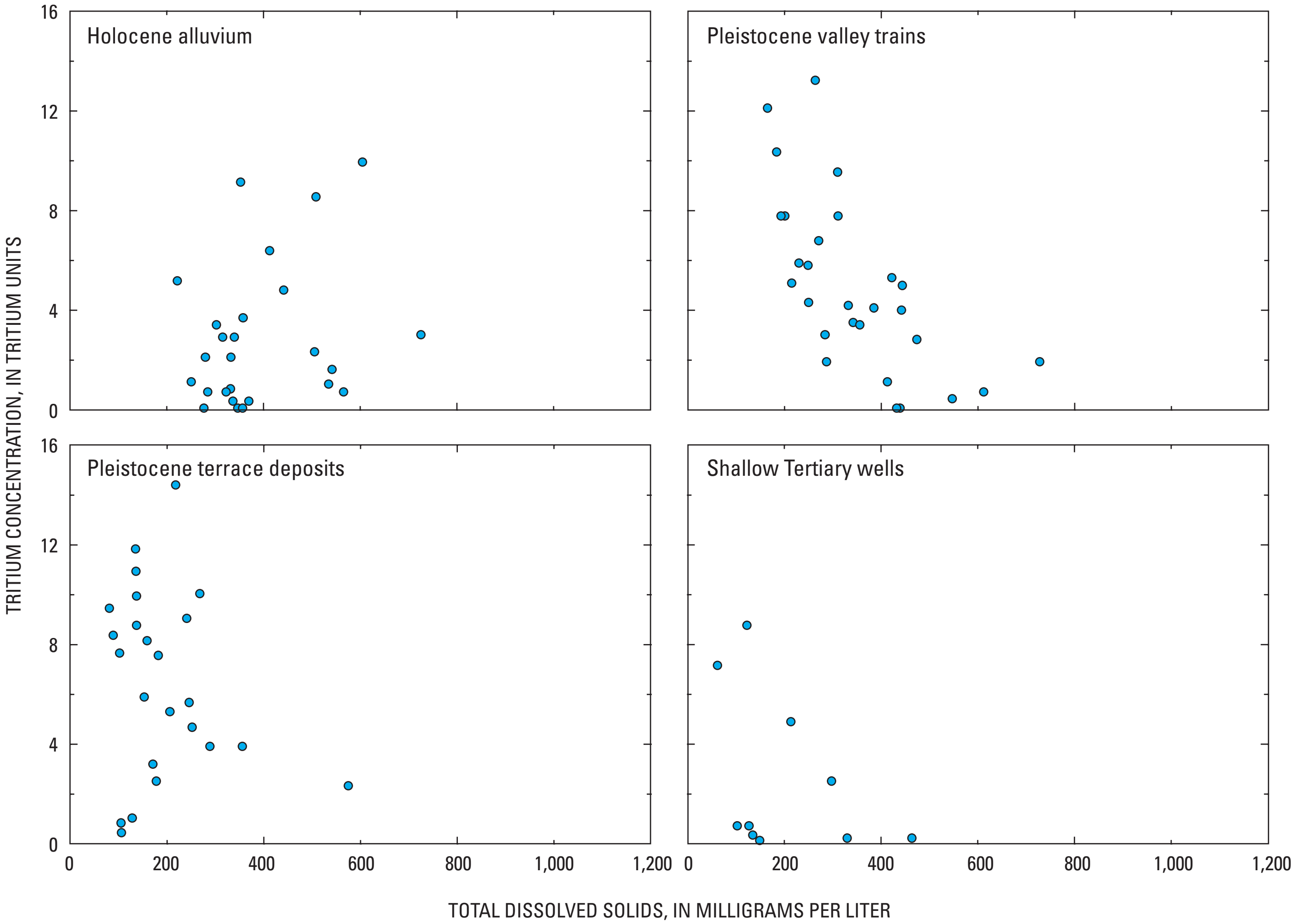


Figure 9. Total dissolved solids and tritium concentrations in samples from four shallow well groups in the Mississippi embayment-Texas coastal uplands aquifer system and Mississippi River Valley alluvial aquifer.

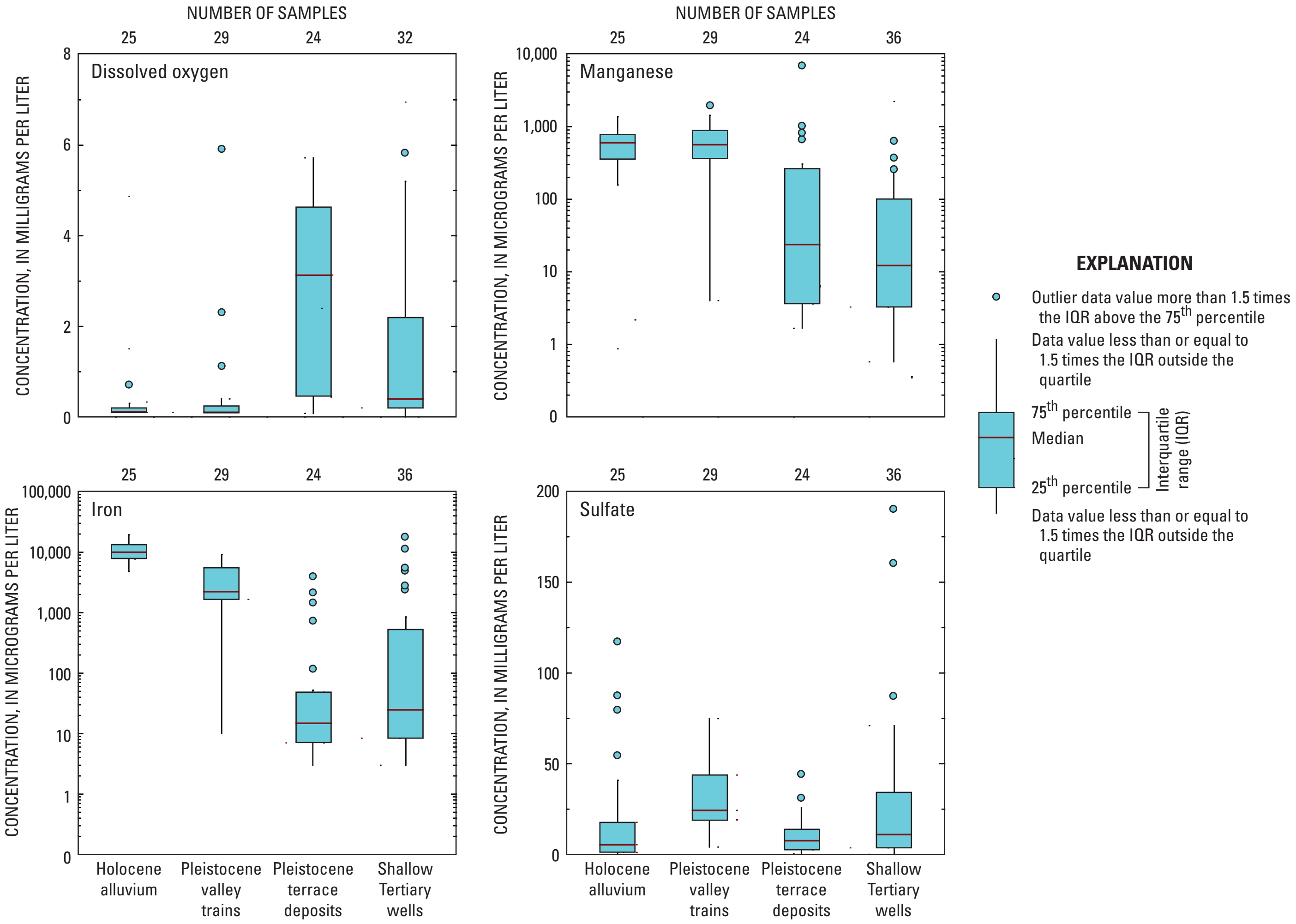


Figure 10. Concentrations of redox-sensitive constituents in samples from four shallow well groups in the Mississippi embayment-Texas coastal uplands aquifer system and Mississippi River Valley alluvial aquifer.

median DO concentration of about 3 mg/L. Median DO concentrations for wells in the shallow Tertiary, Pleistocene valley trains, and Holocene alluvium were all less than 0.5 mg/L, indicating more than half of the groundwater samples from these aquifers were anoxic. However, a number of shallow Tertiary wells had samples that were classified as oxic, with a maximum DO concentration of 5.8 mg/L. Nearly all of the wells sampled in the MRVA (Holocene alluvium and Pleistocene valley trains) were anoxic. Only one well completed in the Holocene alluvium was classified as oxic, with the maximum DO concentration of 0.7 mg/L, and three wells in the Pleistocene valley trains had DO concentrations greater than 0.5 mg/L (fig. 10). A relation between well depth and water level to DO concentrations did not exist, in part because of the narrow range of these characteristics for each of the aquifers (table 1).

The overall redox conditions differ among the shallow well groups (fig. 11). Using redox categories defined by McMahon and Chapelle (2008), concentrations of DO, nitrate, manganese, iron, and sulfate were used to classify the parts of the aquifers sampled by the wells as oxic, suboxic, anoxic, or mixed redox conditions. In anoxic aquifers, nitrate, manganese, iron, and sulfate are the terminal electron acceptors, rather than oxygen (McMahon and Chapelle, 2008). Wells completed in the Holocene alluvium indicated the most reducing conditions, with all but one well being anoxic (fig. 11). Dissolved manganese and iron concentrations, in addition to the generally low sulfate concentrations when iron concentrations are high, suggest iron-reducing to sulfate-reducing redox conditions in this aquifer. Four samples indicated methanogenic conditions in parts of the Holocene alluvium. Redox conditions in the Pleistocene valley trains generally are similar to the Holocene alluvium in that most wells sampled anoxic groundwater, but lower iron and higher sulfate concentrations suggest conditions in this aquifer are not as reducing as in the Holocene alluvium. Redox conditions are more variable in the Pleistocene terrace deposits and Tertiary wells than in the MRVA wells (fig. 11), with redox conditions ranging from oxic to anoxic in both of these groups.

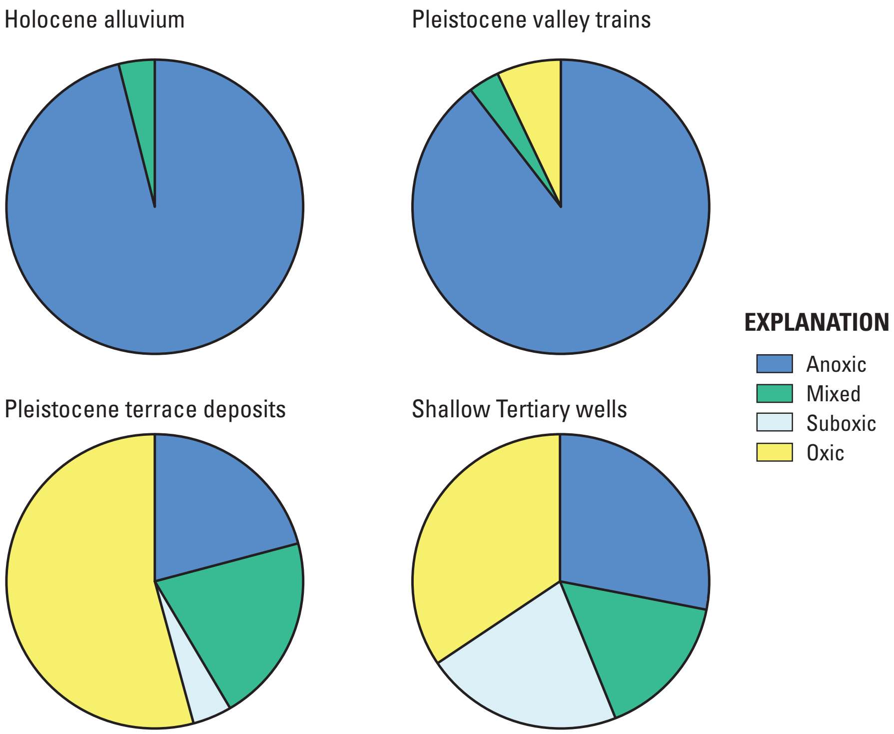


Figure 11. Percentage of samples that were classified as oxic, suboxic, anoxic, or mixed redox state in four shallow well groups in the Mississippi embayment-Texas coastal uplands aquifer system and Mississippi River Valley alluvial aquifer.

Given that the depth to water was less than 50 ft for most of the wells in each of the shallow wells groups and that, with the exception of the Pleistocene terrace deposits, well depths are not substantially different (fig. 12*A* and *B*), differences in apparent groundwater age or residence time likely are a result of differences in recharge and shallow hydrogeology of these aquifers. Detailed lithologic information from sources such as drillers' or geophysical logs was not available for most wells to characterize subsurface geology; however, soil survey data were available. Soil data were used to generally characterize differences in the near surface hydrology of these aquifers (fig. 12*C*–*E*). Soil properties that may affect recharge to these aquifers, such as soil hydrologic groups and average clay content, are shown in figure 12. Soil hydrologic group is a soil grouping based on infiltration and runoff characteristics: soils in group A have the lowest runoff potential and highest infiltration rate, soils in group D have the highest runoff potential and lowest infiltration rates, and groups B and C have intermediate runoff potential and infiltration rates (U.S. Department of Agriculture, 2007). The average clay content was calculated from the lowest and highest percentages of soil particles that were less than 2 millimeters in size (U.S. Department of Agriculture, 2007).

The soils in the buffer areas around wells in the Pleistocene terrace deposits had higher infiltration rates (based on the soil hydrologic group) and lower average clay content than the remaining aquifers (fig. 12). Soils in hydrologic groups B and D accounted for much of the buffer areas around the wells. Hydrologic group B includes soils that have moderate to high infiltration rates with moderately low runoff potential, and hydrologic group D includes soils with very low infiltration rates and high runoff. Differences in these soil properties generally were reflected in the amount of recent water in these shallow well groups. The highest percentage of group B soils for the Pleistocene terrace deposits corresponded to the highest tritium concentrations (fig. 12*C*; fig. 8*A*) among the four aquifers. In turn, the redox conditions also were associated with the overlying soils. The most reducing conditions were in samples from the Holocene alluvium, where the buffer areas included the lowest median percentage of hydrologic group B, the highest median percentage of hydrologic group D, and the highest median average clay content (fig. 12). In contrast, samples from the Pleistocene terrace deposits, which were largely oxic (fig. 11), were characterized by soils with higher infiltration rates and a smaller clay content.

Nutrients

Nutrients, such as nitrogen and phosphorus, are essential elements for plant and animal growth, and various forms of nitrogen and phosphorus occur naturally in the environment. Concentrations of these nutrients generally are low in groundwater; for example, estimated national background concentrations for nitrate and orthophosphate in shallow groundwater are 2.0 and 0.02 mg/L, respectively (Fuhrer and others, 1999). Nitrogen is not a common element in rocks, but phosphorus can be present in accessory minerals in igneous rocks or in sedimentary rocks generally representing less than 0.1 percent of the composition of elements in the rocks (Hem, 1985). Elevated concentrations of both nitrogen and phosphorus in groundwater may be the result of application of fertilizers in agricultural and urban areas, animal waste, leaking sewer lines or septic systems, or the infiltration of treated wastewater into aquifers. The atmosphere is also a nonpoint source for nitrogen, depositing more than 3 million tons nationally each year from chemical reactions or from the combustions of fossil fuels (Fuhrer and others, 1999).

Nitrate usually is the species of nitrogen that is of concern in groundwater systems because of its solubility, mobility, and potential health effects. Nitrate concentrations in shallow wells in the Tertiary aquifers and MRVA aquifers generally were low and less than the national background concentration of 2 mg/L as nitrogen (N), a level that might indicate effects from anthropogenic activities (Mueller and Helsel, 1996). No

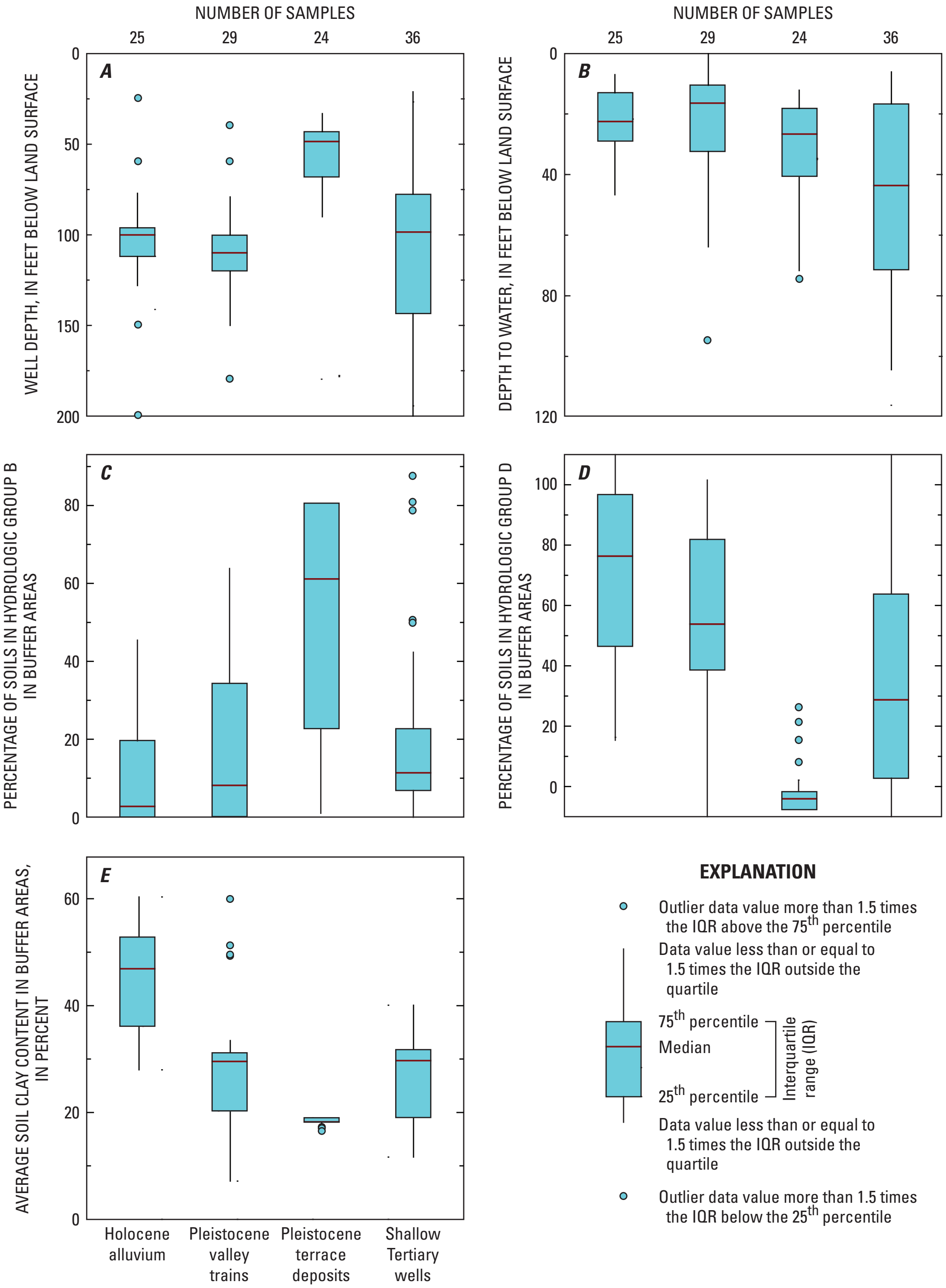


Figure 12. Differences in *(A)* well depth, *(B)* depth to water, *(C)* percentage of soils in hydrologic group B, *(D)* percentage of soils in hydrologic group D, and *(E)* average clay content in four shallow well groups in the Mississippi embayment-Texas coastal uplands aquifer system and Mississippi River Valley alluvial aquifer.

concentrations were greater than the maximum contaminant level of 10 mg/L for drinking water; the maximum concentration measured was 6.8 mg/L in the shallow Tertiary aquifer (table 4). Only samples from the Pleistocene terrace deposits had a median nitrate concentration greater than the reporting level (0.05 mg/L) for nitrate (table 4), and samples from only six wells had nitrate concentrations greater than 2 mg/L.

Nitrate concentrations in groundwater are affected by redox conditions. In anoxic groundwater, nitrate may be reduced as a result of microbial activity to nitrogen gas (N_2) or to ammonia (Stumm and Morgan, 1996). In the Holocene alluvium and Pleistocene valley trains, iron concentrations are high, whereas dissolved oxygen values are low (<0.5 mg/L) indicating a strongly reducing environment (fig. 10). Dissolved oxygen was not measured for all samples, and dissolved iron concentrations are used to illustrate the relation between redox conditions and nitrate concentrations (fig. 13). Generally, when iron concentrations were greater than about 50 g/L (indicating anoxic conditions), nitrate was not detected or was present at concentrations less than 0.5 mg/L. The low nitrate concentrations in the Holocene alluvium and Pleistocene valley trains likely reflect the redox conditions in these aquifers. In these largely anoxic aquifers, nitrate was detected infrequently; only one sample from the Holocene alluvium and eight samples from the Pleistocene valley trains had nitrate concentrations greater than 0.1 mg/L. The highest nitrate concentrations in the Pleistocene valley trains were in samples in which iron concentrations were less than 20 g/L (fig. 13). Any nitrate that moves with recharge into these aquifers likely is subject to denitrification because of the reducing conditions within these aquifers. Ten samples from the shallow Tertiary wells had nitrate concentrations greater than 0.5 mg/L and were associated with oxic conditions (iron <50 µg/L); however, nitrate was not detected in more than half of the samples from the shallow Tertiary wells. In contrast, under the largely oxic conditions in the Pleistocene terrace deposits, nitrate was detected at a concentration greater than 0.5 mg/L in more than half of the samples.

Ammonia is a reduced form of nitrogen and may be present in groundwater naturally as a result of degradation of organic matter (ammonification), or in some cases it may be a result of contamination from sources such as leaking septic systems, infiltration of wastewater, or agricultural sources (Chapelle, 1993). Denitrification is another possible source of ammonia to groundwater. Nitrate is typically converted to nitrogen gas (N_2) during denitrification but also may be converted to ammonia (Chapelle, 1993).

In contrast to nitrate, ammonia concentrations in samples from the Holocene alluvium and Pleistocene valley trains generally were higher than in samples from the Pleistocene terrace deposits and shallow Tertiary aquifer (table 4). The highest concentration of ammonia was 2.6 mg/L in a sample from the Holocene alluvium. Ammonia concentrations in the Holocene alluvium and Pleistocene valley trains were correlated with specific conductance, suggesting concentrations increase with longer average groundwater residence time, particularly in the Pleistocene valley trains samples where a relation between residence time (tritium concentrations) and concentration of inorganic constituents was observed (fig. 9). The relation between ammonia and specific conductance suggests that ammonia likely is stable in these anoxic aquifers.

Although the median amount of nitrogen contributed from various sources within the buffer areas of the Holocene alluvium and Pleistocene valley trains wells was three times greater than the loading around the Pleistocene terrace deposits wells and the Tertiary aquifer wells (table 5), in general most of the total nitrogen concentrations ranged from about 0.05 to 3 mg/L in samples from all four aquifers (fig. 14). Total nitrogen concentrations were somewhat higher in samples from the Pleistocene terrace deposits and shallow Tertiary wells where nitrate was the predominant species of nitrogen in groundwater, likely reflecting the greater solubility and mobility of nitrate compared to other species of nitrogen. The overall lower total nitrogen concentrations in samples from the Holocene alluvium and Pleistocene valley trains, despite the greater input of nitrogen largely from fertilizer use,

Table 4. Summary of selected nutrient concentrations in samples from four shallow well groups in the Mississippi embayment-Texas coastal uplands aquifer system and Mississippi River Valley alluvial aquifer, 1994–2004.

[mg/L, milligram per liter; N, nitrogen; P, phosphorus; min, minimum; max, maximum; <, less than]

Aquifer	Nitrate as N, in mg/L			Ammonia as N, in mg/L			Total nitrogen, in mg/L			Dissolved phosphorus as P, in mg/L		
	min	max	median	min	max	median	min	max	median	min	max	median
Holocene alluvium	<0.06	0.35	<0.06	0.14	2.6	0.58	0.17	2.7	0.65	<0.01	1.3	0.65
Pleistocene valley trains	<0.06	2.6	<0.06	0.024	1.5	0.14	0.06	2.7	0.27	<0.01	1.0	0.11
Pleistocene terrace deposits	<0.06	6.2	0.73	<0.015	0.94	<0.015	<0.01	6.2	0.84	<0.01	0.08	<0.01
Shallow Tertiary wells	<0.06	6.8	<0.06	<0.015	1.4	<0.04	<0.01	6.8	0.46	<0.01	0.87	0.07

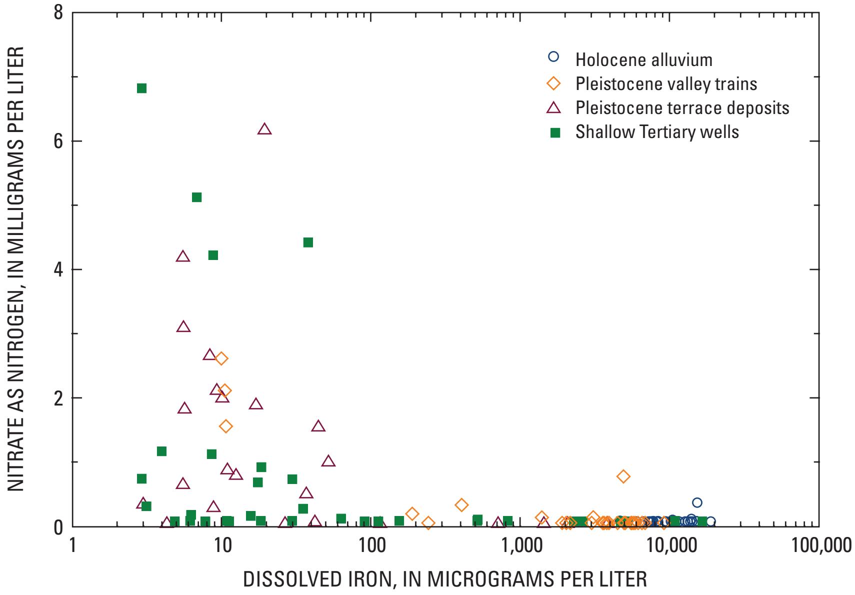


Figure 13. Relation between dissolved iron and nitrate concentrations in samples from four shallow well groups in the Mississippi embayment-Texas coastal uplands aquifer system and Mississippi River Valley alluvial aquifer.

is likely the result of several factors. The fine-grained sediments and clay-rich soils that overlie these units may slow the movement of water and nitrogen into the aquifer. Additionally, much of the nitrate that may be contributed with recharge to these aquifers likely is converted to N_2 or ammonia through denitrification. Dissolved gases were not analyzed in these samples, so the extent of denitrification or the amount of N_2 in these aquifers is not known. Ammonia in groundwater typically is present as ammonium (NH_4^+), and its transport may be slowed because of sorption to aquifer materials (Freeze and Cherry, 1979; DeSimone and Howes, 1998). Total nitrogen concentrations in groundwater in the MRVA may be low, in part because of sorption of ammonia, the dominant species of nitrogen in these aquifers, to aquifer sediments.

Concentrations of dissolved phosphorus in groundwater typically are low because phosphorus tends to sorb to soil and aquifer sediments and is not readily transported in groundwater (Hem, 1985). For example, the estimated background concentration of orthophosphate for 47 shallow wells across the country was 0.02 mg/L as phosphorus (P) (Fuhrer and others, 1999). Wetzel (1983) suggested average groundwater concentrations also were about 0.02 mg/L. Samples from the Pleistocene terrace deposits reflect the general occurrence of phosphorus in groundwater; dissolved phosphorus was detected in only seven samples and the maximum concentration was 0.083 mg/L (table 4). However, dissolved phosphorus concentrations in the three remaining shallow well groups were considerably higher than 0.02 mg/L and higher than concentrations in the Pleistocene terrace deposits (fig. 15). The highest concentrations of dissolved phosphorus were in samples from the Holocene alluvium with a median concentration of 0.65 mg/L and maximum of

Table 5. Sources of nitrogen to the buffer areas surrounding wells in four shallow well groups in the Mississippi embayment-Texas coastal uplands aquifer system and Mississippi River Valley alluvial aquifer.

[Median input from 1,640-foot radius around wells in each shallow aquifer group. Nitrogen, in kilograms per square kilometer per year; <, less than]

Shallow well group	Septic systems[a]	Atmospheric deposition[b]	Non-farm fertilizer use[b]	Farm fertilizer use[b]	Animal manure, confined[b]	Animal manure, unconfined[b]	Total nitrogen input, all sources[c]	Median nitrate concentration[d]
Holocene alluvium	18	610	0	4,500	3.6	41	5,200	<0.05
Pleistocene valley trains	23	620	0	5,700	8.8	73	6,600	<0.05
Pleistocene terrace deposits	0	500	1,030	110	2.1	23	1,900	0.73
Shallow Tertiary wells	37	460	0	510	18	290	1,750	<0.05

[a] Calculated from N_s = Ce x Ve x n, where N_s is the mass of nitrogen input from septic effluent, Ce is concentration of nitrogen in septic effluent (85 milligrams per liter; Miller, 1980), Ve is the volume of septic effluent per person per day (170 liters per day; Miller, 1980), and n is the number of people using septic systems in the areal extent of the zone of contribution to the well (assuming four persons per household and using septic-system density [Kerie J. Hitt, U.S. Geological Survey, written commun., 2005]).

[b] Kerie J. Hitt, U.S. Geological Survey, written commun., 2005.

[c] Totals are medians from study area and do not sum across table.

[d] Concentration in milligrams per liter, as nitrogen.

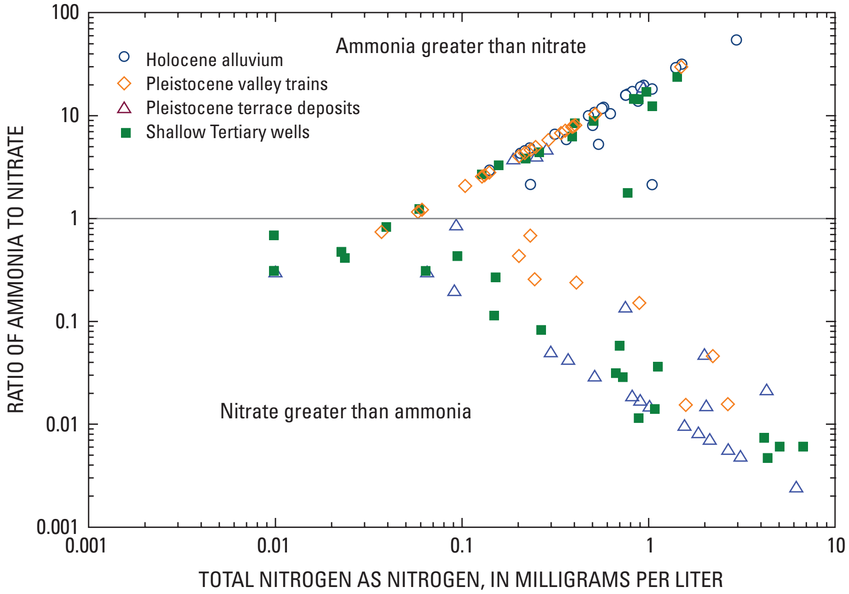


Figure 14. Relation between the ratio of ammonia and nitrate to total nitrogen in samples from four shallow well groups in the Mississippi embayment-Texas coastal uplands aquifer system and Mississippi River Valley alluvial aquifer.

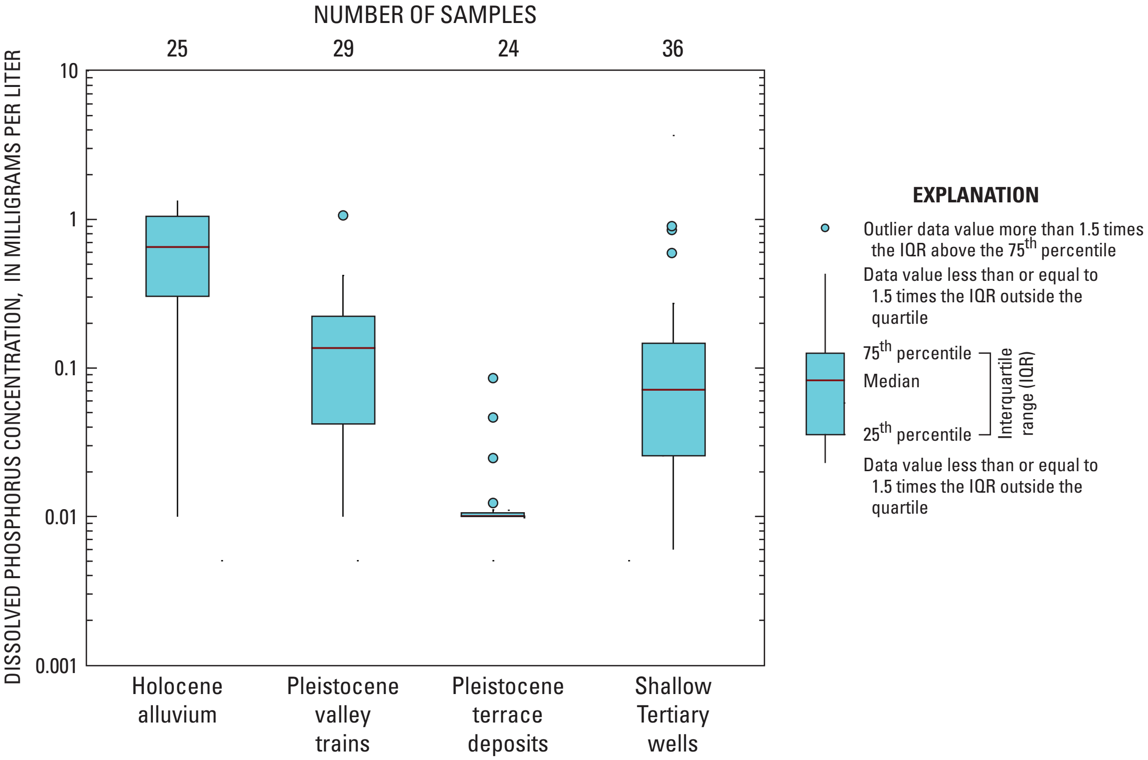


Figure 15. Concentrations of dissolved phosphorus in samples from four shallow well groups in the Mississippi embayment-Texas coastal uplands aquifer system and Mississippi River Valley alluvial aquifer.

1.3 mg/L. Three-quarters of the samples from this aquifer had phosphorus concentrations greater than 0.2 mg/L (fig. 15). Phosphorus concentrations in samples from the Pleistocene valley trains were somewhat lower than in samples from the Holocene alluvium with a median concentration of 0.11 mg/L and a maximum of 1 mg/L (table 4). In the samples from shallow Tertiary wells, phosphorus concentrations ranged from less than 0.01 to 0.87 mg/L with a median concentration of 0.07 mg/L. The occurrence of phosphorus in the three Tertiary aquifers sampled differed somewhat. Phosphorus concentrations were lowest in the middle Claiborne aquifer where it was detected in only four of eight wells in the Memphis area, and the maximum concentration was 0.07 mg/L. The lower Claiborne-upper Wilcox and middle Wilcox aquifers had median concentrations of 0.1 and 0.12 mg/L, respectively, and maximum concentrations of 0.27 and 0.87 mg/L, respectively.

The principal sources of phosphorus to groundwater systems include the overlying soils, dissolution of minerals that contain phosphate in aquifer sediments, agricultural fertilizer, animal waste, and leaking septic systems or infiltration of wastewater (Fuhrer and others, 1999). The widespread occurrence of elevated phosphorus concentrations (greater than 0.02 mg/L) in three of the shallow well groups suggests either a natural source in the soils or aquifer sediments, or nonpoint sources such as fertilizer and animal waste, or a combination of natural and human sources. The elevated concentrations of phosphorus in these aquifers could not be attributed to a specific source; however, phosphorus concentrations in samples from the Holocene alluvium and shallow Tertiary wells were weakly correlated to several inorganic constituents. Dissolved phosphorus concentrations were weakly related to the amount of agricultural land use in buffer areas around wells in the Holocene alluvium (Spearman's rho = 0.34, p = 0.05) but were not related in samples from the Pleistocene valley trains (fig. 16). Phosphorus concentrations were not correlated to soil properties in the surrounding buffer areas for any of the shallow well groups.

Weak correlations between specific conductance and dissolved phosphorus in samples from the Holocene alluvium and shallow Tertiary wells could be interpreted as indicating a contribution of phosphorus from the dissolution of aquifer sediments. In the shallow Tertiary wells, the occurrence of elevated phosphorus in the lower Claiborne-upper Wilcox and middle Wilcox aquifers, in areas of largely forested land use, suggests a geologic source for phosphorus in these aquifers in the absence of a manmade source; however, this interpretation is not conclusive. The relation between specific conductance and phosphorus concentrations also may represent geochemical conditions favorable to phosphorus transport in ground-water, whether the source of phosphorus is natural or manmade.

Although transport in groundwater generally has not been considered to be an important pathway in the environment for phosphorus, its occurrence in groundwater at elevated concentrations has been documented in a few studies (Atkinson, 1974; Burkart and others, 2004). In a number of groundwater studies, the source and transport of phosphorus were localized and related to sewage disposal or animal waste lagoons and downgradient plumes (Walter and others, 1996; Spruill, 1997). In a plume emanating from a sewage lagoon, phosphorus transport occurred in both anoxic and suboxic zones in the aquifer. Phosphorus transport in the anoxic zone was thought to be a result of the reducing conditions in the aquifer. As iron solubility increased and iron oxyhydroxides on the aquifer

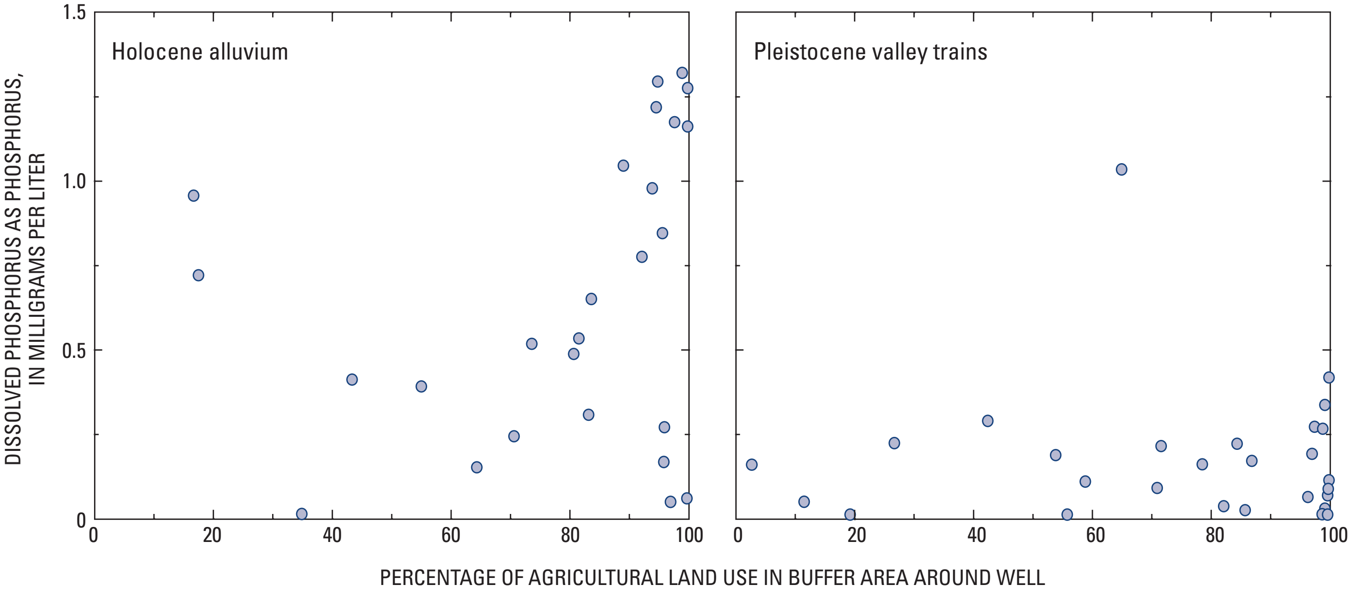


Figure 16. Relation of agricultural land use in buffer areas (1,640-foot radius) surrounding wells to dissolved phosphorus concentrations in water from wells completed in the Holocene alluvium and Pleistocene valley trains.

matrix dissolved, the number of sorption sites decreased (Walter and others, 1996). Continued downgradient transport in the suboxic zone was interpreted to be the result of a lack of available sorption sites in the aquifer matrix. That is, over time phosphorus transported with groundwater had occupied sorption sites and limited the capacity of the sediments to sorb additional phosphorus (Walter and others, 1996). In this dataset, a general association between elevated phosphorus concentrations and dissolved iron suggests that reducing conditions that mobilize iron also may facilitate transport of phosphorus. Although a statistically significant relation between iron and phosphorus concentrations in individual samples did not exist, the relative distribution of iron and phosphorus concentrations was somewhat similar among the shallow well groups (figs. 10 and 15). Both maximum iron and phosphorus concentrations were in samples from the Holocene alluvium and both were lowest in samples from the Pleistocene terrace deposits (figs. 10 and 15). This general association between iron and phosphorus concentrations in the Holocene alluvium, Pleistocene valley trains, and shallow Tertiary wells could be the result of a decrease in the number of sorption sites on the aquifer matrixes as a result of iron dissolution, or iron colloids in groundwater may serve as sorption sites for phosphorus transport with groundwater, or a combination of both processes may account for the dissolved phosphorus concentrations observed.

The elevated concentrations of phosphorus in these aquifers may represent a source of phosphorus to streams and rivers in the study area. Nutrient enrichment of streams in the southeastern United States is a topic of concern because of the hypoxic zone in the Gulf of Mexico (U.S. Environmental Protection Agency, 2007a) as well as the potential effects on local streams and stream ecology. Dissolved phosphorus results for samples from the Tensas River and Bogue Phalia were grouped into streamflow quartiles to generally characterize whether elevated groundwater concentrations may affect surface-water phosphorus concentrations (fig. 17). These basins are 390 and 484 square miles, respectively and do not receive any major point sources of phosphorus (Coupe, 2002). Samples collected during periods where the streamflow consisted primarily of groundwater inflow to the streams are represented by samples in the 25th quartile (low base flow) and probably some of the samples in the 50th quartile (high base flow). Median dissolved phosphorus concentrations for low base-flow samples collected from the Tensas River were about 0.15 mg/L and higher than concentrations in most of the samples collected when streamflow was greater (fig. 17). The maximum measured dissolved phosphorus value at this site was in the lowest streamflow quartile. Base-flow concentrations in samples from the Bogue Phalia were lower than in samples from the Tensas River, but the median concentration of about 0.04 mg/L during base-flow conditions and concentrations between 0.05 and 0.3 mg/L are greater than are usually attributed to groundwater. Although this analysis does not specifically identify groundwater as a major source of phosphorus to these streams, the elevated phosphorus concentrations during base-flow conditions indicate the potential for groundwater discharge to be a contributing source of phosphorus to these streams (fig. 17). Additional study is needed to better understand the extent to which phosphorus in groundwater is a contributing factor to watersheds in the study area having some of the highest phosphorus yields in the Mississippi River basin (Kleiss and others, 2000; Alexander and others, 2008).

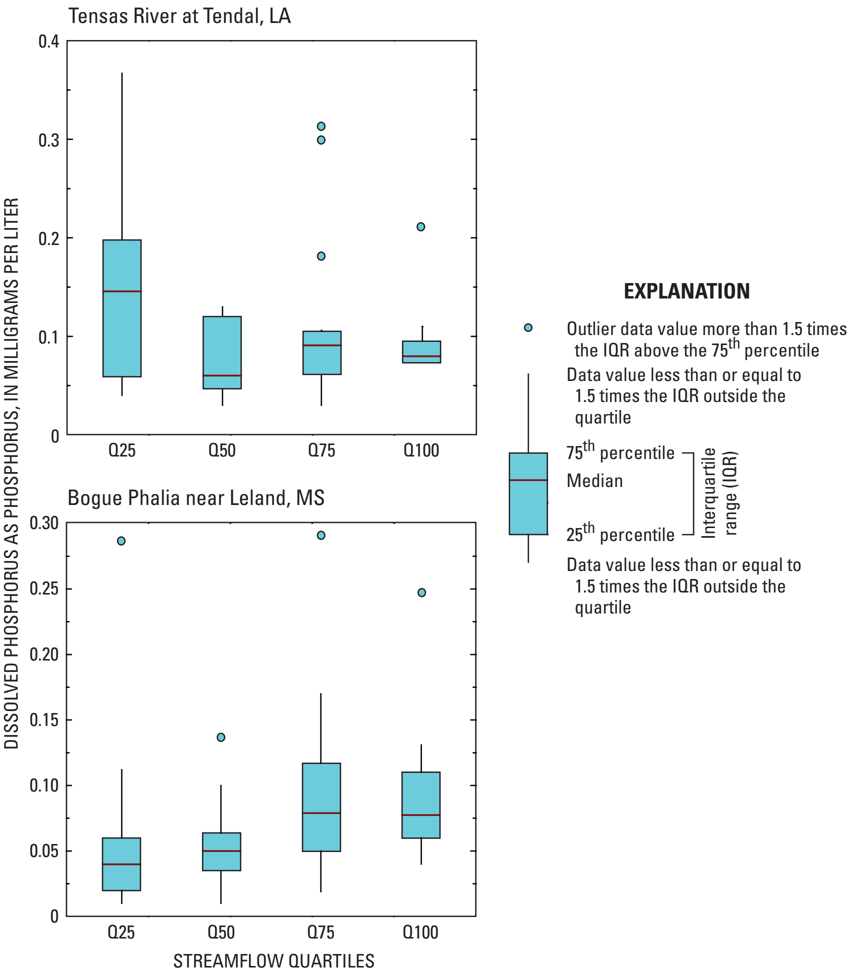


Figure 17. Dissolved phosphorus concentrations by streamflow quartile for samples collected from the Bogue Phalia near Leland, Mississippi (1995–2008), and the Tensas River at Tendal, Louisiana (1996–2000).

Pesticides

A total of 24 pesticides were detected at least once in shallow groundwater; however, one-quarter of these pesticides were detected only once (table 6). Comparatively few pesticides were detected in samples for the Holocene alluvium (6 pesticides) and Pleistocene valley trains (7 pesticides). Bentazon was the only pesticide detected in more than two samples from these aquifers. In both subunits of the MRVA aquifer, agricultural herbicides were the predominant pesticides detected and generally reflected compounds used on the principal crops grown: rice, cotton, and soybeans (table 2). In contrast, 16 different pesticides were detected in samples from both the Pleistocene terrace deposits and shallow Tertiary

Table 6. Detection frequency and maximum concentration for pesticides and pesticide degradates detected in water from four shallow well groups in the Mississippi embayment-Texas coastal uplands aquifer system and Mississippi River Valley alluvial aquifer, 1994–2004.

[N, number of wells sampled; detection frequency, in percent; concentration, in micrograms per liter; —, not detected; E, estimated]

Pesticide	Number of detections in shallow wells	Holocene alluvium N=25		Pleistocene valley trains N=29		Pleistocene terrace deposits N=24		Shallow Tertiary aquifers N=36	
		Detection frequency	Maximum concen-tration	Detection frequency	Maximum concen-tration	Detection frequency	Maximum concen-tration	Detection frequency	Maximum concen-tration
Herbicides									
2,4-D[a]	2	—	—	3	E 0.02	—	—	5[b]	E 14.8
Acetochlor	1	—	—	—	—	—	—	3	0.023
Atrazine	14	—	—	3	0.019	29	0.072	17	0.029
Bentazon[a]	18	24	3.17	28	0.31	8	0.08	9[b]	0.12
Bromacil[a]	2	—	—	—	—	8	0.27	—	—
DCPA	2	—	—	—	—	4	E 0.001	3	0.002
Dicamba[a]	1	—	—	—	—	—	—	5[b]	E 1.46
Diuron[a]	2	—	—	—	—	4	0.19	5[b]	E 0.001
EPTC	1	—	—	—	—	4	0.02	—	—
Fenuron[a]	3	4	E 0.02	—	—	8	0.57	—	—
Fluometuron[a]	4	4	0.28	7	1.22	4	0.11	—	—
Metolachlor	10	—	—	3	0.011	21	0.013	11	0.008
Metribuzin	3	—	—	—	—	4	0.010	6	0.007
Molinate	4	8	0.038	7	0.053	—	—	—	—
Pendimethalin	1	—	—	—	—	—	—	3	E0.017
Picloram[a]	3	—	—	—	—	13	E 3.91	—	—
Prometon	2	—	—	—	—	4	0.051	3	E 0.008
Propanil	2	4	E 0.003	—	—	—	—	3	0.005
Simazine	12	—	—	—	—	29	0.413	14	0.384
Tebuthiuron	4	—	—	—	—	12	1.76	3	0.014
Insecticides									
Diazinon	1	—	—	—	—	—	—	3	0.004
Dieldrin	2	—	—	—	—	8	3.20[c]	—	—
Degradates									
Deethylatrazine	10	—	—	3	E 0.013	25	E 0.046	8	E 0.021
p,p'-DDE	1	4	E 0.002	—	—	—	—	—	—

[a] Pesticide not analyzed for during 2004 sampling of the middle Wilcox aquifer.

[b] Number of wells used to calculate detection frequency was 22.

[c] Exceeds the U.S. Environmental Protection Agency Health Advisory of 0.2 microgram per liter for dieldrin (U.S. Environmental Protection Agency, 2004).

wells, and several pesticides were detected in more than two samples (table 6). The most commonly detected pesticides in samples from the Pleistocene terrace deposits and shallow Tertiary wells were the herbicides atrazine (29 and 17 percent), simazine (29 and 14 percent), and metolachlor (21 and 11 percent). The degradate deethylatrazine also was detected frequently (25 percent) in samples from the Pleistocene terrace deposits but at low, estimated concentrations. Pesticides detected in samples from these aquifers included herbicides with both agricultural and nonagricultural use. For example, atrazine and simazine are used for both agriculture and in urban settings, but tebuthiuron and prometon are not used in agriculture. Generally, the concentrations at which pesticides were detected were low. Only seven pesticides were detected at a concentration greater than 1 µg/L, and a sample from each shallow aquifer had at least one detection greater than 1 µg/L (table 6). Dieldrin was the only pesticide detected at a concentration greater than a human-health benchmark with a maximum concentration of 3.2 µg/L compared to the health-based screening level of 0.2 µg/L. The presence of dieldrin in groundwater at this elevated concentration, 10 years after being banned for use as a termite treatment in 1987, highlights its persistence in the environment.

The occurrence of pesticides was more widespread in samples from the Pleistocene terrace deposits than in samples from the three other shallow well groups (fig. 18). Two-thirds of the samples from wells in the Pleistocene terrace deposits contained at least one pesticide in contrast to between 30 and 43 percent of samples from the remaining shallow aquifers. The maximum number of pesticides detected in a single sample from the Holocene alluvium, Pleistocene valley trains, and shallow Tertiary wells were 3, 4, and 8, respectively. One sample from the Pleistocene terrace deposits contained 10 pesticides.

Agricultural use of pesticides accounts for about 76 percent of the total estimated use across the Nation and about 24 percent is nonagricultural use (Kiely and others, 2004). Agricultural pesticide use of specific pesticides was estimated using average or recommended application rates for crops and the acreage or amount of the crop grown in the buffer area around each well. Data are not available, however, to reliably estimate pesticide use for nonagricultural purposes. For the agricultural pesticides detected in two or more samples, the amount applied in the buffer area around each well was estimated. The median pesticide amount applied in the buffer area for each aquifer is shown in figure 19. Because of the predominance of forest and urban land in areas overlying the Pleistocene terrace deposits and shallow Tertiary wells, the median estimated use of agricultural pesticides is considerably less than in areas overlying the MRVA aquifer because the application rates in buffer zones around the wells for nonagricultural purposes cannot be estimated (fig. 19).

Although the estimated use of several agricultural pesticides applied was larger in buffer areas overlying the MRVA aquifer, most of these herbicides were detected more commonly in samples from the Pleistocene terrace deposits and shallow Tertiary wells. Several herbicides, for example, atrazine, metolachlor, and 2,4-D, may have been used in urban areas and may not have been accounted for by the use estimates; however, it is likely that the systematic and areally extensive estimated use for agricultural purposes is greater than local commercial or residential use of these compounds in buffer areas. Bentazon was the only herbicide detected in all four aquifers that was detected more frequently in samples from the MRVA aquifer. The factors contributing to a relatively high detection frequency of bentazon compared to other herbicides with greater amounts of use in the MRVA is not clear, but its frequent occurrence may be related to its physical properties such as its octanol-water partition and soil sorption coefficients that are lower than those for atrazine and metolachlor. It is also possible that the use of bentazon is greater than the estimated amount applied. Although bentazon is not commonly used in urban areas, it was detected in two wells in the Memphis area. Both of these wells are located near a stream, and bentazon may have been transported downstream from agricultural areas in the watershed. Propanil had the highest estimated use, but was detected in only one sample from the Holocene alluvium and one from the shallow Tertiary aquifer. Propanil was detected in samples from three streams that overlie the MRVA aquifer (Coupe, 2000); however, its detection frequency and the concentrations at which it was detected were lower than other herbicides with smaller amounts of use. Propanil has a short half life (1–3 days; Kamrin, 1997), which may account for its low detection frequency in both groundwater and surface-water samples compared to herbicides with lower amounts of estimated use.

Several herbicides with both agricultural and nonagricultural use, such as simazine, 2,4-D, atrazine, and metolachlor, were detected in samples from the Pleistocene terrace deposits and shallow Tertiary wells more commonly than in the MRVA (fig. 19). Herbicides, such as tebuthiuron and prometon, used for weed control along rights-of-way and other nonagricultural areas were detected in groundwater from both the Pleistocene terrace deposits and shallow Tertiary wells. Most of the detections (about 86 percent) in wells completed in shallow parts of the Tertiary aquifers were in samples from wells screened in the middle Claiborne aquifer with the largest number of different pesticides detected in individual wells in the Memphis area (fig. 18). The remaining 14 percent of the detections in the shallow Tertiary wells was for atrazine, deethylatrazine, and diazinon in samples from the lower Claiborne-upper Wilcox aquifer in Texas, and all concentrations were less than 0.02 µg/L. No pesticides were detected in the middle Wilcox aquifer in the area around Shreveport, Louisiana.

The potential of a pesticide to affect water quality is influenced by several factors including the type and intensity of use, environmental factors such as soil properties and aquifer hydrology, as well as chemical and physical properties that determine mobility and persistence of a pesticide (Gilliom and others, 2006). Estimated use of pesticides in the buffer areas around shallow wells was not a good predictor of occurrence, in part because only pesticides with agricultural

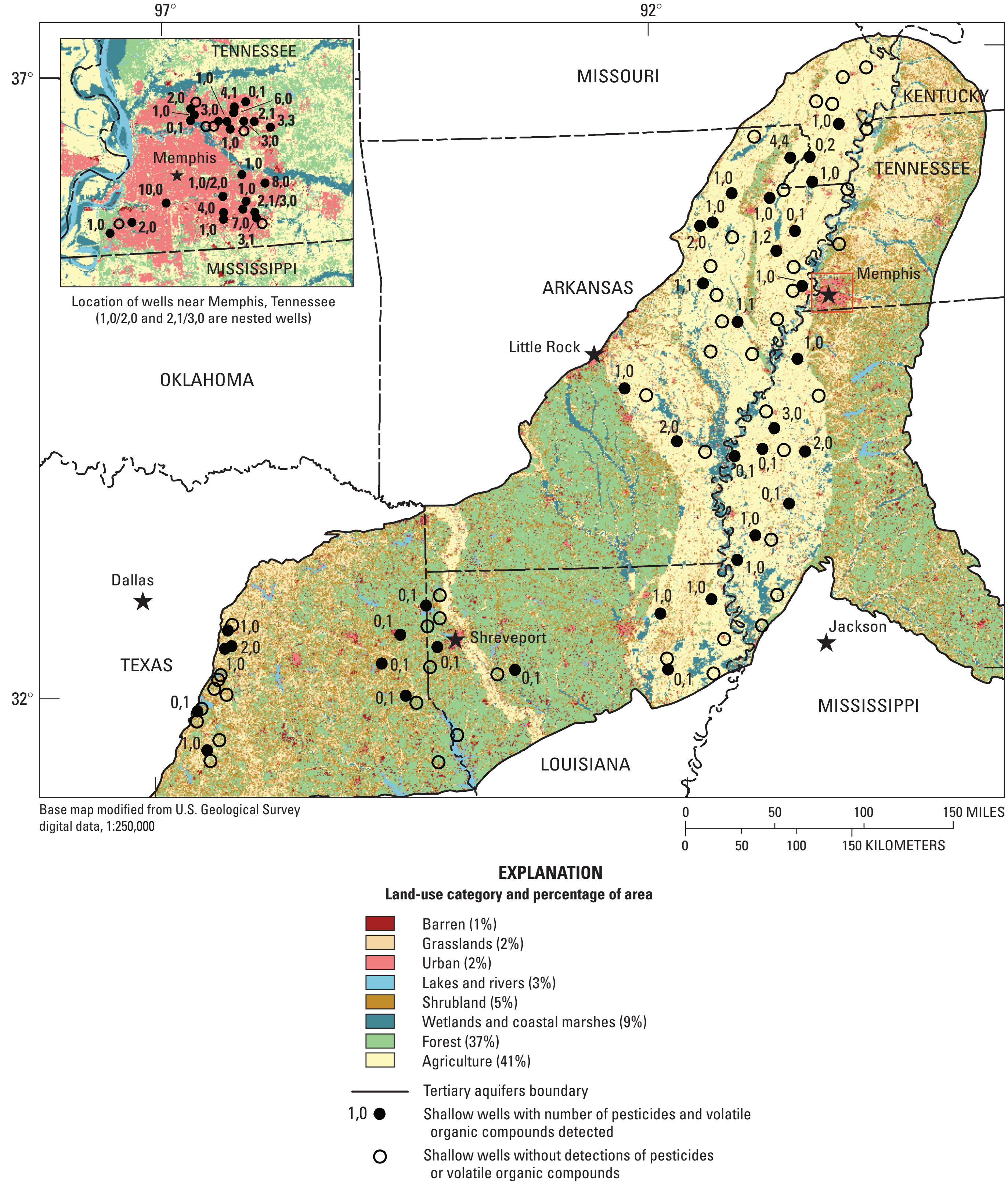


Figure 18. Number of pesticides and volatile organic compounds detected in shallow wells in the Mississippi embayment-Texas coastal uplands aquifer system and Mississippi River Valley alluvial aquifer (land-use data from Vogelmann and others, 1998a, 1998b).

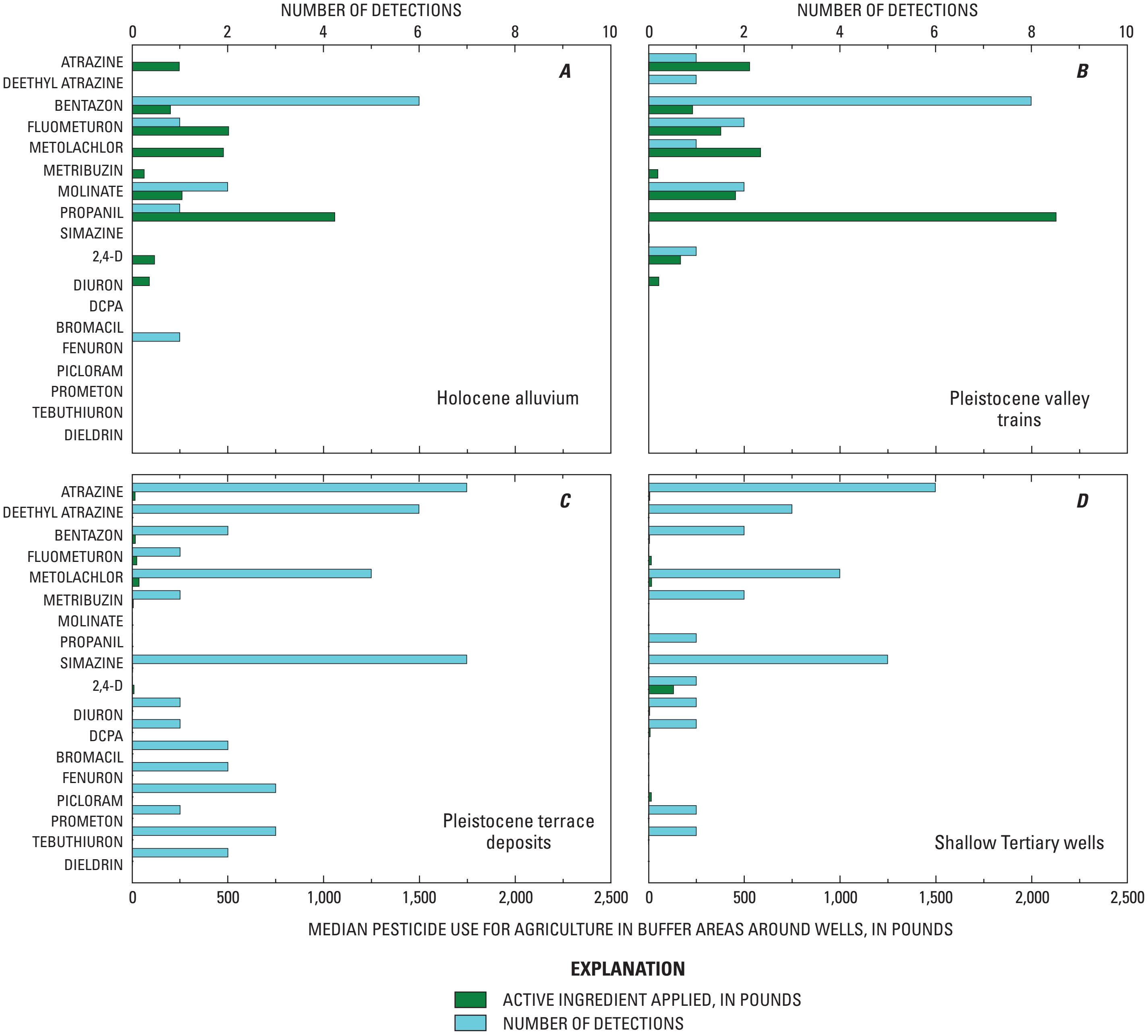


Figure 19. Median estimated agricultural use (1997) of detected pesticides in buffer areas and number of detections in samples from wells in the *(A)* Holocene alluvium, *(B)* Pleistocene valley trains, *(C)* Pleistocene terrace deposits, and *(D)* shallow Tertiary wells in the Mississippi embayment-Texas coastal uplands aquifer system and Mississippi River Valley alluvial aquifer.

use could be estimated. Pesticide occurrence generally was not correlated to other water-quality constituents, apparent residence time (tritium concentrations), well depth, or depth to water in the shallow groundwater. Differences in pesticide occurrence between aquifers and, in some cases, wells screened in the same aquifer generally were associated with differences in the overlying soils (fig. 20). Pesticides were detected in about two-thirds of samples from the Pleistocene terrace deposits compared to about one-third of samples from the other shallow well groups (fig. 20). The soils overlying the Pleistocene terrace deposits aquifer had the highest infiltration rates (lowest percentage of hydrologic group D soils) and lowest organic matter content. Although the relation between soil properties and occurrence do not apply in all of the shallow well groups, generally, pesticides were more commonly detected in samples from wells where the soils had higher infiltration rates based on a lower median percentage of hydrologic group D soils in the buffer area and lower organic matter content (fig. 20). For example, with the exception of the Pleistocene valley trains, the median percentage of the buffer areas around wells where pesticides were detected was lower than in those wells without detections.

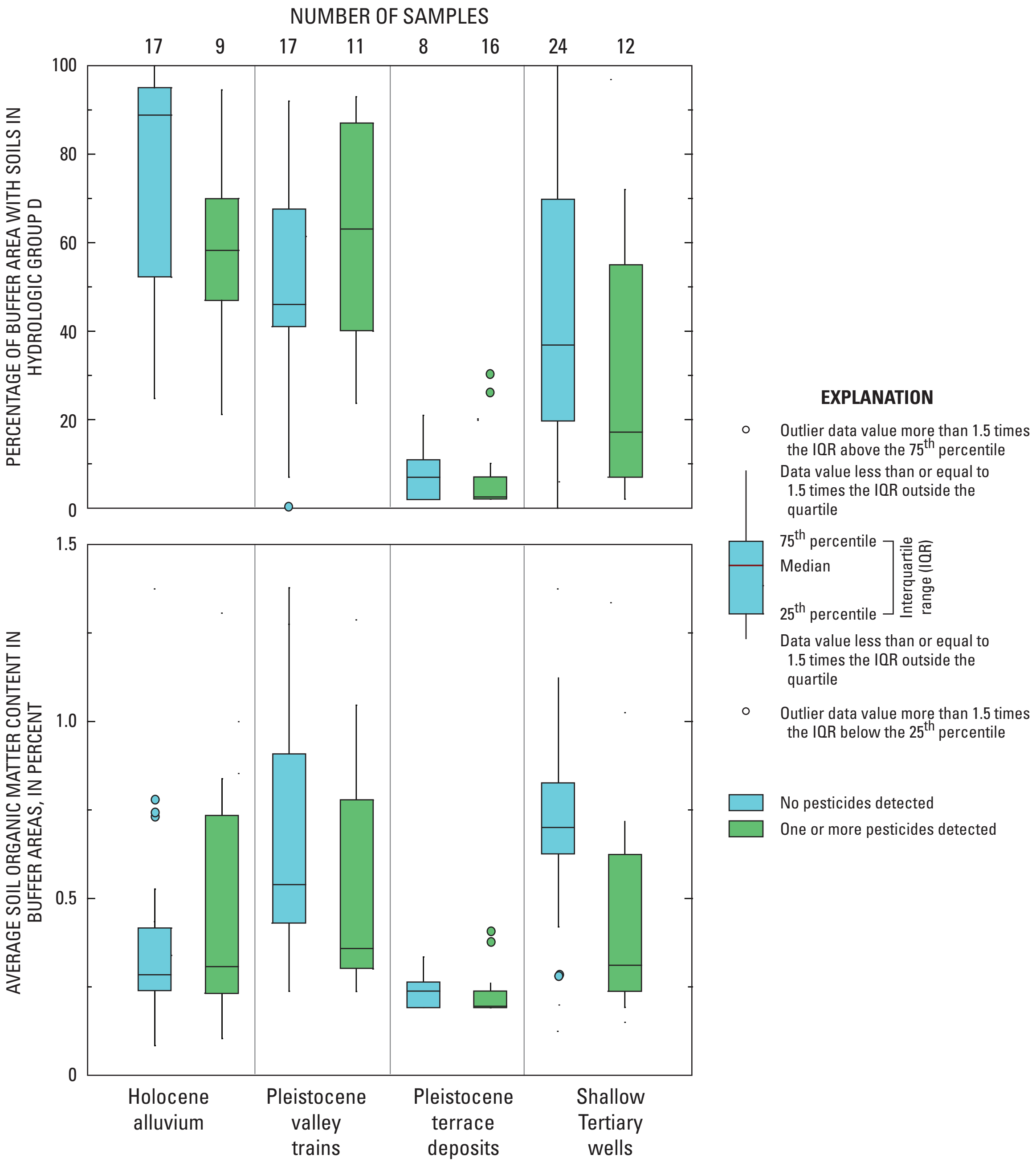


Figure 20. Distribution of soil hydrologic group and average organic matter content for samples with and without pesticide detections from four shallow well groups in the Mississippi embayment-Texas coastal uplands aquifer system and the Mississippi River Valley alluvial aquifer.

Volatile Organic Compounds

Volatile organic compounds are highly soluble, mobile, and persistent in groundwater, and many are suspected carcinogens (Lapham and Tadayon, 1996). Commonly used products, such as gasoline, refrigerants, paints, solvents, and plastics, contain VOCs. VOCs are used as fumigants in agriculture to control insects, worms, and other pests (Zogorski and others, 2006) and are also found in fuels used in farming equipment. Leaking underground storage tanks (USTs), supply pipelines, and improper waste disposal are potential point sources of VOCs to groundwater.

A relatively small number of VOCs were detected in each of the shallow well groups at a common assessment level of 0.2 g/L (table 7; fig. 18). The number of detections of VOCs in each shallow well group ranged from 3 in samples from the Holocene alluvium to 12 in samples from the Pleistocene valley trains (table 7). The most frequently detected VOC was dichlorodifluoromethane, which was detected in five samples collected from the Pleistocene valley trains and Pleistocene terrace deposits. Tetrahydrofuran was detected four times,

Table 7. Detection frequency and maximum concentration for volatile organic compounds detected in water from four shallow well groups in the Mississippi embayment-Texas coastal uplands aquifer system and Mississippi River Valley alluvial aquifer, 1994–2004.

[N, number of wells sampled; detection frequency, in percent; concentration, in micrograms per liter; —, not detected; E, estimated]

Volatile organic compound	Number of detections in shallow wells	Holocene alluvium N=25		Pleistocene valley trains N=29		Pleistocene terrace deposits N=24		Shallow Tertiary aquifers N=35	
		Detection frequency	Maximum concen-tration	Detection frequency	Maximum concen-tration	Detection frequency	Maximum concen-tration	Detection frequency	Maximum concen-tration
Trihalomethanes									
Trichloromethane (Chloroform)	3	—	—	—	—	4	2.06	6	0.91
Chlorinated solvents									
1,1,-Dichloroethane	1	—	—	—	—	4	0.20	—	—
1,2-Dichloroethane	1	—	—	3	2.68	—	—	—	—
cis-1,2-Dichloroethene	1	—	—	—	—	4	0.57	—	—
Tetrachloroethene (PCE)	1	—	—	—	—	4	0.44	—	—
Gasoline hydrocarbons									
1,2,4-Trimethylbenzene	1	—	—	3	0.25	—	—	—	—
2-Ethyltoluene	1	4	0.38	—	—	—	—	—	—
Benzene	1	—	—	—	—	—	—	3	0.36
Toluene	2	—	—	—	—	4	0.27	3	0.28
Gasoline oxygenates									
Diisopropyl ether	2	—	—	7	22	—	—	—	—
Methyl tert-butyl ether (MTBE)	3	—	—	10	6.4	—	—	—	—
Methyl tert-pentyl ether	1	—	—	3	0.79	—	—	—	—
Refrigerants									
Dichlorodifluoromethane	5	—	—	14	E 1.18	4	E 0.3	—	—
Trichlorofluoromethane	2	—	—	—	—	4	0.23	3	0.30
Other solvents – ether based									
Acetone[a]	1	—	—	—	—	—	—	5[b]	0.6
Diethyl ether	1	4	1.11	—	—	—	—	—	—
Tetrahydrofuran[a]	4	4	3.58	—	—	—	—	13[b]	1.35

[a] Volatile organic compound not analyzed for during 1994 sampling of the lower Claiborne-upper Wilcox aquifer.

[b] Number of wells used to calculate detection frequency was 22.

and methyl tert-butyl ether (MTBE) and chloroform were each detected three times overall (table 7). Given the variety and localized nature of potential sources (for example, USTs, machine shops, and dry cleaners), relating the occurrence of these few detections to explanatory factors is not feasible. However, one general observation is that five of the nine VOCs detected in samples from wells in the Holocene alluvium and Pleistocene valley trains were compounds that are associated with motor fuels, either gasoline oxygenates such as MTBE, or hydrocarbons in gasoline such as 2-ethyltoluene (table 7). One sample from a domestic well completed in the Pleistocene valley trains accounted for two of the highest concentrations of VOCs measured. Detections of MTBE, methyl tert-pentyl ether, and diisopropyl ether in this sample may be related to the storage and use of fuels near the well. Tetrahydrofuran is a solvent that is used in polyvinyl chloride (PVC) glues, and its occurrence in four samples may be from PVC plumbing at the well head rather than its occurrence in groundwater.

The occurrence of chlorinated solvents in samples from the Pleistocene terrace deposits (table 7) is likely a consequence of the overlying land use. Chlorinated solvents are used in industrial, commercial, and domestic applications, and the wells in the Pleistocene terrace deposits are in a predominantly urban setting (table 7). Wells in which chlorinated solvents were detected were oxic with DO concentrations between 1.9 and 4.9 mg/L, and chlorinated solvents generally are stable in oxic groundwater (Wiedemeier and others, 1998).

The Quality of Drinking Water in the Mississippi Embayment-Texas Coastal Uplands Aquifer System

Fifty-five wells completed in the Tertiary aquifers and sampled as part of these studies were deeper than 200 ft and generally are representative of drinking-water resources in the study area. These wells were screened in several different aquifers: the upper Claiborne (2 wells), middle Claiborne (17 wells), lower Claiborne-upper Wilcox (12 wells), and middle Wilcox (24 wells) aquifers. Fifty-four of these wells were used for domestic or public supply, and one well was used for stock supply; however, all 55 wells are referred to as drinking-water wells for the purposes of this report. Well depths ranged from 208 to 1,466 ft and the median depth was 395 ft. The wells were screened in both confined and unconfined parts of these aquifers, and tritium samples collected at 11 wells did not indicate a significant component of recent water at those 11 wells.

Inorganic Constituents

Concentrations of most inorganic constituents were less than available water-quality criteria for drinking water. Inorganic constituents were compared to available MCLs, secondary drinking-water standards, and health-based screening levels to generally assess the quality of water in the drinking-water wells. No constituents were detected at concentrations greater than an available MCL. Ten of the 55 samples had total dissolved solids concentrations greater than the SMCL of 500 mg/L (U.S. Environmental Protection Agency, 2004), with a maximum concentration of 1,000 mg/L. High concentrations of total dissolved solids can limit the use of groundwater for drinking water, irrigation, and industry because the water can be corrosive, have a salty or brackish taste, or result in scale formation in pipes. Most of the total dissolved solids concentrations (80 percent) in the deep drinking-water wells were between 27 and 492 mg/L, with an overall median of 291 mg/L. Dissolved iron and manganese concentrations were greater than their SMCLs of 300 and 50 µg/L (U.S. Environmental Protection Agency, 2004) in samples from 20 and 17 wells, respectively. High levels of iron and manganese are largely an aesthetic issue related to staining of fixtures and plumbing. Concentrations in the drinking-water wells ranged from 3 to 8,100 µg/L, with a median of 78 µg/L for iron, and ranged from 2.2 to 410 µg/L, with a median value of 15 µg/L for manganese. In many samples, the reducing conditions in the aquifer resulted in elevated iron and manganese concentrations. Samples from 13 wells had both iron and manganese concentrations that exceeded their SMCL. One sample had a concentration of fluoride of 3.8 mg/L, which exceeded the SMCL of 2 mg/L. Radon was the only other inorganic constituent that had concentrations greater than a health-related benchmark. The USEPA has proposed that public water supplies treat groundwater that has radon concentrations greater than 300 picocuries per liter (pCi/L) if a multimedia mitigation (MMM) program is not undertaken by a State (U.S. Environmental Protection Agency, 2007b). The recommended level of radon in drinking water is 4,000 pCi/L or less if a MMM program that addresses indoor air, the primary exposure route, is in place. Radon concentrations ranged from 46 to 518 pCi/L, with a median value of 98 pCi/L. Samples from 10 domestic wells screened in the middle Wilcox aquifer of northeastern Texas and northwestern Louisiana accounted for all radon concentrations greater than 300 pCi/L.

Nutrients

When detected, nitrate concentrations in samples from the deep drinking-water wells were low. Nitrate was detected in only 19 of the 55 wells with concentrations ranging from 0.05 to 3.8 mg/L and most of these wells were less than 500 ft deep (fig. 21). Concentrations of nitrate were low, in part, because DO concentrations were low, and nitrate is subject to denitrification in anoxic groundwater. All wells greater than 500 ft deep were anoxic (DO less than 0.5 mg/L), and overall, more than 75 percent of the samples were anoxic. The maximum nitrate concentration was in a sample that had a DO concentration of 7.40 mg/L (fig. 21). Ammonia was the predominant form of nitrogen in the deep wells. Ammonia was present in 52 of the 55 samples, and concentrations ranged from 0.02 to 1.8 mg/L. Similar to results for shallow Tertiary wells, concentrations were positively correlated to dissolved solids (Spearman's $\text{rho} = 0.75$, $p < 0.001$). Although this relation is relatively strong and might suggest a geologic source of nitrogen, sediments that compose these aquifers are not a likely source of nitrogen. A possible source of ammonia is from ammonification of organic matter in the aquifer resulting in increases in ammonia concentration with residence time in the aquifer.

Phosphorus was detected in 50 of the 55 wells, and 46 of those concentrations were greater than 0.02 mg/L. Dissolved phosphorus concentrations in the drinking-water wells ranged from 0.008 to 1.45 mg/L. The median concentration was 0.16 mg/L, which is greater than the median concentration measured in samples from the shallow Tertiary wells (table 4). Although elevated phosphorus concentrations occurred throughout the Tertiary aquifers, high concentrations were prevalent in parts of the study area. For example, some of the

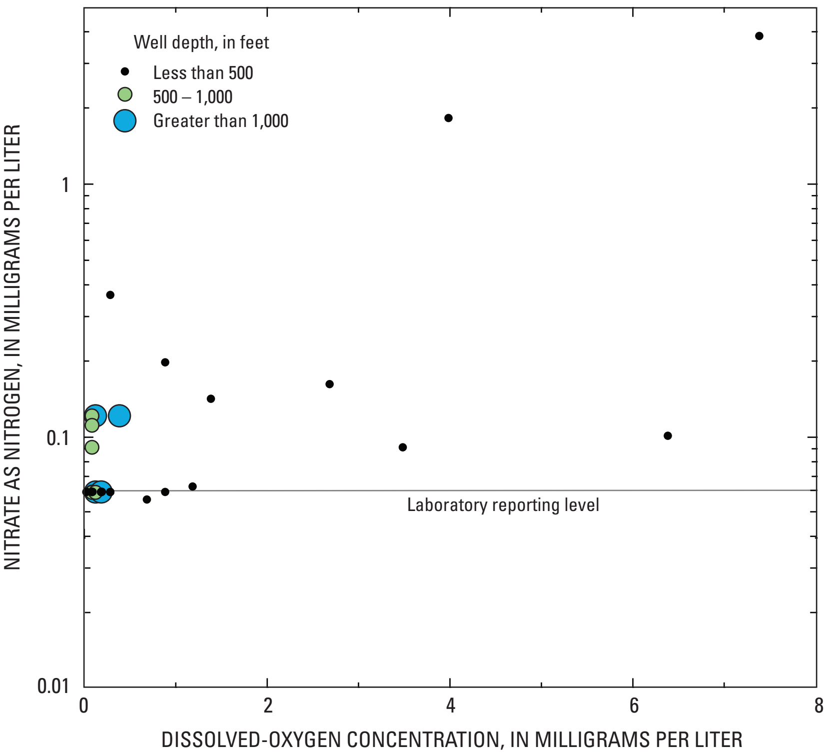


Figure 21. Relation between nitrate and dissolved-oxygen concentrations in drinking-water wells in the Mississippi embayment-Texas coastal uplands aquifer system.

highest phosphorus concentrations were in wells completed in the middle Wilcox aquifer wells in northwestern Louisiana (fig. 22). In addition, deep Tertiary wells in the southern part of the Mississippi Valley generally had higher phosphorus concentrations than wells in the northern part of the study area (fig. 22). Elevated concentrations of phosphorus were not limited to one of the Tertiary aquifers; concentrations greater than 0.1 mg/L occurred in several samples from each aquifer, with the exception of the upper Claiborne aquifer. However, only two wells from the upper Claiborne aquifer were sampled.

Dissolved phosphorus concentrations were correlated to total dissolved solids, and three depth ranges of wells had comparable ranges in phosphorus concentrations (fig. 23). This relation, the widespread occurrence of phosphorus, the absence of recent water in wells with tritium samples, and the fact that concentrations were not related to the depth of these wells (fig. 23), suggest that the aquifer sediments may be the predominant source of phosphorus in these samples. Relatively few minerals contain phosphorus, and a relation between fluoride and phosphorus concentrations (Spearman's rho = 0.6, $p < 0.001$) suggests that fluoroapatite is a possible source of phosphorus in these aquifers (fig. 23); however, apatite was not identified in heavy mineral separates from several of the units of Tertiary age (Lonsdale and others, 1931; Blankenship, 1956). In general, a relation between phosphorus and fluoride did not exist in samples from the shallow wells with the exception of a weak relation in the shallow Tertiary wells (Spearman's rho = 0.27, $p = 0.06$). Fluoride is relatively reactive in groundwater; for example, if a sufficient amount of calcium is present, the water may be in equilibrium with respect to fluorite and limit dissolved fluoride concentrations (Hem, 1985).

Pesticides and Volatile Organic Compounds

Pesticides and VOCs were detected infrequently in samples from deep drinking-water wells. When detected, both pesticide and VOC concentrations in most instances were considerably less than 1 µg/L (table 8), and no concentrations were greater than available drinking-water criteria. Two pesticides and two pesticide degradates were detected in 5 of the 55 drinking-water wells. Diazinon, an insecticide used predominantly in residential areas (discontinued in 2004), was detected in three samples from wells screened in the lower Claiborne-upper Wilcox aquifer in eastern Texas at concentrations of 0.017 µg/L or less (table 8). No other pesticide was detected more than once in samples from the deep wells. The compound p,p'-DDE, a degradate of the insecticide DDT, was detected in water from a lower Claiborne-upper Wilcox well in Texas. The use of DDT was banned in 1972. Bromacil and deethyl atrazine were both detected in one sample from a well screened in the middle Wilcox aquifer in eastern Arkansas. The five wells with pesticide detections were less than 500 ft deep. These pesticides also were detected in shallow wells, generally at comparable concentrations (table 6). Three of the four wells where pesticides were detected were in areas where the aquifers were unconfined.

Volatile organic compounds were detected at concentrations above 0.2 µg/L in samples from four of the drinking-water wells. Two of the five VOC detections were in a sample from a well completed in the middle Claiborne aquifer at a depth of 737 ft. The two VOCs, m- plus p-xylene and isobutyl methyl ketone, were not detected in any shallow samples. Chloroform was detected twice and was among the most commonly detected VOCs in shallow wells. The highest VOC concentration, 10.1 µg/L of tetrahydrofuran, was collected from a domestic well. Tetrahydrofuran may have been from the PVC plumbing at the wellhead, similar to the relatively high concentrations detected in shallow well samples.

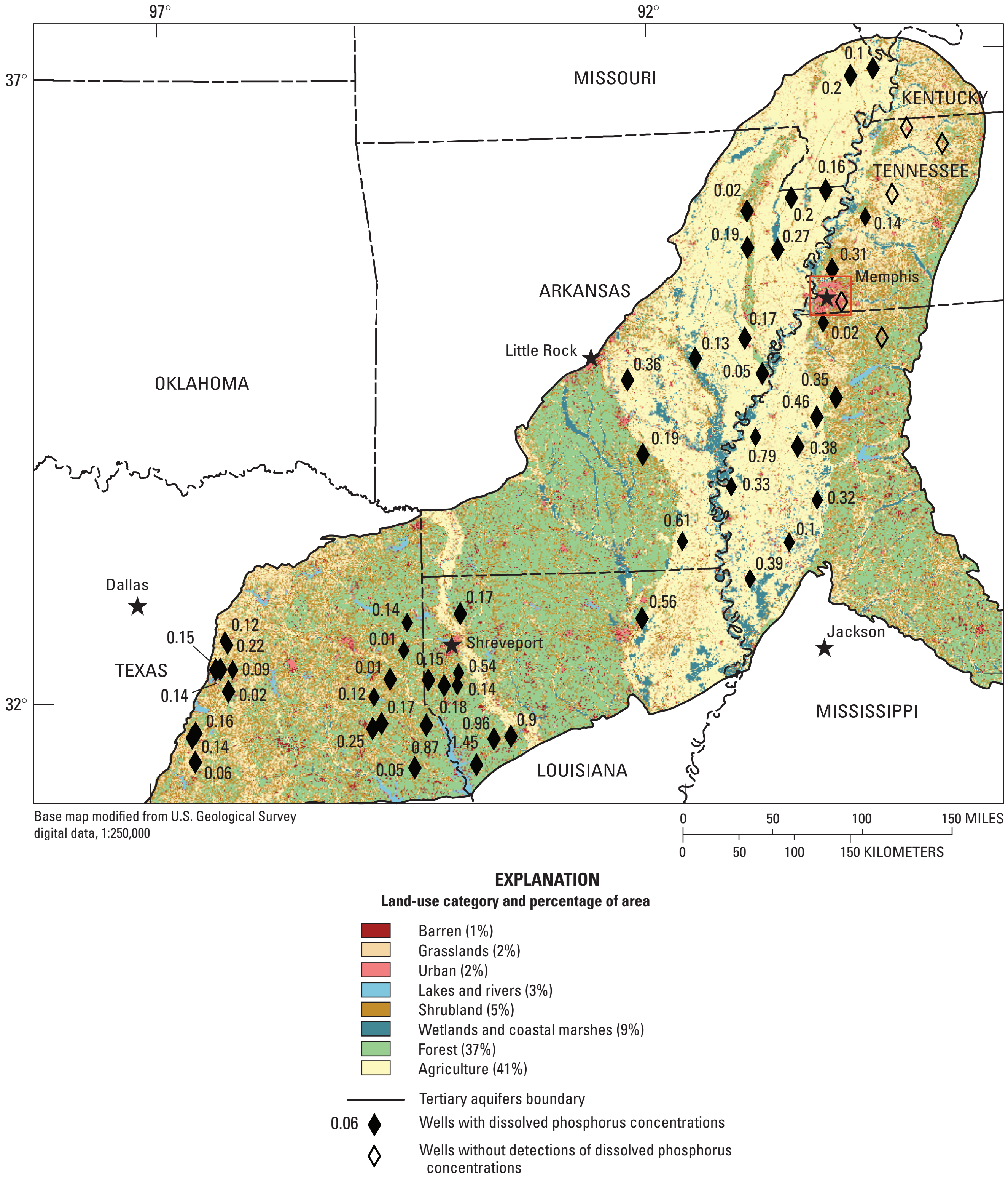


Figure 22. Dissolved phosphorus concentrations in samples from 55 drinking-water wells in the Mississippi embayment-Texas coastal uplands aquifer system (land-use data from Vogelmann and others, 1998a, 1998b).

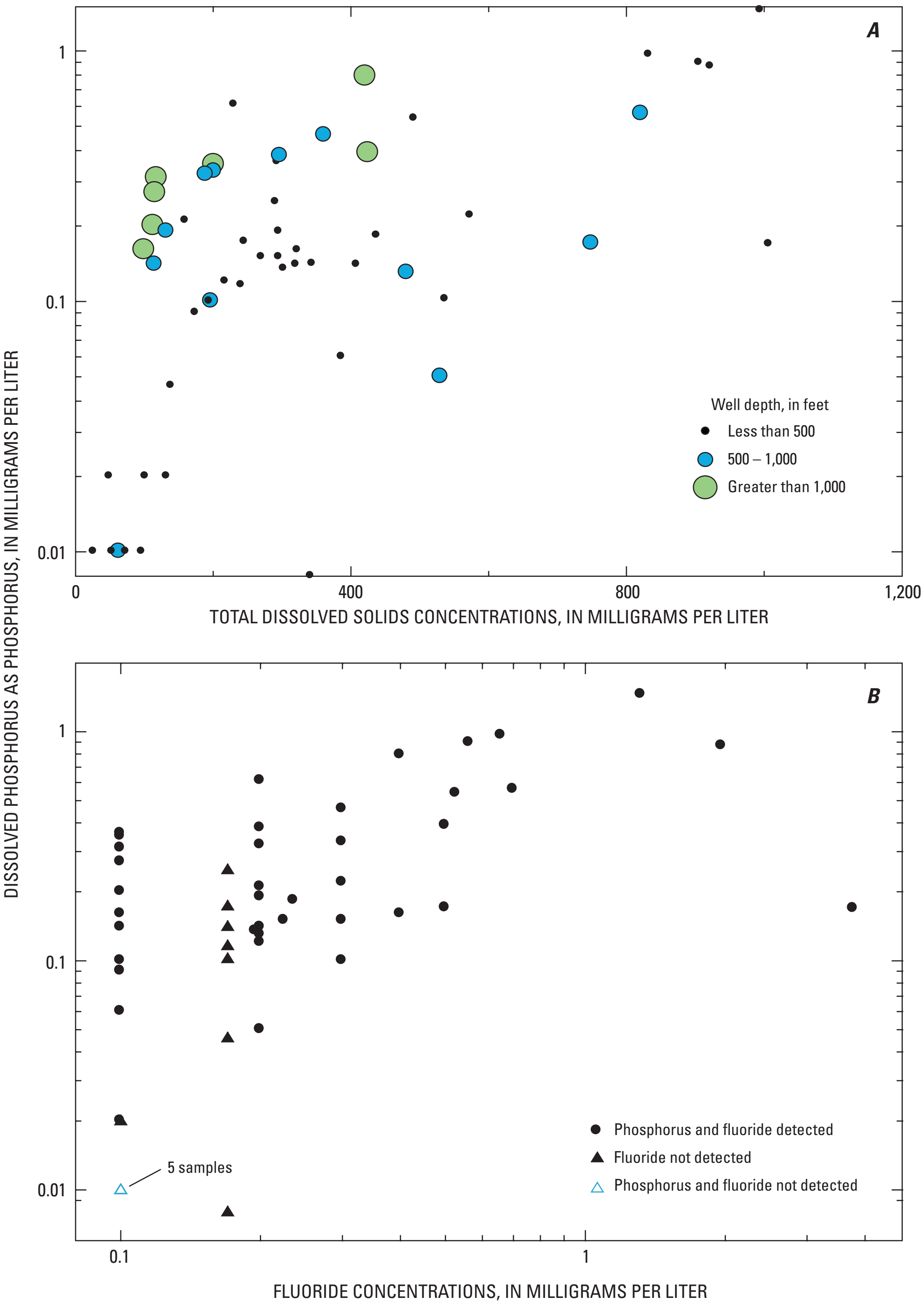


Figure 23. Relation between dissolved phosphorus and *(A)* total dissolved solids and *(B)* fluoride concentrations in drinking-water wells in the Mississippi embayment-Texas coastal uplands aquifer system.

Table 8. Detection frequency and maximum concentrations for pesticides, pesticide degradates, and volatile organic compounds detected in water from 55 drinking-water wells greater than 200 feet deep in the Mississippi embayment-Texas coastal uplands aquifer system, 1994–2004.

[N, number of wells; detection frequency, in percent; concentration, in micrograms per liter; E, estimated. There were no exceedances of a U.S. Environmental Protection Agency drinking-water standard (U.S. Environmental Protection Agency, 2004) or U.S. Geological Survey health-based screening level (Toccalino and others, 2003)]

Compound	Number of detections in drinking-water wells	Drinking-water wells N=55	
		Detection frequency	Maximum concentration
	Herbicides		
Bromacil	1	2	0.16
	Insecticides		
Diazinon	3	5	0.017
	Degradates		
Deethyl atrazine	1	2	E 0.004
p,p'-DDE	1	2	E 0.001
	Volatile organic compounds		
Isobutyl methyl ketone	1	2	E 0.20
m- plus p-xylene	1	2	0.43
Tetrahydrofuran	1	2	10.1
Trichloromethane (Chloroform)	2	4	0.72

Vulnerability of Drinking-Water Aquifers to Shallow Groundwater Leakage—An Example

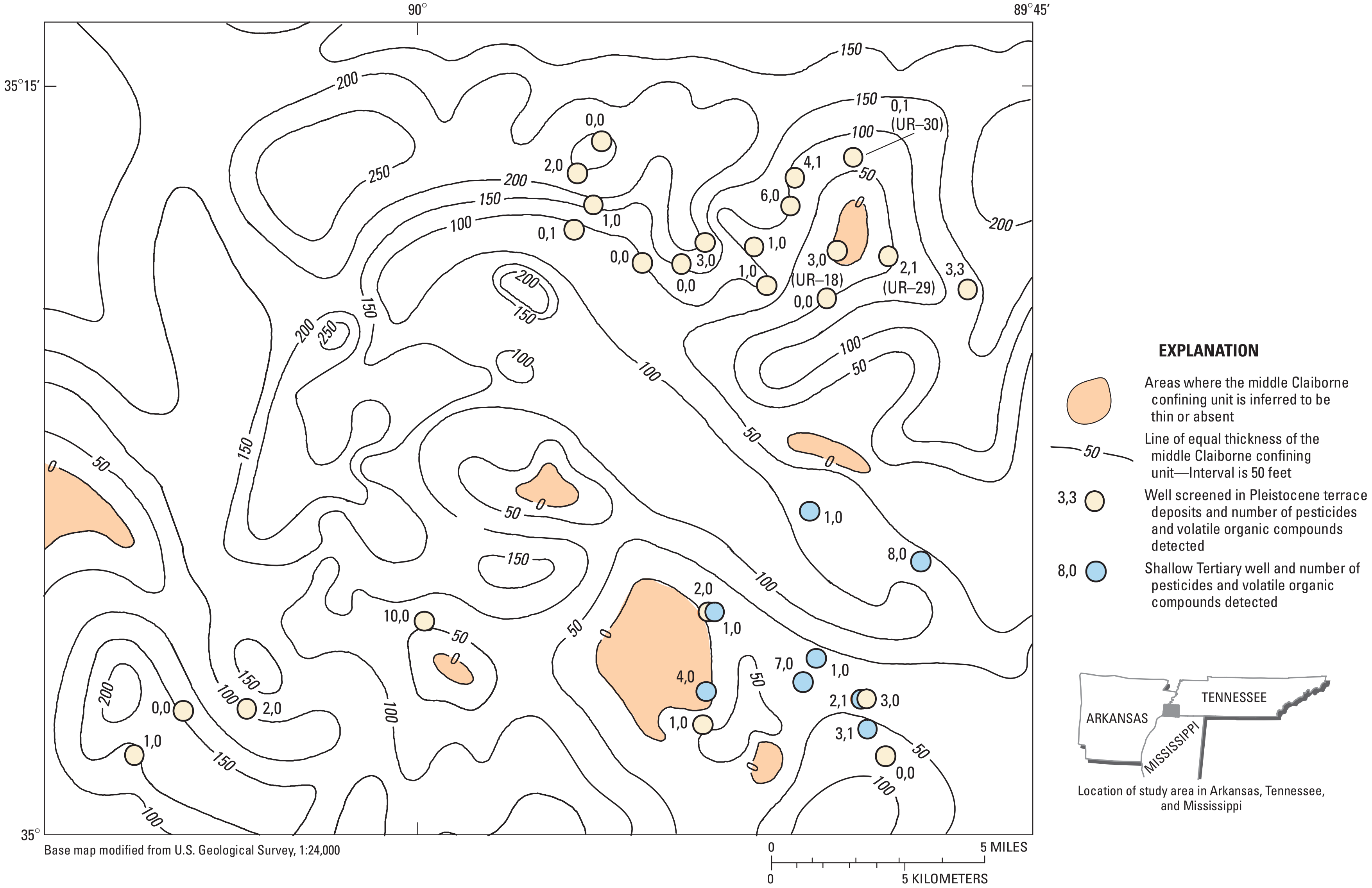
Although the quality of deep drinking water throughout the study area is good, the occurrence of pesticides and VOCs at low concentrations locally indicates that the deeper aquifers, particularly where unconfined, are vulnerable to contamination if contaminant sources are present. Groundwater withdrawals for water supply have lowered water levels in the Tertiary aquifers throughout much of the study area such that gradients in the areas of water-level decline are downward from surficial aquifers to deeper aquifers that are used as sources of drinking water. Increases in water use in the future may increase the potential for downward movement of water and contaminants from shallow sources.

The groundwater hydrology of the Memphis, TN, area has been characterized in a number of studies. Throughout most of the area, the middle Claiborne confining unit separates the shallow water-table aquifer (Pleistocene terrace deposits) from the underlying middle Claiborne aquifer, locally called the Memphis aquifer. Hydrogeologic studies by Graham and Parks (1986) and Parks (1990) characterized the potential for leakage in the Memphis area, documented the occurrence of recent water in parts of the middle Claiborne aquifer (Memphis aquifer) using tritium data, and identified areas where hydraulic heads between the water-table aquifer and the middle Claiborne aquifer were similar, indicating a hydraulic connection between the aquifers. Parks (1990) constructed a map of the thickness of the confining unit separating the two aquifers based on geophysical logs and inferred areas where the confining unit was thin or absent. Changes in water quality were characterized in local-scale studies at a landfill (Bradley, 1991) and a well field (Parks and others, 1995) in the Memphis area. These changes were associated with the downward movement of water from the water table in both the western and eastern parts of the Memphis area.

In this study, pesticides and VOCs were detected in samples from 16 and 5 wells, respectively, in the Pleistocene terrace deposits in the Memphis area (fig. 24). Only six wells in this shallow aquifer did not have a detection of either a pesticide or VOC, highlighting the widespread occurrence of these organic compounds in shallow groundwater in the Memphis area. In addition, pesticides also were detected in samples from five wells completed in the Pleistocene terrace deposits located in proximity to areas where the underlying confining unit is thin or absent (fig. 24), representing the potential for contaminants to move downward into the upper part of the middle Claiborne aquifer.

In the southeastern part of the Memphis area, samples from each of the eight wells completed in the upper part of the middle Claiborne aquifer contained at least one pesticide, and samples from two wells also contained VOCs (fig. 24). The occurrence of these organic compounds in the upper part of the middle Claiborne aquifer indicates that this aquifer is vulnerable to contamination, corroborating conclusions of previous studies of largely point sources of contamination in the area (Parks, 1990; Bradley, 1991; Parks and others, 1995).

Water-level data collected from 24 shallow Pleistocene terrace deposits wells and 8 shallow Tertiary middle Claiborne wells during the spring 1997 were compared to a potentiometric-surface map of the middle Claiborne aquifer (Kingsbury, 1996; fig. 25). The potentiometric-surface map was drawn using water-level data collected during September 1995 when water levels in the Memphis area were generally at their lowest for the year. Water levels in the eight shallow Tertiary aquifer wells in the southeastern part of the Memphis area generally were 4 to 10 ft higher than nearby water-level contours (fig. 25). The difference likely is because of the different seasons in which the water levels were measured. Most of the water levels from shallow Pleistocene terrace deposits wells were considerably higher, in much of the area more than about 50 to 140 ft, than water



Base map modified from U.S. Geological Survey, 1:24,000

Figure 24. Thickness of the middle Claiborne confining unit and number of pesticides and volatile organic compounds detected in samples from the Pleistocene terrace deposits and shallow Tertiary wells in the Memphis, Tennessee, area (modified from Parks, 1990).

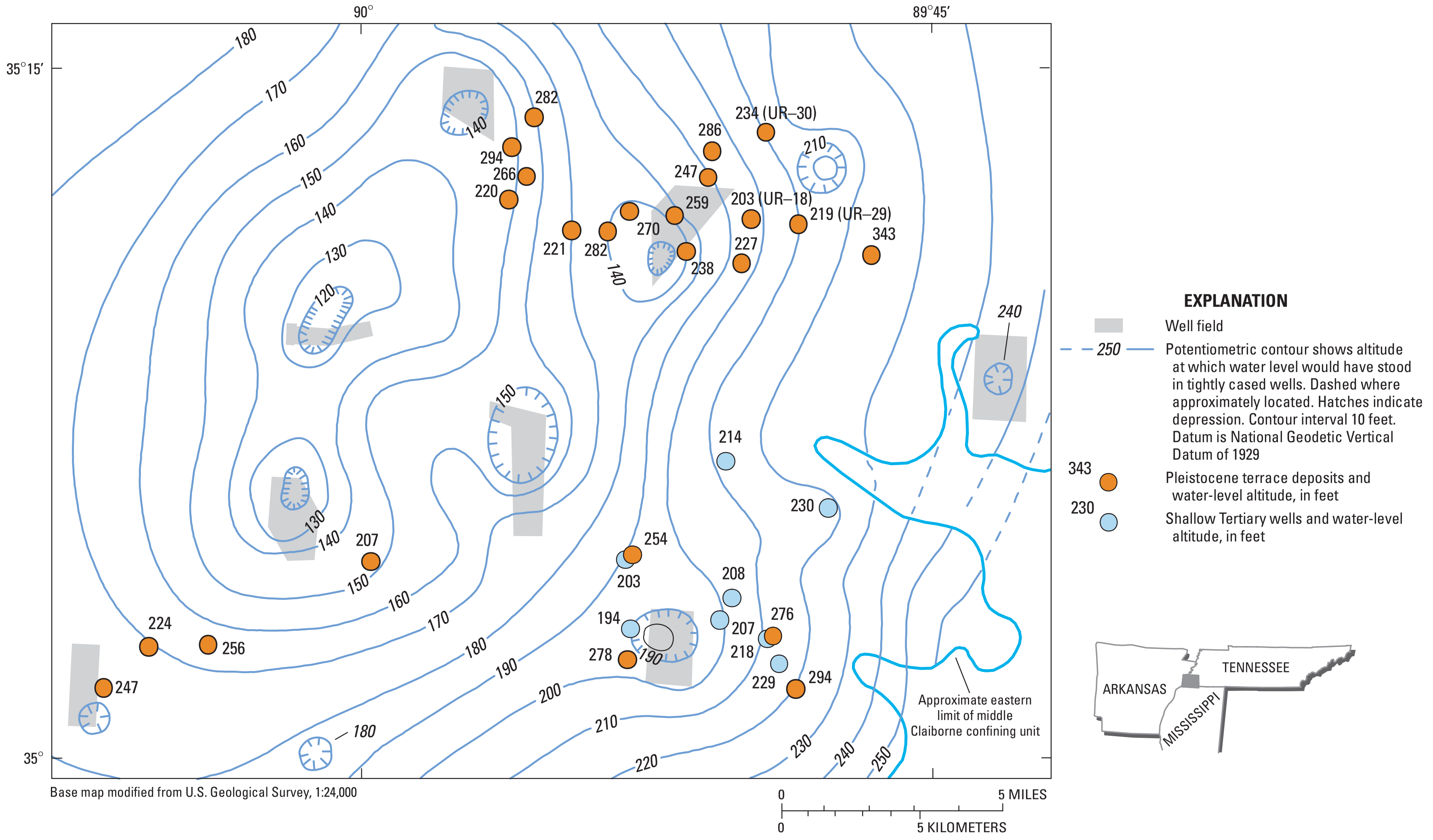


Figure 25. Potentiometric surface of the middle Claiborne aquifer, 1995, and water levels in the Pleistocene terrace deposits and shallow Tertiary wells, 1997 (modified from Kingsbury, 1996).

levels in the middle Claiborne aquifer (as indicated by nearby contours). Two well pairs in this dataset, with one well in Pleistocene terrace deposits and one middle Claiborne well, in the southeastern Memphis area, indicated a difference of about 50 ft in water levels with between 20 to 30 ft of middle Claiborne confining unit present at these locations (Strom, 1997). Although these differences in head favor the downward movement of water, where the confining unit is present, the potential for leakage is considered to be less than in areas where the confining unit is thin or absent.

The difference between water levels at two Pleistocene terrace deposits wells (UR-18 and UR-29) and the middle Claiborne aquifer, however, was less than 10 ft (fig. 25). The water level at a third well (UR-30), located in the same general area, was only about 25 ft higher than water levels in the middle Claiborne aquifer. These shallow wells are located near two cones of depression in the potentiometric surface of the middle Claiborne aquifer formed by groundwater withdrawals. The low water levels in wells UR-18, UR-29, and UR-30 in an area where the middle Claiborne confining unit is interpreted as being thin or absent (fig. 24) suggest an area of potential leakage from the shallow aquifer to the middle Claiborne aquifer. Additionally, the pesticides and VOCs detected in these shallow wells have the potential to move into the deeper drinking-water aquifer in this area.

Summary

Water-quality data collected for 169 wells as part of the National Water-Quality Assessment (NAWQA) Program from 1994 to 2004 were aggregated to better understand factors that affect the quality of groundwater in the Mississippi embayment-Texas coastal uplands aquifer system and Mississippi River Valley alluvial (MRVA) aquifer. The wells sampled included public-supply, domestic use, irrigation, and monitoring wells and were completed in four regional aquifers of the Mississippi embayment-Texas coastal uplands aquifer system, two subunits of the MRVA aquifer (Holocene alluvium and Pleistocene valley trains), and a shallow water-table aquifer in the Memphis, TN, area (Pleistocene terrace deposits).

Because of the large range in depths (21 to 1,466 ft) of the wells sampled for this study and because many of the constituents analyzed likely originate from activities at land surface, a subset of 114 wells 200 ft deep or less was selected to characterize the occurrence of many of the constituents in shallow groundwater. These wells were subdivided into four groups—the Holocene alluvium and Pleistocene valley trains units of the Mississippi River Valley alluvial aquifer; the Pleistocene terrace deposits in Memphis, TN; and the shallow Tertiary wells, which included wells in the middle Claiborne, lower Claiborne-upper Wilcox, and middle Wilcox aquifers.

Although the ranges in well depth and depth to water generally were similar among the four shallow well groups, differences in water quality were observed. Groundwater in the two subunits of the MRVA aquifer generally is more mineralized than groundwater in the Pleistocene terrace deposits and shallow Tertiary wells. In addition, tritium concentrations in samples from the Holocene alluvium, Pleistocene valley trains, and shallow Tertiary wells indicated a smaller component of recent groundwater than samples from the Pleistocene terrace deposits. Samples from the Pleistocene terrace deposits had the highest median and maximum tritium concentrations, likely indicating that this group had the largest component of recent recharge. In samples from the Pleistocene valley trains and shallow Tertiary wells, tritium concentrations were inversely related to total dissolved solids, suggesting increases in inorganic constituent concentrations with longer groundwater residence times in these aquifers.

The redox conditions, as indicated by concentrations of dissolved oxygen, nitrate, manganese, iron, and sulfate, differed considerably among the four shallow well groups. The majority of the samples from the Holocene alluvium and Pleistocene valley trains were anoxic (dissolved oxygen less than 0.5 mg/L). Redox conditions in the Holocene alluvium were strongly reducing, and several samples had iron concentrations as high as 14,000 µg/L. Samples from the Pleistocene valley trains indicated somewhat less reducing conditions with a few oxic wells. In contrast, more than half of the samples from the Pleistocene terrace deposits were oxic, as were about one-third of the samples from the shallow Tertiary wells. Iron and manganese concentrations in the Pleistocene terrace deposits and shallow Tertiary wells were considerably lower than in the subunits of the MRVA.

Differences in apparent age of water or residence time and redox conditions were associated with differences in soil properties within 1,640-ft (500-meter) buffer areas around the wells. Soils near the Pleistocene terrace deposits wells had higher infiltration rates and lower amounts of clay than the other three shallow well groups. Soils overlying wells in the two subunits of the MRVA aquifer had the highest average clay content and lowest infiltration rates.

The estimated loading of nitrogen from various sources, including farm and non-farm fertilizer use, animal manure, septic systems and atmospheric deposition, was about three times higher in the buffer areas surrounding the Holocene alluvium and Pleistocene valley trains than in the buffer areas surrounding the remaining shallow well groups. Nitrate, however, was not detected in most samples from the Holocene alluvium and Pleistocene valley train aquifers. Nitrate was more commonly detected in samples from the shallow Tertiary and Pleistocene terrace deposits, which both had maximum concentrations of about 6 mg/L. Reducing conditions in the MRVA aquifer likely result in denitrification of most nitrate that moves with recharge, and soils overlying these aquifers likely slow the movement of water and facilitate denitrification.

Dissolved phosphorus concentrations in samples from the Holocene alluvium, Pleistocene valley trains, and shallow Tertiary wells were considerably higher than 0.02 mg/L, a concentration typical of many groundwater systems. The highest concentrations (maximum 1.3 mg/L; median 0.65 mg/L) were in samples from the Holocene alluvium. Median concentrations of dissolved phosphorus were 0.11 mg/L in the Pleistocene valley trains and 0.07 mg/L in the shallow Tertiary wells. Phosphorus was detected in only seven samples from the Pleistocene terrace deposits and had a maximum concentration of 0.08 mg/L.

The widespread occurrence of elevated phosphorus concentrations in three of the four shallow well groups suggests a natural source and(or) a nonpoint source and also indicates groundwater is a potential source of phosphorus to streams in these areas. Although phosphorus concentrations in samples from the Holocene alluvium showed a weak correlation to several inorganic constituents and to the amount of agricultural land use in the buffer area, the elevated concentrations could not be attributed to a specific source. The highest phosphorus concentrations in the shallow wells tended to be associated with water that had high iron concentrations, suggesting reducing conditions that mobilize iron might facilitate the transport of phosphorus in these aquifers. Data for dissolved phosphorus concentrations and stream discharge for two streams in the study area indicate that groundwater discharge may be a contributing source of phosphorus to these streams. Additional study is needed to better understand the sources and transport of phosphorus in these shallow aquifers.

A total of 24 pesticides were detected at least once in shallow groundwater; however, one-quarter of these pesticides were detected only once. Relatively few pesticides were detected in samples from the Holocene alluvium and Pleistocene valley trains, although the estimated use for agricultural purposes was considerably higher in areas overlying wells in these aquifers than near the shallow Tertiary and Pleistocene terrace deposits wells. Bentazon was the only herbicide detected in more than two samples from wells completed in the MRVA aquifer, although its estimated use was lower than other herbicides. The most commonly detected pesticides in samples from the Pleistocene terrace deposits and shallow Tertiary wells were the herbicides atrazine, simazine, and metolachlor. The degradate, deethylatrazine, also was detected in about 25 percent of the samples from the Pleistocene terrace deposits. Generally, the concentrations at which pesticides were detected were low. Only seven compounds were detected at a concentration greater than 1 µg/L, and a sample from each shallow aquifer had at least one detection greater than 1 µg/L. Dieldrin was the only pesticide detected at a concentration greater than a human-health benchmark with a maximum concentration of 3.2 µg/L, compared to the health-based screening level of 0.2 µg/L. Differences in the number of pesticides detected among the shallow well groups generally corresponded to differences in the soil properties near the wells. Pesticides were detected more commonly in samples from wells in the Pleistocene terrace deposits where soils had higher infiltration rates and lower organic matter content.

Volatile organic compounds were not detected commonly at an assessment level of 0.2 µg/L in shallow groundwater. The number of detections of volatile organic compounds in shallow groundwater ranged from 3 in samples from the Holocene alluvium to 12 in samples from the Pleistocene valley trains. The most commonly detected VOC was dichlorodifluoromethane, which was detected in a total of five samples collected from the Pleistocene valley trains and Pleistocene terrace deposits aquifers. Methyl tert-butyl ether (MTBE), chloroform, and tetrahydrofuran were each detected three times overall.

Fifty-five wells deeper than 200 ft completed in the Mississippi embayment-Texas coastal uplands aquifer system were sampled as part of this study. Tritium samples collected at 11 of these wells did not indicate a component of recent recharge. Nearly all of these deep wells were used for public supply or were domestic wells. The quality of the water generally was good, and concentrations of most inorganic constituents were less than water-quality criteria for drinking water. Secondary maximum contaminant levels (SMCLs) were exceeded for total dissolved solids in 10 wells, iron in 20 wells, and manganese in 17 wells. Samples from 13 wells had both iron and manganese concentrations that exceeded their SMCL. Radon activities in samples from 10 wells located in the middle Wilcox aquifer of northeastern Texas and northwestern Louisiana were greater than 300 picocuries per liter (pCi/L). Nitrate concentrations were low, only two samples had nitrate concentrations that were greater than 1 mg/L. Low nitrate concentrations corresponded to the anoxic conditions sampled in most wells. Ammonia was the predominant form of nitrogen in drinking-water wells. Few pesticides (six) and volatile organic compounds (five) were detected, and concentrations were generally less than 1 µg/L, except for one detection of tetrahydrofuran that was 10.1 µg/L. Tetrahydrofuran is found in glues used for polyvinyl chloride pipes, and its occurrence may be from plumbing at the wellhead.

Phosphorus was detected in 91 percent of the drinking-water wells, and 84 percent of the concentrations were greater than 0.02 mg/L. The highest concentrations generally were in samples from the middle Wilcox aquifers in northwestern Louisiana and the middle Claiborne aquifer in the southern part of the Mississippi Valley. Dissolved phosphorus was correlated with total dissolved solids as well as fluoride. These relations and the fact that phosphorus was detected at depth suggest a geologic source may be the predominant source of phosphorus in drinking-water wells.

Groundwater withdrawals from the Tertiary aquifers have lowered water levels, which increases the potential of movement of shallow groundwater to deep aquifers. Water-level data for a few wells in the Pleistocene terrace deposits in the Memphis area suggest a hydraulic connection between this shallow aquifer and the deeper middle Claiborne aquifer, locally named the Memphis aquifer, that is used for public supply. Pesticides and volatile organic compounds were detected in samples from Pleistocene terrace deposits wells and middle Claiborne aquifer wells, further illustrating the potential for the downward migration of the compounds to the drinking-water aquifer. Eight shallow Tertiary wells screened in the upper part of the middle Claiborne aquifer contained at least one pesticide, and two of these wells contained a volatile organic compound. The occurrence of these organic compounds in the upper part of the middle Claiborne aquifer indicate that, in some locations, this aquifer is vulnerable to contamination, corroborating conclusions of previous studies.

References

Alexander, R.B., Smith, R.A., Schwarz, G.E., Boyer, E.W., Nolan, J.V., and Brakebill, J.W., 2008, Differences in phosphorus and nitrogen delivery to the Gulf of Mexico from the Mississippi River basin: Environmental Science and Technology, v. 42, no. 3, p. 822–830.

Arthur, J.K., 2001, Hydrogeology, model description, and flow analysis of the Mississippi River alluvial aquifer in northwestern Mississippi: U.S. Geological Survey Water-Resources Investigations Report 01–4035, 47 p.

Atkinson, J.C., 1974, Orthophosphate in ground water: Ground Water, v. 12, no. 5, p. 291–295.

Blankenship, R.R., 1956, Heavy-mineral suites in unconsolidated Paleocene and younger sands, western Tennessee: Journal of Sedimentary Petrology, v. 26, no. 4, p. 356–362.

Bradley, M.W., 1991, Ground-water hydrology and the effects of vertical leakage and leachate migration on ground-water quality near the Shelby County landfill, Memphis, Tennessee: U.S. Geological Survey Water-Resources Investigations Report 90–4075, 42 p.

Burkart, M.R., Simpkins, W.W., Morrow, A.J., and Gannon, J.M., 2004, Occurrence of total dissolved phosphorus in unconsolidated aquifers and aquitards in Iowa: Journal of the American Water Resources Association, v. 40, no. 3, p. 827–834.

Chapelle, F.H., 1993, Ground-water microbiology and geochemistry: New York, John Wiley & Sons, Inc., 424 p.

Childress, C.J.O., Foreman, W.T., Connor, B.F., and Maloney, T.J., 1999, New reporting procedures based on long-term method detection levels and some considerations for interpretations of water-quality data provided by the U.S. Geological Survey National Water Quality Laboratory: U.S. Geological Survey Open-File Report 99–193, 19 p.

Coupe, R.H., 2000, Occurrence of pesticides in five rivers of the Mississippi Embayment study unit, 1996–98: U.S. Geological Survey Water-Resources Investigations Report 99–4159, 55 p.

Coupe, R.H., 2002, Nitrogen and phosphorus concentrations and fluxes of streams in the Mississippi Embayment study unit, 1996–1998: U.S. Geological Survey Water-Resources Investigations Report 01–4024, 65 p.

Criner, J.H., and Parks, W.S., 1976, Historic water-level changes and pumpage from the principal aquifers of the Memphis area, Tennessee: U.S. Geological Survey Water-Resources Investigations Report 76–67, 45 p.

DeSimone, L.A., and Howes, B.L., 1998, Nitrogen transport and transformations in a shallow aquifer receiving wastewater discharge: A mass balance approach: Water Resources Research, v. 34, no. 2, p. 271–285.

Edds, Joe, and Fitzpatrick, D.J., 1984, Maps showing altitude of the potentiometric surface and changes in water levels of the Sparta Sand and Memphis Sand aquifers in eastern Arkansas, spring 1983: U.S. Geological Survey Water-Resources Investigations Report 84–4265, 1 sheet.

Freeze, R.A., and Cherry, J.A., 1979, Groundwater: Englewood Cliffs, NJ, Prentice-Hall, 604 p.

Fuhrer, G.J., Gilliom, R.J., Hamilton, P.A., Morace, J.L., Nowell, L.H., Rinella, J.F., Stoner, J.D., and Wentz, D.A., 1999, The quality of our Nation's waters: Nutrients and pesticides: U.S. Geological Survey Circular 1225, 82 p.

Gilliom, R.J., Alley, W.M., and Gurtz, M.E., 1995, Design of the National Water-Quality Assessment Program—Occurrence and distribution of water-quality conditions: U.S. Geological Survey Circular 1112, 33 p.

Gilliom, R.J., Barbash, J.E., Crawford, C.G., Hamilton, P.A., Martin, J.D., Nakagaki, N., Nowell, L.H., Scott, J.C., Stackelberg, P.E., Thelin, G.P., and Wolock, D.M., 2006, Pesticides in the Nation's streams and ground water, 1992–2001: U.S. Geological Survey Circular 1291, 170 p.

Gonthier, G.J., 2000, Water quality in the deep tertiary aquifers of the Mississippi embayment, 1996: U.S. Geological Survey Water-Resources Investigations Report 99–4131, 91 p.

Gonthier, G.J., 2002, Quality of shallow ground water in recently developed residential and commercial areas, Memphis vicinity, Tennessee, 1997: U.S. Geological Survey Water-Resources Investigations Report 02–4294, 105 p.

Gonthier, G.J., 2003, Quality of ground water in Pleistocene and Holocene subunits of the Mississippi River Valley alluvial aquifer, 1998: U.S. Geological Survey Water-Resources Investigations Report 03–4202, 80 p.

Graham, D.D., and Parks, W.S., 1986, Potential for leakage among principal aquifers in the Memphis area, Tennessee: U.S. Geological Survey Water-Resources Investigations Report 85–4295, 46 p.

Halde, M.J., Delzer, G.C., and Zogorski, J.S., 1998, Study design and analytical results used to evaluate a surface-water point sampler for volatile organic compounds: U.S. Geological Survey Open-File Report 98–651, 31 p.

Hem, J.D., 1985, Study and interpretation of the chemical characteristics of natural water (3d ed.): U.S. Geological Survey Water-Supply Paper 2254, 264 p.

Hirsch, R.M., Alley, W.M., and Wilber, W.G., 1988, Concepts for a National Water-Quality Assessment Program: U.S. Geological Survey Circular 1021, 42 p.

Hosman, R.L., and Weiss, J.S., 1991, Geohydrologic units of the Mississippi embayment and Texas coastal uplands aquifer systems, south-central United States: U.S. Geological Survey Professional Paper 1416–B, 19 p.

Kamrin, M.A., 1997, Pesticide profiles: Toxicity, environmental impact, and fate: New York, CRC Lewis Publishers, p. 516.

Kiely, T., Donaldson, D., and Grube, A., 2004, Pesticides industry sales and usage—2000 and 2001 market estimates: U.S. Environmental Protection Agency, Office of Prevention, Pesticides, and Toxic Substances, EPA–733–R–04–001, 33 p.

Kingsbury, J.A., 1996, Altitude of the potentiometric surfaces, September 1995, and historical water-level changes in the Memphis and Fort Pillow aquifers in the Memphis area, Tennessee: U.S. Geological Survey Water-Resources Investigations Report 96–4278, 1 sheet.

Kleiss, B.A., Coupe, R.H., Gonthier, G.J., and Justus, B.G., 2000, Water quality in the Mississippi embayment, Mississippi, Louisiana, Arkansas, Missouri, Tennessee, and Kentucky, 1995–98: U.S. Geological Survey Circular 1208, 36 p.

Lapham, W.W,. and Tadayon, S., 1996, Plan for assessment of the occurrence, status, and distribution of volatile organic compounds in aquifers of the United States: U.S. Geological Survey Open-File Report 96–199, 44 p.

Lloyd, O.B., Jr., and Lyke, W.L., 1995, Ground water atlas of the United States: Segment 10, Illinois, Indiana, Kentucky, Ohio, Tennessee: U.S. Geological Survey Hydrologic Investigations Atlas 730–K, 30 p.

Lonsdale, J.T., Metz, M.S., and Halbouty, M.T., 1931, The petrographic characteristics of some Eocene sands from southwest Texas: Journal of Sedimentary Petrology, v. 1, no. 2, p. 73–81.

Majewski, M., 1997, National and study unit pesticide use: U.S. Geological Survey Pesticide National Synthesis Project accessed May 3, 1997, at http://water.wr.usgs.gov/pnsp/natsu/

Maupin, M.A., and Barber, N.L., 2005, Estimated withdrawals from principal aquifers in the United States, 2000: U.S. Geological Survey Circular 1279, 46 p.

McMahon, P.B., and Chapelle, F.H., 2008, Redox processes and water quality of selected principal aquifer systems: Ground Water, v. 46, no. 2, p. 259–271.

Michel, R.L., 1989, Tritium deposition in the continental United States, 1953–1983: U.S. Geological Survey Water-Resources Investigations Report 89–4072, 46 p.

Miller, D.W., 1980, Waste disposal effects on ground water—A comprehensive survey of the occurrence and control of ground-water contamination resulting from waste-disposal practices: Berkeley, CA, Premier Press, 512 p.

Miller, J.A., 1990, Ground water atlas of the United States: Segment 6, Alabama, Florida, Georgia, South Carolina: U.S. Geological Survey Hydrologic Investigations Atlas 730–G, 28 p.

Moran, M.J., Zogorski, J.S., and Rowe, B.L., 2006, Approach to an assessment of volatile organic compounds in the Nation's ground water and drinking-water supply wells: U.S. Geological Survey Open-File Report 2005–1452, 36 p.

Morris, E.E., and Bush, W.V., 1986, Extent and source of saltwater intrusion into the alluvial aquifer near Brinkley, Arkansas, 1984: U.S. Geological Survey Water-Resources Investigations Report 85–4322, 123 p.

Mueller, D.K., and Helsel, D.R., 1996, Nutrients in the Nation's waters—Too much of a good thing?: U.S. Geological Survey Circular 1136, 24 p.

Nakagaki, N., Price, C.P., Falcone, J.A., Hitt, K.J., and Ruddy, B.C., 2007, Enhanced national land cover data 1992 (NLCDe 92), edition 1.0, (digital map), accessed May 22, 2009, at http://water.usgs.gov/lookup/getspatial?nlcde92

Page, L.V., and May, H.G., 1964, Water resources of Bossier and Caddo Parishes, Louisiana: Louisiana Department of Public Works Water Resources Bulletin No. 5, 105 p.

Parks, W.S., 1990, Hydrogeology and preliminary assessment of the potential for contamination of the Memphis aquifer in the Memphis area, Tennessee: U.S. Geological Survey Water-Resources Investigations Report 90–4092, 39 p.

Parks, W.S., Mirecki, J.E., and Kingsbury, J.A., 1995, Hydrogeology, ground-water quality, and source of ground water causing water-quality changes in the Davis well field at Memphis, Tennessee: U.S. Geological Survey Water-Resources Investigations Report 94–4212, 58 p.

Payne, J.N., 1975, Geohydrologic significance of lithofacies of the Carrizo Sand of Arkansas, Louisiana, and Texas, and the Meridian Sand of Mississippi: U.S. Geological Survey Professional Paper 569–D, 10 p.

Pettijohn, R.A., 1996, Geochemistry of ground water in the Gulf Coast aquifer systems, South-Central United States: U.S. Geological Survey Water-Resources Investigations Report 96–4107, 158 p.

Rapp, T.R., 1996, Ground-water resources of Caddo Parish, Louisiana, 1992: Louisiana Department of Transportation and Development Water Resources Technical Report No. 58, 89 p.

Renken, R.A., 1998, Ground water atlas of the United States: Segment 5, Arkansas, Louisiana, Mississippi: U.S. Geological Survey Hydrologic Investigations Atlas 730–F, 28 p.

Reutter, D.C., and Dunn, D.D., 2000, Water-quality assessment of the Trinity River Basin, Texas—Ground-water quality of the Trinity, Carrizo-Wilcox, and Gulf Coast aquifers, February–August 1994: U.S. Geological Survey Water-Resources Investigations Report 99–4233, 56 p.

Ruddy, B.C., Lorenz, D.L., and Mueller, D.K., 2006, County-level estimates of nutrient inputs to the land surface of the conterminous United States, 1982–2001: U.S. Geological Survey Scientific Investigations Report 2006–5012, 17 p.

Ryder, P.D., 1996, Ground water atlas of the United States: Segment 4, Oklahoma, Texas: U.S. Geological Survey Hydrologic Investigations Atlas 730–E, 30 p.

Snider, J.L., 1982, Premining hydrology of the lignite area in southeastern De Soto Parish, Louisiana: Louisiana Department of Transportation and Development Water Resources Technical Report No. 29, 40 p.

Spruill, T.B., 1997, Geologic sources of phosphorus in the Neuse River and implications for management: Albemarle-Pamlico Estuarine Study Comprehensive Conservation and Management Plan Implementation Forum, June 5–6.

Strom, E.W., 1997, Hydrogeologic interpretations of natural gamma logs for 31 shallow wells in the Memphis, Tennessee, area: U.S. Geological Survey Water-Resources Investigations Report 97–4181, 43 p.

Stumm, W., and Morgan, J.J., 1996, Aquatic chemistry, chemical equilibria and rates in natural waters: New York, John Wiley & Sons, Inc., 1022 p.

Toccalino, P., Nowell, L., Wilber, W., Zogorski, J., Donohue, J., Eiden, C., Krietzman, S., and Post, G., 2003, Development of health-based screening levels for use in state- or local-scale water-quality assessments: U.S. Geological Survey Water-Resources Investigations Report 03–4054, 22 p.

Trapp, H., Jr., and Horn, M.A., 1997, Ground water atlas of the United States: Segment 11, Delaware, Maryland, New Jersey, North Carolina, Pennsylvania, Virginia, West Virginia: U.S. Geological Survey Hydrologic Atlas 730–L, 24 p.

U.S. Census Bureau, 2002, United States Census 2000, accessed January 31, 2006, at http://www.census.gov/

U.S. Department of Agriculture, 1995, State soil geographic (STATSGO) data base, data use information: Natural Resources Conservation Service, National Soil Survey Center Miscellaneous Publication Number 1492, 113 p.

U.S. Department of Agriculture, 2007, National engineering handbook, part 630, Hydrology, Chapter 7, Hydrologic soil groups: Natural Resources Conservation Service, 14 p.

U.S. Environmental Protection Agency, 2003, Clean Water Act Module—Watershed Academy: U.S. Environmental Protection Agency, accessed February 13, 2007, at http://www.epa.gov/watertrain/cwa/rightindex.htm

U.S. Environmental Protection Agency, 2004, 2004 edition of the drinking water standards and health advisories: U.S. Environmental Protection Agency, EPA 822–R–04–005, accessed September 13, 2005, at http://www.epa.gov/waterscience/criteria/drinking/standards/dwstandards.pdf

U.S. Environmental Protection Agency, 2006, Safe Drinking Water Act (SDWA): U.S. Environmental Protection Agency, accessed February 13, 2007, at http://www/epa.gov/safewater/sdwa/basicinformation.html

U.S. Environmental Protection Agency, 2007a, Mississippi River basin and Gulf of Mexico hypoxia: U.S. Environmental Protection Agency, accessed October 1, 2008, at http://www.epa.gov/msbasin/taskforce/gulf.htm

U.S. Environmental Protection Agency, 2007b, Proposed radon in drinking water rule, Ground water & drinking water: U.S. Environmental Protection Agency, accessed September 26, 2008, at http://www.epa.gov/safewater/radon/proposal.html

U.S. Geological Survey, 1999, Strategic directions for the U.S. Geological Survey ground-water resources program—A report to Congress, November 30, 1998: Reston, VA, U.S. Geological Survey Office of Ground Water, 14 p.

U.S. Geological Survey, 2003, Principal aquifers of the 48 conterminous United States, Hawaii, Puerto Rico, and the U.S. Virgin Islands, accessed August 19, 2008, at http://www-atlas.usgs.gov/metadata/aquifrp025.html

U.S. Geological Survey, 2008, Ground water GIS ancillary data calculated using national GIS data layers, accessed July 16, 2008, at http://water.usgs.gov/nawqa-only/gis/data/gw/gwdata_2008/metadata/nlcdebuf2008_meta.html

Vogelmann, J.E., Sohl, T., and Howard, S.M., 1998a, Regional characterization of land cover using multiple sources of data: Photogrammetric Engineering and Remote Sensing, v. 64, p. 45–57.

Vogelmann, J.E., Sohl, T., Howard, S.M., and Shaw, D.M., 1998b, Regional land cover characterization using Landsat thematic mapper data and ancillary data sources: Environmental Monitoring and Assessment, v. 51, p. 415–428.

Walter, D.A., Rea, B.A., Stollenwerk, K.G., and Savoie, J., 1996, Geochemical and hydrologic controls on phosphorus transport in a sewage-contaminated sand and gravel aquifer near Ashumet Pond, Cape Cod, Massachusetts: U.S. Geological Survey Water-Supply Paper 2463, 89 p.

Warwick, P.D., San Filipo, J.R., Crowley, S.S., Thomas, R.E., Freid, John, and Tulley, J.K., 1997, Map showing outcrop of the coal-bearing units and land use in the Gulf Coast region: U.S. Geological Survey Open-File Report 97–172.

Wetzel, R.G., 1983, Limnology: Philadelphia, PA, Sauders College Publishing, 767 p.

Wiedemeier, T.H., Swanson, M.A., Moutoux, D.E., Gordon, E.K., Wilson, J.T., Wilson, B.H., Kampbell, D.H., Haas, P.E., Miller, R.N., Hansen, J.E., and Chapelle, F.H., 1998, Technical protocol for evaluating natural attenuation of chlorinated solvents in ground water: Cincinnati, OH, U.S. Environmental Protection Agency, National Risk Management Research Laboratory, Office of Research and Development, EPA/600/R–98/128, 244 p.

Zogorski, J.S., Carter, J.M., Ivahnenko, T.I., Lapham, W.W., Moran, M.J., Rowe, B.L., Squillace, P.J., and Toccalino, P.L., 2006, Volatile organic compounds in the Nation’s ground water and drinking-water supply wells: U.S. Geological Survey Circular 1292, 101 p.

Appendix 1. Detection frequencies of volatile organic compounds, 1994–2004, in the Mississippi embayment-Texas coastal uplands aquifer system and Mississippi River Valley alluvial aquifer with and without the 0.2 microgram per liter assessment level.

[µg/L, micrograms per liter; MCL, maximum contaminant level; —, none; N/A, not applicable; HBSL, health based screening level]

Name	Detection frequency for concentrations greater than or equal to 0.2 µg/L (percent)	Number of analyses	Maximum concentration (µg/L)	Benchmark level (µg/L)	Benchmark type[a]	Detection frequency with no assessment level (percent)
Shallow wells						
Chloroform	2.7	113	2.06	80[b]	MCL	15.9
Tetrahydrofuran	4.0	100	3.58	—	N/A	34.0
Tetrachloroethene (PCE)	0.9	113	0.44	5	MCL	7.0
Toluene[c]	1.8	113	0.28	1,000	MCL	7.0
Acetone	1.0	100	0.60	6,000	HBSL	1.0
Methyl tert-butyl ether (MTBE)	2.7	113	6.40	—	N/A	3.5
Trichloroethene (TCE)	0.0	113	0.05	5	MCL	1.8
1,1,1-Trichloroethane	0.0	113	0.03	200	MCL	1.8
1,2,4-Trimethylbenzene[d]	0.9	113	0.25	—	N/A	10.6
cis-1,2-Dichloroethene	0.9	113	0.57	—	N/A	2.7
Carbon disulfide	0.0	100	0.18	700	HBSL	16.0
Dichlorodifluoromethane (CFC-12)	4.4	113	1.18	1,000	HBSL	6.2
Bromodichloromethane	0.0	113	0.17	80[b]	MCL	1.8
1,1-Dichloroethane	0.9	113	0.20	—	N/A	5.3
Dichloromethane	0.0	113	0.15	0	MCL	0.9
Benzene	0.9	113	0.36	5	MCL	7.1
Trichlorofluoromethane (CFC-11)	1.8	113	0.30	2,000	HBSL	1.8
Diisopropyl ether (DIPE)	2.0	100	22.0	—	N/A	5.0
1,1-Dichloroethene	0.0	113	0.07	7	MCL	2.7
1,3,5-Trimethylbenzene	0.0	113	0.01	—	N/A	5.3
Chlorobenzene	0.0	113	0.003	100	MCL	0.9
Ethylbenzene	0.0	113	0.01	700	MCL	0.9
1,2,3-Trimethylbenzene	0.0	100	0.01	—	N/A	3.0
2-Ethyltoluene	0.9	100	0.38	—	N/A	1.0
m- + p-Xylene	0.0	100	0.05	—	N/A	12.0
o-Xylene	0.0	100	0.01	—	N/A	2.0
Styrene	0.0	100	0.02	100	MCL	1.0
1,2-Dichloroethane	0.9	113	2.68	5	MCL	0.9
Chloroethane	0.0	113	0.02	—	N/A	0.9
Chloromethane	0.0	113	0.06	—	N/A	5.3
Diethyl ether	0.9	100	1.11	—	N/A	0.9
Methyl tert-pentyl ether	0.9	100	0.79	—	N/A	1.0
trans-1,2-Dichloroethene	0.0	113	0.01	100	MCL	0.9

Appendix 1. Detection frequencies of volatile organic compounds, 1994–2004, in the Mississippi embayment-Texas coastal uplands aquifer system and Mississippi River Valley alluvial aquifer with and without the 0.2 microgram per liter assessment level.—Continued

[µg/L, micrograms per liter; MCL, maximum contaminant level; —, none; N/A, not applicable; HBSL, health based screening level]

Name	Detection frequency for concentrations greater than or equal to 0.2 µg/L (percent)	Number of analyses	Maximum concentration (µg/L)	Benchmark level (µg/L)	Benchmark type[a]	Detection frequency with no assessment level (percent)
Drinking-water wells						
Methyl ethyl ketone	15.3	46	1.30	—	N/A	15.3
Chloroform	3.7	54	0.72	80[b]	MCL	18.5
m- + p-Xylene	2.2	46	0.43	—	N/A	4.3
Isobutyl methyl ketone	2.2	46	0.20	—	N/A	2.2
Tetrahydrofuran	2.2	46	10.11	—	N/A	2.2
1,2,4-Trimethylbenzene[d]	0.0	54	0.12	—	N/A	13.0
Acetone	0.0	46	0.30	6,000	HBSL	2.2
Bromodichloromethane	0.0	54	0.02	80[b]	MCL	1.9
Carbon disulfide	0.0	46	0.18	700	HBSL	28.3
Chloromethane	0.0	54	0.10	—	N/A	3.7
Diisopropyl ether (DIPE)	0.0	46	0.10	—	N/A	2.2
Ethylbenzene	0.0	54	0.16	700	MCL	1.9
o-Xylene	0.0	46	0.16	—	N/A	2.2
Tetrachloroethene (PCE)	0.0	54	0.18	5	MCL	3.7
Trichloroethene (TCE)	0.0	54	0.05	5	MCL	1.9

[a] U.S. Environmental Protection Agency, 2004; Toccalino and others, 2003.

[b] Maximum contaminant level of 80 µg/L for total trihalomethanes used for comparison.

[c] Included concentrations greater than or equal to 0.03 µg/L.

[d] Included concentrations greater than or equal to 0.05 µg/L.

Appendix 2. Water-quality standards and human-health benchmarks for selected constituents analyzed for in the Mississippi embayment-Texas coastal uplands aquifer system and Mississippi River Valley alluvial aquifer, 1994–2004.

[MCL, maximum contaminant level; SMCL, secondary maximum contaminant level; HA, health advisory; HBSL, health-based screening level; —, not available; mg/L, milligrams per liter; µS/cm, microsiemen per centimeter; °C, degree Celsius; µg/L, microgram per liter; pCi/L, picocurie per liter; AMCL, alternative maximum contaminant level. Compounds in italics were compared to U.S. Geological Survey health-based screening levels (Toccalino and others, 2003). All other compounds were compared to U.S. Environmental Protection Agency drinking-water standards (U.S. Environmental Protection Agency, 2004) as a frame of reference]

Property or constituent	MCL	SMCL	HA	HBSL
Physical properties				
pH, field, in standard units	—	6.5 – 8.5	—	—
Dissolved solids and major inorganic ions, in mg/L				
Dissolved solids, residue on evaporation, 180 °C	—	500	—	—
Sodium, as Na	—	30 – 60 (taste)	—	—
Chloride, as Cl	—	250	—	—
Fluoride, as Fl	4	2	—	—
Sulfate, as SO_4	—	250	—	—
Trace elements, in µg/L				
Aluminum, as Al	—	50–200	—	—
Antimony, as Sb	6	—	—	—
Arsenic, as As	10	—	—	—
Barium, as Ba	2,000	—	—	—
Beryllium, as Be	4	—	—	—
Cadmium, as Cd	5	—	—	—
Chromium, as Cr	100 (total)	—	—	10,000
Copper, as Cu	1,300 (action level)	1,000	—	—
Iron, as Fe		300	—	—
Lead, as Pb	15 (action level)	—	—	—
Manganese, as Mn	—	50	300	300
Molybdenum, as Mo	—	—	40	40
Nickel, as Ni	—	—	100	100
Selenium, as Se	50	—	—	—
Uranium, as Ur	30	—	20	
Zinc, as Zn	—	5,000	2,000	2,000
Radon, in pCi/L				
Radon[a]	300 (AMCL 4,000 pCi/L)	—	—	—
Nutrients, in mg/L				
Ammonia, as N	—	—	30	—
Nitrite plus nitrate, as N	10	—	—	—
Nitrite, as N	1	—	—	—

Appendix 2. Water-quality standards and human-health benchmarks for selected constituents analyzed for in the Mississippi embayment-Texas coastal uplands aquifer system and Mississippi River Valley alluvial aquifer, 1994–2004.—Continued

[MCL, maximum contaminant level; SMCL, secondary maximum contaminant level; HA, health advisory; HBSL, health-based screening level; —, not available; mg/L, milligrams per liter; µS/cm, microsiemen per centimeter; °C, degree Celsius; µg/L, microgram per liter; pCi/L, picocurie per liter; AMCL, alternative maximum contaminant level. Compounds in italics were compared to U.S. Geological Survey health-based screening levels (Toccalino and others, 2003). All other compounds were compared to U.S. Environmental Protection Agency drinking-water standards (U.S. Environmental Protection Agency, 2004) as a frame of reference]

Property or constituent	MCL	SMCL	HA	HBSL
Pesticides, in µg/L				
Herbicides				
2,4-D	70	—	—	
Acetochlor	—	—		1–100
Alachlor	2.0	—	10	—
Atrazine	3.0	—	—	—
Bentazon	—	—	200	200
Bromacil	—	—	70	70
DCPA	—	—	70	70
Dicamba	—	—	4,000	3,000
Diuron	—	—	200	2–200
EPTC	—	—	—	200
Fluometuron	—	—	500	4
Metolachlor	—	—	700	70
Metribuzin	—	—	70	90
Molinate	—	—	—	0.7
Pendimethalin	—	—	—	70
Picloram	500	—	—	—
Prometon	—	—	100	100
Propanil	—	—	—	6
Simazine	4	—	—	—
Tebuthiuron	—	—	500	1,000
Thiobencarb	—	—	—	70
Trifluralin	—	—	10	20
Insecticides				
Carbofuran	40	—	—	—
Diazinon	—	—	1	1
Dieldrin	—	—	0.2	0.002–0.2
Oxamyl	200	—	—	—

Appendix 2. Water-quality standards and human-health benchmarks for selected constituents analyzed for in the Mississippi embayment-Texas coastal uplands aquifer system and Mississippi River Valley alluvial aquifer, 1994–2004.—Continued

[MCL, maximum contaminant level; SMCL, secondary maximum contaminant level; HA, health advisory; HBSL, health-based screening level; —, not available; mg/L, milligrams per liter; µS/cm, microsiemen per centimeter; °C, degree Celsius; µg/L, microgram per liter; pCi/L, picocurie per liter; AMCL, alternative maximum contaminant level. Compounds in italics were compared to U.S. Geological Survey health-based screening levels (Toccalino and others, 2003). All other compounds were compared to U.S. Environmental Protection Agency drinking-water standards (U.S. Environmental Protection Agency, 2004) as a frame of reference]

Property or constituent	MCL	SMCL	HA	HBSL
Volatile organic compounds, in µg/L				
1,1,1-Trichloroethane	200	—	—	—
1,2-Dichloroethane	5	—	—	—
Acetone	—	—	—	6,000
Benzene	5	—	—	—
Bromodichloromethane	80	—	—	—
Carbon disulfide	—	—	—	700
Chloromethane (Methyl chloride)	—	—	30	30
Dichlorodifluoromethane	—	—	1000	1,000
Dichloromethane (Methylene chloride)	5	—	—	—
Methyl ethyl ketone (2-Butanone)	—	—	4,000	4,000
Ethylbenzene	700	—	—	—
Methyl tert-butyl ether (MTBE)	—	20 (odor) 40 (taste)	—	—
Styrene	100	—	—	—
Tetrachloroethene (PCE)	5	—	—	—
Toluene	1,000	—	—	—
trans-1,2-Dichloroethylene	100	—	—	—
Trichloroethene (TCE)	5	—	—	—
Trichlorofluoromethane	—	—	2,000	2,000
Trichloromethane (Chloroform)	80	—	—	—

[a] The U.S. Environmental Protection Agency has a proposed MCL for radon in ground water of 300 pCi/L for States without a multimedia mitigation program and an alternate maximum contaminant level of 4,000 pCi/L for States with a multimedia mitigation program.

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Welch and others—**Quality of Shallow Groundwater and Drinking Water in Aquifers, South-Central United States, 1994–2004**—Scientific Investigations Report 2009–5091