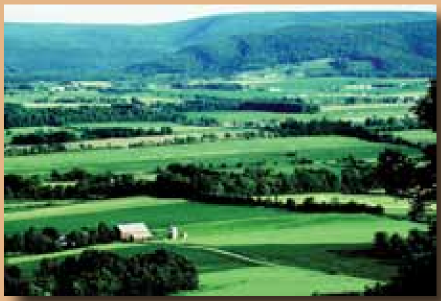
NATIONAL WATER QUALITY ASSESSMENT PROGRAM

Factors Affecting Water Quality in Selected Carbonate Aquifers in the United States, 1993–2005




Scientific Investigations Report 2008–5240

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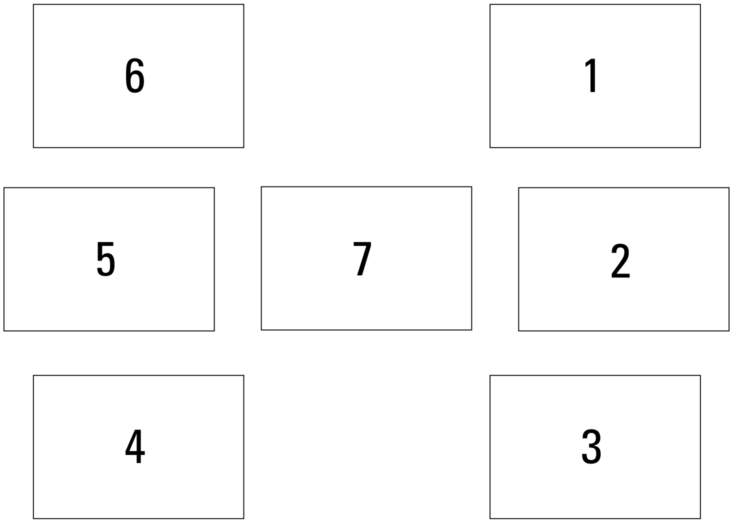

Cover.

1. Penns Creek Valley in Centre County, Pa., in the Valley and Ridge carbonate aquifer (Photograph by Albert E. Becher, U.S. Geological Survey)

2. Yates Spring in Decatur County, Ga., in the Floridan aquifer (Photograph by Alan M. Cressler, U.S. Geological Survey)

3. Housing development in southwestern Florida, near Tampa, Fla., in the Floridan aquifer (Photograph by Harley Means, Florida Geological Survey)

4. Range land in Uvalde County, Tex., in the Edwards-Trinity aquifer (Photograph by George Ozuma)

5. Shoshone springs in Great Basin National Park, Nev., in the Basin and Range carbonate aquifer (Photograph by Philip Gardner, U.S. Geological Survey)

6. Malone Spring near Niota, Tenn., in the Valley and Ridge carbonate aquifer (Photograph by Gregory C. Johnson, U.S. Geological Survey)

7. A sinkhole in Cumberland County, Pa., in the Valley and Ridge carbonate aquifer (Photograph by William E. Kochanov, Pennsylvania Geological Survey)

Factors Affecting Water Quality in Selected Carbonate Aquifers in the United States, 1993–2005

By Bruce D. Lindsey, Marian P. Berndt, Brian G. Katz, Ann F. Ardis, and
Kenneth A. Skach

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U.S. Department of the Interior
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Conversion Factors, Abbreviations, and Datums

Multiply	By	To obtain
	Length	
inch (in.)	2.54	centimeter (cm)
inch (in.)	25.4	millimeter (mm)
foot (ft)	0.3048	meter (m)
mile (mi)	1.609	kilometer (km)
	Area	
square mile (mi^2)	259.0	hectare (ha)
square mile (mi^2)	2.590	square kilometer (km^2)
	Flow rate	
cubic foot per second (ft^3/s)	0.02832	cubic meter per second (m^3/s)
million gallons per day (Mgal/d)	0.04381	cubic meter per second (m^3/s)
inch per year (in/yr)	25.4	millimeter per year (mm/yr)
	Radioactivity	
picocurie per liter (pCi/L)	0.037	becquerel per liter (Bq/L)
	Transmissivity*	
foot squared per day (ft^2/d)	0.09290	meter squared per day (m^2/d)

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

$$°F=(1.8\times°C)+32$$

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

$$°C=(°F-32)/1.8$$

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

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

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

*Transmissivity: The standard unit for transmissivity is cubic foot per day per square foot times foot of aquifer thickness $[(ft^3/d)/ft^2]ft$. In this report, the mathematically reduced form, foot squared per day (ft^2/d), is used for convenience.

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).

FOREWORD

The U.S. Geological Survey (USGS) is committed to providing the Nation with credible 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, now 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 condition 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 1991-2001, 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*).

Multiple national and regional assessments are ongoing in the second decade (2001–2012) of the NAWQA Program as 42 of the 51 Study Units are reassessed. These assessments extend the findings in the Study Units by determining status and trends at sites that have been consistently monitored for more than a decade, and filling critical gaps in characterizing the quality of surface water and ground water. For example, increased emphasis has been placed on assessing the quality of source water and finished water associated with many of the Nation's largest community water systems. During the second decade, NAWQA is addressing five national priority topics that build an understanding of how natural features and human activities affect water quality, and establish links between *sources* of contaminants, the *transport* of those contaminants through the hydrologic system, and the potential *effects* of contaminants on humans and aquatic ecosystems. Included are topics on the fate of agricultural chemicals, effects of urbanization on stream ecosystems, bioaccumulation of mercury in stream ecosystems, effects of nutrient enrichment on aquatic ecosystems, and transport of contaminants to public-supply wells. These topical studies are conducted in those Study Units most affected by these issues; they comprise a set of multi-Study-Unit designs for systematic national assessment. In addition, national syntheses of information on pesticides, volatile organic compounds (VOCs), nutrients, selected trace elements, and aquatic ecology are continuing.

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

Factors Affecting Water Quality in Selected Carbonate Aquifers in the United States, 1993–2005

By Bruce D. Lindsey, Marian P. Berndt, Brian G. Katz, Ann F. Ardis, and Kenneth A. Skach

Abstract

Carbonate aquifers are an important source of water in the United States; however, these aquifers can be particularly susceptible to contamination from the land surface. The U.S. Geological Survey National Water-Quality Assessment (NAWQA) Program collected samples from wells and springs in 12 carbonate aquifers across the country during 1993–2005; water-quality results for 1,042 samples were available to assess the factors affecting ground-water quality. These aquifers represent a wide range of climate, land-use types, degrees of confinement, and other characteristics that were compared and evaluated to assess the effect of those factors on water quality. Differences and similarities among the aquifers were also identified. Samples were analyzed for major ions, radon, nutrients, 47 pesticides, and 54 volatile organic compounds (VOCs).

Geochemical analysis helped to identify dominant processes that may contribute to the differences in aquifer susceptibility to anthropogenic contamination. Differences in concentrations of dissolved oxygen and dissolved organic carbon and in ground-water age were directly related to the occurrence of anthropogenic contaminants. Other geochemical indicators, such as mineral saturation indexes and calcium-magnesium molar ratio, were used to infer residence time, an indirect indicator of potential for anthropogenic contamination. Radon exceeded the U.S. Environmental Protection Agency proposed Maximum Contaminant Level (MCL) of 300 picocuries per liter in 423 of 735 wells sampled, of which 309 were drinking-water wells.

In general, land use, oxidation-reduction (redox) status, and degree of aquifer confinement were the most important factors affecting the occurrence of anthropogenic contaminants. Although none of these factors individually accounts for all the variation in water quality among the aquifers, a combination of these characteristics accounts for the majority of the variation. Unconfined carbonate aquifers that had high percentages of urban or agricultural land, or a combination of both, had higher concentrations and higher frequency of detections for most of the anthropogenic contaminants than areas with other combinations of land use and degree of aquifer confinement. Redox status is an indicator of more recently recharged water and affects the fate of some contaminants.

Median concentrations of nitrate were highest in the Valley and Ridge and Piedmont aquifers and lowest in the Biscayne, Castle Hayne, and Silurian-Devonian/Upper carbonate aquifers. Nitrate concentrations were significantly higher in unconfined aquifers than in confined aquifers and semiconfined/mixed confined aquifers (wells in aquifers with breached confining layers or wells open to both a confined and an unconfined aquifer). Water recharged after 1953 had significantly higher concentrations of nitrate than water recharged prior to 1953. Redox status was also a key factor affecting nitrate concentrations; in recently recharged waters, samples in oxic waters had significantly higher concentrations of nitrate than anoxic waters, regardless of land use in the area around the well. Samples from 54 wells (5 percent) exceeded the U.S. Environmental Protection Agency MCL of 10 mg/L for nitrate in drinking water. Most of the samples exceeding the drinking-water standard (52 samples, or 5 percent) were in domestic supply wells in agricultural areas. The Piedmont and Valley and Ridge aquifers had the largest number of samples (45) exceeding the MCL; in the remaining aquifers only 9 samples had concentrations of nitrate that exceeded the MCL (about 1 percent). None of the water recharged prior to 1953 and only a single sample from a confined aquifer had nitrate concentrations that exceeded 10 mg/L as N.

Wells were sampled for a minimum of 47 pesticides. Detection frequencies and comparisons varied depending on the assessment level used. At least 1 of the 47 pesticides was detected at 509 (50 percent) of the 1,027 sites where pesticide data were available using the ‘all detections’ assessment level—that is, including any quantified detection as well as any estimated values where the compound was definitively detected. Multiple pesticides were frequently detected in a sample of water from a site; 39 percent of the samples had two or more pesticides detected in the same sample, and 4 percent of the samples had six or more pesticides detected. Dieldrin was detected at 20 sites, 9 of which were from either domestic or public supply wells, at a concentration above the Health-Based Screening Level (HBSL) of 0.002 µg/L. Diazinon was detected at a concentration greater than the HBSL of 1 µg/L at a single site, which was also a domestic supply well. These are the only samples where a pesticide exceeded a human-health benchmark.

The most frequently occurring pesticide compounds were four herbicides—atrazine, simazine, metolachlor, and prometon—and deethylatrazine, a degradate of atrazine. These pesticides typically were detected at concentrations that were less than 10 percent of a human-health benchmark. Of the four frequently occurring pesticides, only samples for atrazine (4 percent) and simazine (0.1 percent) had concentrations that exceeded 10 percent of the human-health benchmark; most of these cases were in agricultural areas. It is important to note, however, that the most frequently occurring pesticide degradate compound—deethylatrazine—has no human-health benchmark. Using a common assessment level of 0.01 µg/L, four of the aquifers—Biscayne, Mississippian, Piedmont, and Valley and Ridge—had at least one of these five compounds detected in more than 30 percent of the wells sampled. These four aquifers, along with the Ordovician, Ozark Plateaus, and Prairie du Chien aquifers were the aquifers or aquifer systems that had concentrations of pesticides that exceeded 10 percent of a human-health benchmark. Water recharged after 1953 had a significantly higher percentage of detections of pesticides than water recharged before 1953, and water from unconfined aquifers had a significantly higher percentage of detections of pesticides than water from confined or semiconfined/mixed confined aquifers. Water from sites in unconfined aquifers, where land use was agricultural or urban, accounted for the vast majority of detections of pesticides. Dissolved oxygen concentration was positively related to pesticide occurrence, which likely reflects the positive association between dissolved oxygen concentration and recently recharged water.

Water samples were collected for analysis of VOCs at 793 sites—154 samples were analyzed for 54 VOCs from 1993 through 1995 and 639 samples were analyzed for 86 VOCs from 1996 through 2005. Twenty percent of samples contained one or more VOCs at concentrations greater than or equal to 0.2 µg/L (159 of 793 samples). The aquifers with the highest percentage of samples containing one or more VOCs were the Castle Hayne (about 41 percent of samples) and Biscayne aquifers (34 percent). The most frequently detected VOCs were chloroform, tetrahydrofuran, tetrachloroethene (PCE), toluene, acetone, ethylmethylketone, methyl tert-butyl ether (MTBE), and trichloroethene (TCE). Low-level concentrations of VOCs occurred in a much larger percentage of a subset of the data (the 639 samples analyzed using a low-level analytical method). In these samples, 69 percent of the 639 samples contained 1 or more VOCs, indicating the vulnerability of the carbonate aquifers to low-level VOC contamination. Four VOCs were detected at concentrations exceeding their respective MCLs in five samples, all of which were from drinking-water wells. Vinyl chloride concentrations exceeded the MCL of 2 µg/L in two samples from urban areas in the unconfined Biscayne aquifer. PCE, TCE, and 1,2-dichloropropane each had one sample with a concentration greater than their MCLs of 5 µg/L; these samples were from agricultural and urban areas in the unconfined Mississippian aquifer.

Water quality in the 12 carbonate aquifers was highly variable. Most of the samples met drinking-water standards. The occurrence of anthropogenic contaminants was related to contaminant sources but also was affected by degree of aquifer confinement, ground-water age, and redox status. Areas with higher amounts of agricultural or urban land in unconfined aquifers were the most likely to have elevated concentrations of anthropogenic contaminants.

Introduction

Carbonate aquifers and aquifer systems are an important global water resource, providing 25 percent of drinking-water supplies to the global population (Quinlan and Ewers, 1989), and in the contiguous United States, carbonate rocks cover 17 percent of the land surface (fig. 1) (Davies and others, 1984). Carbonate aquifers provide 22 percent of the United States public ground-water supply (fig. 2) (Maupin and Barber, 2005). The U.S. Geological Survey (USGS) has delineated the extent and composition of principal aquifers of the United States (U.S. Geological Survey, 2003), and 17 of these are designated as carbonate or sandstone and carbonate aquifers or aquifer systems (two or more related aquifers). The USGS National Water-Quality Assessment (NAWQA) Program has collected water-quality samples in many of these carbonate aquifers, and this report presents an analysis of the results of that sampling. These carbonate aquifers sampled as a part of the NAWQA Program have consistent and comparable data available on hydrogeology and geochemistry, and these data provide transferable scientific knowledge that could be applied to other carbonate aquifer systems. Carbonate aquifers considered in this study are not inclusive of all carbonate aquifers in the United States but rather represent a selection of aquifers studied by the NAWQA Program, which consequently allows for comparative study.

Carbonate aquifers commonly are referred to as karst aquifers. Karst is a term for the unique landscape that forms from the dissolution of carbonate rocks and other soluble rocks such as gypsum, which are more soluble than other types of geologic media. A karst aquifer is defined as an aquifer in which the flow of water is or can be appreciable through one or more of the following: joints, faults, bedding-plane partings, and cavities—any or all of which have been enlarged by dissolution (Field, 2002). Although karst aquifers can be in other bedrock types, most karst aquifers in the United States are in carbonate bedrock (White, 1993; Weary, 2006). Conversely, according to Quinlan and others (1991), “If there is carbonate rock, there is almost certainly some type of karst.” So, for purposes of this report, the carbonate aquifers can be considered karst aquifers as well, although they may have varying degrees of development of karst features.

Most of the permeability and hence transmissivity of the carbonate strata is formed when slightly acidic meteoric water dissolves and enlarges solution openings in the rock. White

(1993) describes the three levels of permeability types that can be found in karst aquifers, ranging from pores and vugs, to solutionally enlarged joints, fractures, and bedding-plane partings, to an integrated system of conduits of various sizes. Karst terranes are also characterized by features such as sinkholes, caves, springs, sinking streams, and underground drainage systems. The hydrologic properties of carbonate aquifers are highly variable, most notably in their heterogeneous permeability (Brahana and others, 1988). These aquifers are characterized by large fluctuations in water recharge and water supply, and respond rapidly to meteorological and hydrologic events.

Because of the features of karst aquifers, every component of the aquifer can differ from a traditional porous medium: recharge can be focused through sinkholes or losing streams; transport can be non-Darcian (turbulent) in solution-enlarged conduits, with directions of flow dictated by geologic structure rather than gradient; and discharge can be focused at large springs. Furthermore, the porosity and permeability of the rock mass is continually evolving as a result of the chemical interactions between the rock and water moving through it. Most of these features that differ from a traditional porous medium increase the susceptibility of the carbonate aquifer to contamination. Water can enter the carbonate aquifers rapidly through sinkholes and travel rapidly through cracks, fissures, and conduits, hence making the system extremely susceptible to contamination. A better understanding of karst water resources requires an understanding of the unique features of carbonate aquifers and the differences and similarities between different carbonate aquifers.

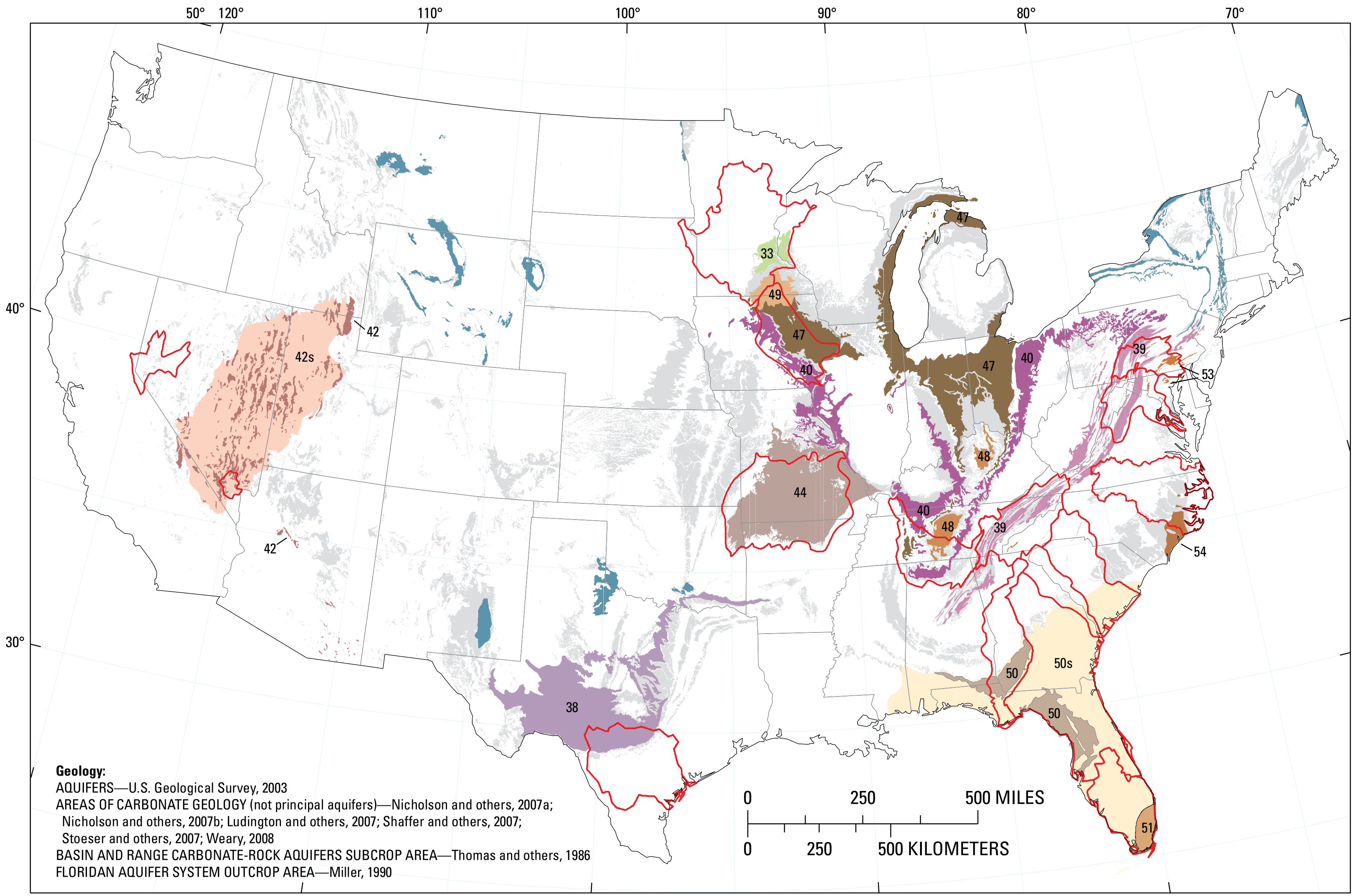
Purpose and Scope

This report describes the factors affecting water quality in 12 selected carbonate aquifers in the United States. The carbonate aquifers detailed in this report were sampled as part of the NAWQA Program, implemented in 1991 to assess the condition of the nation's streams and ground water. The carbonate aquifers sampled are (in alphabetical order): Basin and Range carbonate-rock aquifers, Biscayne aquifer, Castle Hayne aquifer, Edwards-Trinity aquifer system, Floridan aquifer system, Mississippian aquifers, Ordovician aquifers, Ozark Plateaus aquifer system, Piedmont and Blue Ridge carbonate-rock aquifers, Prairie du Chien aquifer of the Cambrian-Ordovician aquifer system, Silurian-Devonian aquifers and Upper carbonate aquifer (combined), and Valley and Ridge carbonate-rock aquifers. Analytical results from ground-water samples from 865 wells and 177 springs from 14 NAWQA study units form the basis of this study. Samples were collected from 1993 to 2005. Properties and constituents analyzed include physical properties, major ions, nutrients, radon, 47 pesticides, and 54 volatile organic compounds (VOCs).

Description of Study Area

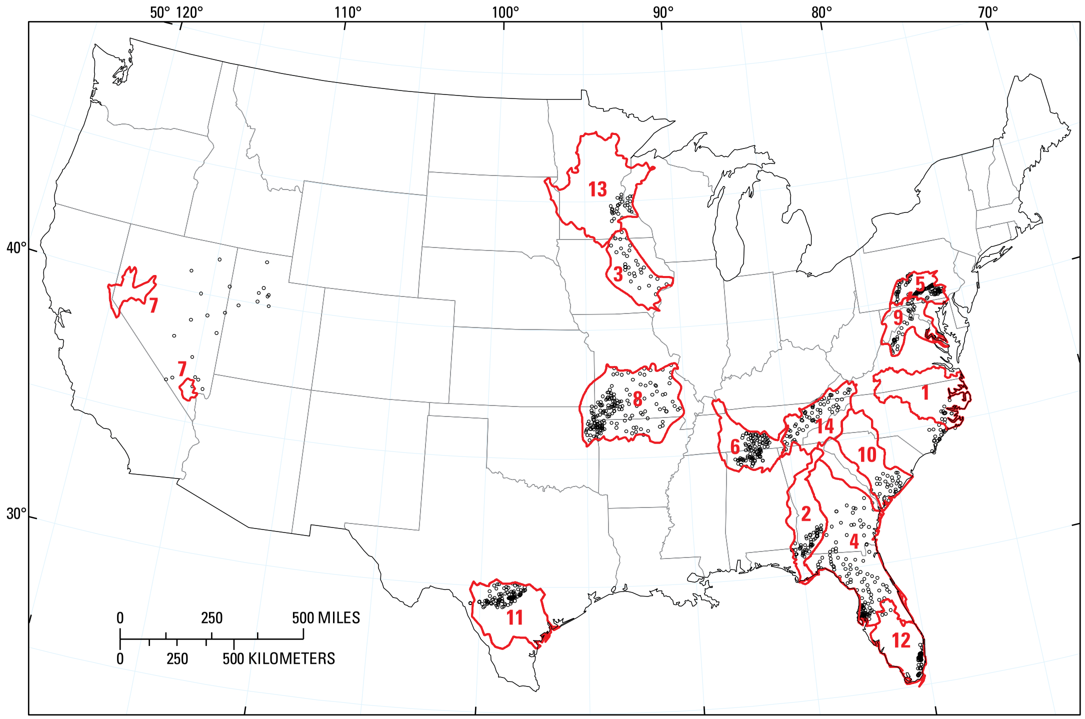
The areas selected for this study included all aquifers in the United States designated on the USGS principal aquifer map (U.S. Geological Survey, 2003) as carbonate-rock or sandstone and carbonate-rock aquifers where the USGS NAWQA Program collected data (fig. 1). In principal aquifers designated as sandstone and carbonate, only that part of the aquifer that was carbonate was included in the study. The Cambrian-Ordovician aquifer is designated as a sandstone aquifer (U.S. Geological Survey, 2003); however, the Prairie du Chien aquifer is a part of the Cambrian-Ordovician aquifer that has carbonate lithology, so that aquifer was included in the study as well. The Silurian-Devonian and Upper carbonate aquifers are each principal aquifers; however, they were sampled as a single unit and are referred to as a single entity in this study. The study included data from all but 5 of the 17 principal aquifers in the conterminous United States designated as carbonate or sandstone and carbonate. The Silurian-Devonian and Mississippian aquifers are included in the study but have large areas without samples and are underrepresented with respect to the aquifer size (fig. 1). The sampling in the Edwards-Trinity aquifer system is concentrated in the southeastern part of the aquifer (fig. 1) where the majority of the water is used. Although a fairly substantial amount of the land area of the United States underlain by carbonate bedrock was not included in the study, only a relatively small amount of the areas designated as principal aquifers was not included in this study (fig. 1). This suggests that much of the land area of the United States that is underlain by carbonate bedrock and that is used as a substantial source of water was included in this study. Water-use data (fig. 2, table 1) indicate the importance of these aquifers as sources of drinking-water supply.

Carbonate aquifers are more extensive in the eastern United States, although the NAWQA Program also sampled water from carbonate aquifers in Texas, Nevada, and western Utah. The NAWQA study units that sampled carbonate aquifers included the Albemarle-Pamlico Drainages, Apalachicola-Chattahoochee-Flint River Basins, Eastern Iowa Basins, Georgia-Florida Coastal Plain Drainages, Lower Susquehanna River Basin, Lower Tennessee River Basin, Nevada Basin and Range, Ozark Plateaus, Potomac River Basin, Santee River Basin and Coastal Drainages, South-Central Texas, Southern Florida Drainages, Upper Mississippi River Basin, and Upper Tennessee River Basin (fig. 1). The geographic distribution of these study units not only includes many of the carbonate aquifers, it also provides for a substantial amount of variability in precipitation, recharge, population density, and land use that allows comparisons of the effect of these characteristics on water quality.



Geology:
AQUIFERS—U.S. Geological Survey, 2003
AREAS OF CARBONATE GEOLOGY (not principal aquifers)—Nicholson and others, 2007a; Nicholson and others, 2007b; Ludington and others, 2007; Shaffer and others, 2007; Stoeser and others, 2007; Weary, 2008
BASIN AND RANGE CARBONATE-ROCK AQUIFERS SUBCROP AREA—Thomas and others, 1986
FLORIDAN AQUIFER SYSTEM OUTCROP AREA—Miller, 1990

Figure 1. Locations of 12 selected carbonate aquifers or aquifer systems, other carbonate principal aquifers, areas of carbonate geology that are not principal aquifers, sampling sites, and National Water-Quality Assessment (NAWQA) Program study units included in this study.



Base from U.S. Geological Survey digital data, 2003, 1:2,000,000
Albers Equal-Area Conic projection
Standard parallels 25°00'N and 50°00'N, central meridian 96°00'W

EXPLANATION

PRINCIPAL AQUIFERS WITH SAMPLES IN STUDY

Carbonate-rock Aquifers

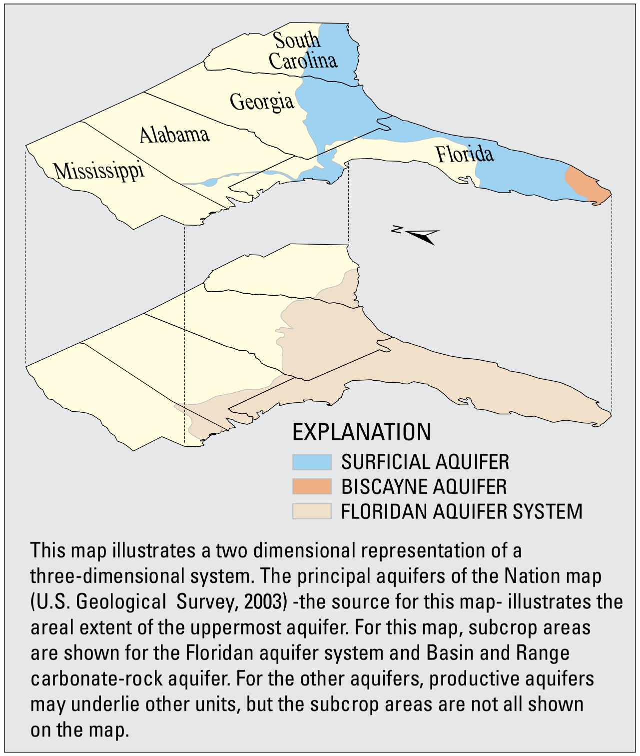
42 Basin and Range carbonate-rock aquifers
42s Basin and Range carbonate-rock aquifers - Subcrop area
51 Biscayne aquifer
54 Castle Hayne aquifer
50 Floridan aquifer system
50s Floridan aquifer system - Subcrop area
48 Ordovician aquifers
44 Ozark Plateaus aquifer system
53 Piedmont and Blue Ridge carbonate-rock aquifers
47 Silurian-Devonian aquifers
49 Upper carbonate aquifer

Sandstone and Carbonate-rock Aquifers

38 Edwards-Trinity aquifer system
40 Mississippian aquifers
39 Valley and Ridge aquifers -- Carbonate-rock aquifer
33 Cambrian-Ordovician aquifer system - Prairie du Chien

▬ CARBONATE OR SANDSTONE AND CARBONATE PRINCIPAL AQUIFER NOT INCLUDED IN STUDY
▭ AREAS OF CARBONATE GEOLOGY THAT ARE NOT PRINCIPAL AQUIFERS
— NAWQA STUDY UNIT BOUNDARY
◦ SAMPLING LOCATION

NAWQA Study Unit Boundaries	Number on map
Albemarle-Pamlico Drainages	1
Apalachicola Chattahoochee Flint River Basins	2
Eastern Iowa Basins	3
Georgia-Florida Coastal Plains Drainages	4
Lower Susquehanna River Basin	5
Lower Tennessee River Basin	6
Nevada Basin and Range	7
Ozark Plateaus	8
Potomac River Basin	9
Santee River Basin and Coastal Drainages	10
South-Central Texas	11
Southern Florida Drainages	12
Upper Mississippi River Basin	13
Upper Tennessee River Basin	14



EXPLANATION
🟦 SURFICIAL AQUIFER
🟧 BISCAYNE AQUIFER
▨ FLORIDAN AQUIFER SYSTEM

This map illustrates a two dimensional representation of a three-dimensional system. The principal aquifers of the Nation map (U.S. Geological Survey, 2003) -the source for this map- illustrates the areal extent of the uppermost aquifer. For this map, subcrop areas are shown for the Floridan aquifer system and Basin and Range carbonate-rock aquifer. For the other aquifers, productive aquifers may underlie other units, but the subcrop areas are not all shown on the map.

Base modified from Miller, 1990

Geology from U.S. Geological Survey, 2003

Figure 1. Locations of 12 selected carbonate aquifers or aquifer systems, other carbonate principal aquifers, areas of carbonate geology that are not principal aquifers, sampling sites, and National Water-Quality Assessment (NAWQA) Program study units included in this study.—Continued

Table 1. Total ground-water withdrawals for 12 carbonate aquifers or aquifer systems, by aquifer and state, for irrigation, public-supply, and self-supplied industrial water uses, 2000.

[Withdrawal data from Maupin and Barber (2005); Bold indicates totals for the aquifer; shading indicates states where samples were collected for current study]

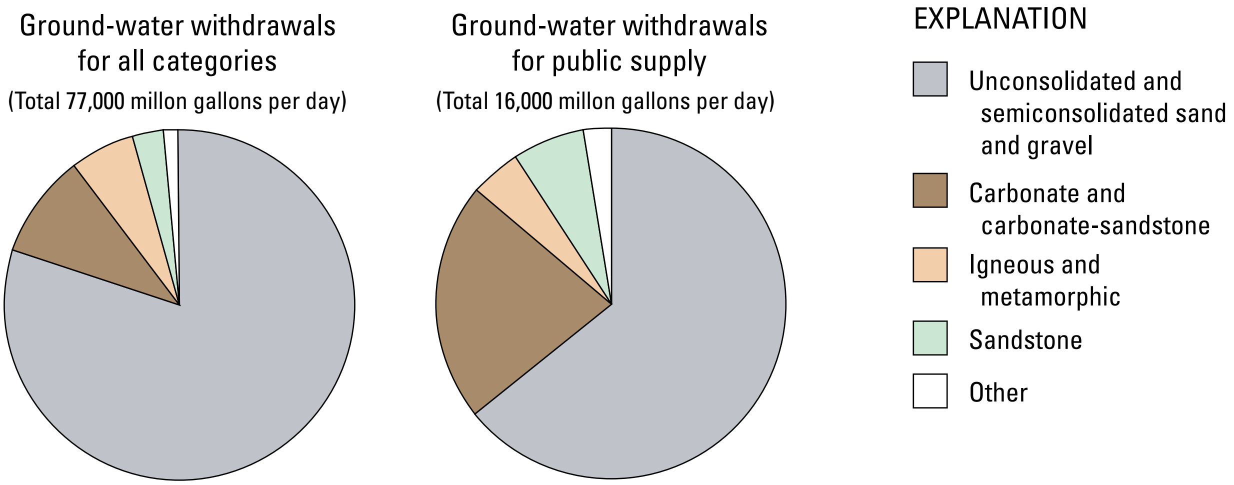
Aquifer or aquifer system (name used in report)	State	Total withdrawals	Irrigation	Public supply	Self-supplied industrial
		Million gallons per day			
Basin and Range carbonate-rock aquifers (Basin and Range)		**73.6**	**0.50**	**71.2**	**1.92**
	Idaho	.77	.00	.77	.00
	Nevada	.50	.50	.00	.00
	Utah	72.3	.00	70.4	1.92
Biscayne aquifer (Biscayne)		**812**	**114**	**698**	**.00**
	Florida	812	114	698	.00
Castle Hayne aquifer (Castle Hayne)		**33.1**	**7.64**	**23.4**	**2.07**
	North Carolina	33.1	7.64	23.4	2.07
Edwards-Trinity aquifer system (Edwards-Trinity)[1]		**740**	**282**	**411**	**47.2**
	Arkansas	7.54	.00	7.31	.23
	Oklahoma	4.26	1.96	2.12	.18
	Texas	729	280	402	46.8
Floridan aquifer system (Floridan)		**3,640**	**1,930**	**1,330**	**385**
	Alabama	5.91	1.46	2.33	2.15
	Florida	2,790	1,460	1,160	173
	Georgia	782	436	142	205
	South Carolina	57.6	28.5	24.5	4.61
Missippian aquifers (Mississippian)[1]		**286**	**6.31**	**211**	**6.79**
	Alabama	42.3	1.64	34.6	6.12
	Illinois	4.38	0	1.20	3.18
	Indiana	2.88	.37	1.16	1.35
	Iowa	7.01	.47	4.89	1.65
	Kentucky	17.4	0	9.06	8.30
	Maryland	1.08	.01	1.00	.07
	Missouri	22.5	3.29	18.7	.48
	Ohio	158	0	119	38.6
	Pennsylvania	5.36	.06	3.74	1.56
	Tennessee	24.1	.47	17.3	6.35
	Virginia	.07	0	.02	.05
	West Virginia	.88	0	.69	.19
Ordovician aquifers (Ordovician)		**5.79**	**0.56**	**4.85**	**0.38**
	Kentucky	2.32	.00	1.94	.38
	Tennessee	3.47	.56	2.91	.00
Ozark Plateaus aquifer system (Ozark Plateaus)		**165**	**20.5**	**131**	**14.0**
	Arkansas	8.44	1.23	7.16	.05
	Kansas	7.12	.06	6.77	.29
	Missouri	145	19.2	113	13.4
	Oklahoma	4.30	.00	4.02	.28

Table 1. Total ground-water withdrawals for 12 carbonate aquifers or aquifer systems, by aquifer and state, for irrigation, public-supply, and self-supplied industrial water uses, 2000.—Continued

[Withdrawal data from Maupin and Barber (2005); Bold indicates totals for the aquifer; shading indicates states where samples were collected for current study]

Aquifer or aquifer system (name used in report)	State	Total withdrawals	Irrigation	Public supply	Self-supplied industrial
		Million gallons per day			
Piedmont and Blue Ridge carbonate-rock aquifers (Piedmont)		**29.9**	**.35**	**17.8**	**11.8**
	Maryland	2.92	.25	.81	1.86
	Pennsylvania	27.0	.10	17.0	9.93
Prairie du Chien of the Cambrian-Ordovician aquifer System (Prairie du Chien)[1]		**932**	**92.4**	**590**	**251**
	Illinois	149	3.79	116	29.8
	Iowa	195	.40	61.0	134
	Michigan	1.13	.35	.64	.14
	Minnesota	271	26.4	209	35.6
	Missouri	22.5	3.29	18.7	.48
	Wisconsin	294	58.2	185	50.6
Silurian-Devonian/Upper carbonate aquifer (Silurian-Devonian/Upper carbonate)		**256**	**27.8**	**172**	**56.4**
Silurian-Devonian	Illinois	55.9	5.77	47.6	2.51
Silurian-Devonian	Indiana	41.7	4.53	33.8	3.37
Silurian-Devonian	Iowa	49.8	.99	37.2	11.7
Silurian-Devonian	Michigan	30.0	3.99	5.63	20.4
Silurian-Devonian	Ohio	35.6	4.79	23.2	7.55
Silurian-Devonian	Wisconsin	32.9	7.28	16.5	9.12
Upper carbonate	Minnesota	9.55	.35	7.52	1.68
Valley and Ridge carbonate-rock aquifers (Valley and Ridge)		**267**	**5.65**	**177**	**83.9**
	Alabama	71.2	.49	66.5	3.95
	Georgia	39.7	3.35	24.4	11.9
	Maryland	2.08	.17	1.64	.27
	New Jersey	12.8	.12	9.66	3.07
	Pennsylvania	69.9	.16	25.7	44.0
	Tennessee	33.0	1.17	28.7	3.19
	Virginia	30.8	.18	13.3	17.4
	West Virginia	7.23	.01	7.08	.14

[1] Aquifers are of mixed lithology, only the portion of these aquifers that are of carbonate lithology are included in the study; however, water-use totals are not broken out by the lithologic categories.


Ground-water withdrawals for all categories
(Total 77,000 millon gallons per day)

Ground-water withdrawals for public supply
(Total 16,000 millon gallons per day)

Figure 2. Ground-water withdrawals in the United States and the relative importance of carbonate aquifers or aquifer systems, 2000 (Maupin and Barber, 2005).

Aquifer Characteristics and Factors for Data Analysis

In order to provide adequate background about the aquifers included in this study, information on the characteristics of the aquifers and other factors that can affect water quality is provided. Basic information about each aquifer is followed by a summary of important hydrogeologic characteristics of carbonate aquifers. The characteristics of the sampling networks with background information on the types and characteristics of sampling sites are summarized.

Description of Aquifers

Each of the 12 carbonate aquifers sampled for this study has unique characteristics. Information on the characteristics of the aquifers provides background that is useful in understanding the results of the water-quality analyses from each aquifer. The geography, lithology, climate, water use, and land use for each aquifer are described in this section.

Basin and Range Carbonate-Rock Aquifers

The Basin and Range carbonate-rock aquifers (hereafter referred to as the Basin and Range aquifer) of Nevada and Utah is one of the largest regional aquifers in the country, covering 92,000 mi^2 of the Great Basin (Schaefer and others, 2005). The Great Basin is in the northern part of the Basin and Range Physiographic Province, a large area in the western United States with north-trending mountains separated by basins or valleys. The subcrop extent of the aquifer is much larger than its outcrop area (fig. 1). The Great Basin contains two aquifer systems: an upper basin-fill aquifer and a lower carbonate-rock aquifer. The Basin and Range aquifer is comprised of thick sequences of limestone and dolomite with some shale, sandstone, and quartzite that underlie several topographic basins (Planert and Williams, 1995). The mountains commonly range in altitude from 8,000 to 10,000 ft above NAVD 88, and the topographic basins commonly range in altitude from 4,000 to 6,000 ft (Schaefer and others, 2005).

The climate in the area is generally arid to semiarid, although the mountains cause some climatic variability. Mean annual precipitation ranges from less than 5 in/yr in the basins and valleys in the south to 16 in/yr in the mountainous regions in the north (Prudic and others, 1995). Mean annual temperatures range from about 30°F in the northern valleys to about 60°F in the extreme southern valleys.

Although land use in the area is primarily rangeland (Schaefer and others, 2005), with less forest and a smaller percentage of urban land, Las Vegas and Salt Lake City are located within the boundaries of the Basin and Range aquifer and are two of the fastest-growing cities in the western United States (Schaefer and others, 2005). Along with anticipated future population growth comes increased demands on the ground water. The carbonate-aquifer system represents a likely source of water for Las Vegas and Salt Lake City. Total ground-water withdrawal in 2000 for the Basin and Range aquifer was 73.6 Mgal/d, most of which (71.2 Mgal/d) was used for public supply (table 1).

Biscayne Aquifer

The Biscayne aquifer underlies an area of approximately 4,000 mi^2 in four counties in southeastern and southernmost Florida (fig. 1). The Pleistocene-age rocks of the Biscayne aquifer are predominantly highly permeable limestone, as well as some less permeable sandstone and sand. The Biscayne aquifer is shallow and unconfined, covered generally by a thin veneer of soil. It is thickest near the coast, particularly at its northeast extent, and thins to the west. A clayey confining unit about 1,000 ft thick separates the Biscayne aquifer from the stratigraphically older Floridan aquifer system. Altitude in the area studied ranges from about 0 to 300 ft above NAVD 88.

Climate is humid subtropical characterized by relatively high annual temperatures averaging from about 72°F to 77°F. Annual precipitation ranges from 40 to 65 in. (McPherson and others, 2000).

Land use is primarily urban along the Atlantic coast; intense agricultural development exists along the southeastern edge of the Everglades as well as around Lake Okeechobee. There are also vast regions of wetlands in southern Florida.

The Biscayne aquifer is the sole source of drinking water for approximately 3 million people in a rapidly growing urban area along the Atlantic coast—from Boca Raton to the Florida Keys, including the major population center of Miami. Most of the drinking water along the southeastern Florida coast is pumped from the Biscayne aquifer (McPherson and others, 2000). In 2000, about 812 Mgal/d was withdrawn from the Biscayne aquifer; of this, more than three quarters of the total water withdrawal (698 Mgal/d) is used for public supply (table 1).

Castle Hayne Aquifer

The North Atlantic Coastal Plain aquifer system underlies an area of approximately 50,000 mi^2 extending along the Coastal Plain Physiographic Province from the North Carolina-South Carolina border to southern New Jersey (fig. 1). The North Atlantic Coastal Plain aquifer system comprises six regional aquifers in early Cretaceous- to Holocene-age deposits (Trapp and Horn, 1997). The vertical sequence of aquifers is as follows: the surficial aquifer, the Chesapeake aquifer, the Castle Hayne-Aquia aquifer, the Severn-Magothy aquifer, the Peedee-upper Cape Fear aquifer, and the Potomac aquifer. The productive limestone rocks of the Castle Hayne aquifer in the North Carolina Coastal Plain, a local part of the Castle Hayne-Aquia aquifer, comprise the only carbonate aquifer within the North Atlantic Coastal Plain aquifer system. The Castle Hayne aquifer is Eocene-Oligocene-age limestone (Trapp and Meisler, 1992), sandy marl, and limey sand and is considered to be a major aquifer except for areas where the transmissivity of the aquifer is less than 1,000 ft^2/d. The aquifer consists of a thick section of highly permeable limestone in southeastern North Carolina. The province borders the Atlantic Ocean; land surface is generally flat; altitudes increase slightly away from the coast. Land use in the area is a patchwork of wetlands, forested, and agricultural lands (Spruill and others, 1998).

Climate in the Coastal Plain Physiographic Province is characterized as humid subtropical. Precipitation in most of the Coastal Plain ranges from about 44–48 in/yr (Trapp and Meisler, 1992); average annual temperature is about 55°F.

The Castle Hayne aquifer is the primary source of ground water for industrial, agricultural, and domestic users in the eastern coastal plain. Ground-water withdrawals in North Carolina for the year 2000 were 33.1 Mgal/d (table 1). About 70 percent of total withdrawals (23.4 Mgal/d) are for public supply; about a quarter of the total is used for irrigation.

Edwards-Trinity Aquifer System

The Edwards-Trinity aquifer system comprises an area of approximately 77,000 mi^2 extending from southeastern Oklahoma through much of west and central Texas (fig. 1). Most of the aquifer system is in the Great Plains Physiographic Province. In Texas, the Edwards-Trinity aquifer system is comprised of Cretaceous-age rocks (Barker and Ardis, 1996) and includes three interrelated aquifers: the Edwards-Trinity aquifer, the Edwards (Balcones Fault Zone) aquifer, and the Trinity aquifer (Ryder, 1996). The Edwards-Trinity and Trinity aquifers are partly stratigraphically equivalent and exhibit some hydraulic connectivity.

The Edwards-Trinity aquifer underlies an area of approximately 34,000 mi^2 in west-central Texas. The Edwards (Balcones Fault Zone) aquifer stretches in a narrow band across approximately 3,000 mi^2 in south-central Texas and consists of highly fractured and faulted limestone and dolomite. The Trinity aquifer underlies an area of approximately 41,000 mi^2 from south-central Texas to southeastern Oklahoma and consists of interbedded sandstone, sand, limestone, and shale. For this national study, ground-water samples were collected from the Edwards aquifer and the Trinity aquifer only in Texas. Within the area of study, altitudes range from about 2,000 ft in the north to less than 1,000 ft above NAVD 88 on its southeastern margin (Barker and Ardis, 1996). In this report 'Edwards-Trinity' refers to the aquifer system rather than the aquifer of the same name.

Climate in the area is classified as subhumid, subtropical in the eastern part, and semiarid in the west. Almost all precipitation occurs as rainfall, ranging from west to east from less than 12 in. to about 30 in., respectively (Ryder, 1996). Mean annual temperature varies geographically from about 66°F to 69°F. Land use in the study area is about half forested, with slightly less than half agricultural and grassland and less than 5 percent urban. The San Antonio metropolitan area (2000 population was 1.7 million) dominates the distribution of urban population in the study area.

The Edwards aquifer of the Balcones Fault Zone is one of the most productive carbonate aquifers in the United States (Maclay, 1995). The U.S. Environmental Protection Agency (USEPA) designated the Edwards aquifer as a sole-source aquifer in the San Antonio area, where it provides water to more than 1.5 million people. The total ground-water withdrawal from the Edwards-Trinity aquifer system in 2000 was 740 Mgal/d of which withdrawal for public supply was 411 Mgal/d (table 1).

Floridan Aquifer System

The Floridan aquifer system underlies an area of approximately 100,000 mi^2 in the Coastal Plain Physiographic Province. The aquifer covers a large area that includes most of Florida, southeastern Georgia, and parts of southern Alabama, Mississippi, and South Carolina (Johnston and Bush, 1988) (fig. 1). The Floridan aquifer system is composed of a thick sequence of Tertiary-age carbonate rocks. These formations are hydraulically connected in varying degrees and form a regional hydrologic unit, albeit with substantial differences in the water-bearing properties. Aquifer thicknesses generally increase seaward and are thin near the northern limit of the aquifer. The Floridan aquifer system is hydrologically defined on the basis of permeability (Miller, 1986). In most places, the aquifer system is divided into the Lower and Upper Floridan aquifers, which are separated by a confining unit called the middle confining unit or semiconfining unit (where it is less than 100 ft thick). Numerous large springs, which are major discharge points, issue from the Upper Floridan aquifer, mostly in unconfined or thinly confined areas. Altitudes vary slightly from north to south; topography is hilly in South Georgia, and relief is flat southward.

The climate ranges from temperate in the north to subtropical in the south. Average annual temperatures range from 60°F to 70°F from north to south. Precipitation averages about 55 in/yr, but varies with land-surface altitude. For instance, in the east-central area, average annual precipitation is 45 in/yr, whereas in the Florida panhandle, the average annual precipitation is 60 in/yr (U.S. Geological Survey, 1986).

The predominant land-use categories on the Floridan aquifer system are forest (about 38 percent), agriculture (about 26 percent), wetlands (almost 20 percent), and urban (less than 10 percent).

The Floridan aquifer system is one of the most productive aquifers in the world (Miller, 1990). It is a multi-use system; in addition to providing water to several large cities (Daytona Beach, Jacksonville, Orlando, Tallahassee, and St. Petersburg in Florida, and Brunswick and Savannah in Georgia) and extensive rural regions, the aquifer is extensively pumped for industrial and irrigation water supplies (Johnston and Bush, 1988; Marella and Berndt, 2005). In 2000, the irrigation and public-supply withdrawals from the Floridan aquifer system were 1,930 Mgal/d and 1,330 Mgal/d, respectively (table 1).

Mississippian Aquifers

The Mississippian aquifers cover a large part of the central United States, but the part included in this study lies predominantly within the Interior Low Plateaus Physiographic Province (Fenneman and Johnson, 1946), which extends from Indiana south to northern Alabama (fig. 1). The Mississippian-age carbonates are predominantly limestone, but some dolostones and chert are also present.

These limestone aquifers are referred to locally as the Mississippian Plateau aquifers in Kentucky (Plebuch and others, 1985) and the Highland Rim aquifer system in Tennessee (Brahana and Bradley, 1986a). The limestone aquifers that yield the largest quantities of water are the Upper Mississippian Monteagle Limestone, the Ste. Genevieve Limestone, and the St. Louis Limestone. Where the Monteagle, the Ste. Genevieve, and the St. Louis are thin or missing, such as in the southwestern part of central Tennessee, the Warsaw Limestone along with chert and limestone beds of the Fort Payne Formation are the principal aquifers. Land-surface altitudes range from 500 to 1,300 ft above NAVD 88. Average annual precipitation is about 55 in/yr.

Predominant land use in the area is agricultural (pasture and cropland) (Kingsbury and Shelton, 2002), although chicken production is a growing industry.

As part of the NAWQA Program, ground water was sampled from carbonate aquifers underlying the Eastern Highland Rim, where these aquifers are an important source of drinking-water supply (Woodside and others, 2004). In Alabama and Tennessee, the estimated ground-water withdrawal from the Mississippian aquifers was 66.4 Mgal/d in 2000. Public supply was 51.9 Mgal/d, of which the City of Huntsville, Ala., is a major user (table 1).

Ordovician Aquifers

Carbonate rocks of Ordovician age are the principal aquifers in large areas of central Kentucky and central Tennessee in the Interior Low Plateaus Physiographic Province (fig. 1). These carbonate-rock aquifers consist of limestone with some dolomite (Brahana and Bradley, 1986b). The aquifers are separated by confining units of shale and shaly limestone. The Middle Ordovician High Bridge and Stones River Groups and the Lexington Limestone and equivalent rocks are the most important carbonate-rock aquifers. The Ordovician carbonates are the predominant geologic units in the Outer and Inner Nashville Basin.

The NAWQA Program sampled ground water from the Ordovician aquifer within the Nashville Basin in Tennessee. Climate in the area is temperate, warm, and humid. Average temperatures range from 56°F to 61°F; the average annual temperature is about 59°F (U.S. Department of Commerce, 1995). The area has low to moderate relief with some small hills and knobs. Land-surface altitudes generally are about 700 ft above NAVD 88.

Average annual precipitation in the lower Tennessee River Basin is about 56 in. (U.S. Department of Commerce, 1995). Precipitation increases from west to east, generally corresponding to the increase in altitude from west to east.

Land use in the Outer and Inner Nashville Basin, approximately the same geographic extent of the Ordovician aquifers in the area included in the study, is 60 percent agricultural (Kingsbury and others, 1999). The majority of the agricultural land is pasture. The predominant crops in the area are corn and soybeans. Urban land overlies about 1 percent of the area.

Total ground-water withdrawals from the Ordovician aquifers for Tennessee and Kentucky are 3.47 and 2.32 Mgal/d, respectively (table 1), most of which is used for public supply.

Ozark Plateaus Aquifer System

The Ozark Plateaus aquifer system underlies most of southern Missouri, a large area of northern Arkansas, and small areas of southeastern Kansas and northeastern Oklahoma (fig. 1). Ozark Plateaus aquifer system rocks are Cambrian- to Mississippian-age limestones and dolomites that also contain beds of sandstone and chert. The confining units are mostly shale but also contain low permeability carbonates and sandstone.

The Ozark Plateaus aquifer system is composed of three individual aquifers; from shallowest Springfield Plateau aquifer (Mississippian age rocks), to the Ozark aquifer (comprised largely of Ordovician rocks with some Devonian rocks), to the deepest St. Francois aquifer (Cambrian rocks). These three aquifers are stratigraphically separated by two confining units. Ground water from the Springfield Plateau and Ozark aquifers was sampled for the NAWQA study. The Springfield Plateau aquifer is unconfined (except in its westernmost extent) and crops out in southwestern Missouri. The Ozark aquifer, the thicker (thick sequences of dolomites, sandstones, and shales) and more widespread of the aquifers, is the primary water source regionally (Miller and Appel, 1997; Renken, 1998). The term “Ozark Plateaus” is the name of an aquifer system, a NAWQA study unit, and a physiographic province. As used in this report, the term “Ozark Plateaus” refers to the aquifer system unless otherwise noted.

Topography in the Ozark Plateaus ranges from flat-lying to rugged; altitudes reach 1,772 ft above NAVD 88. The climate of the area is temperate. Mean annual precipitation ranges from about 38 to 48 in. (Adamski and others, 1995), and mean annual temperature ranges from 56 to 60ºF.

Land use in the Ozark Plateaus study area is a mix of forested land and agricultural land (Adamski and others, 1995). Agricultural land is commonly pastureland. Urban areas are minor, representing less than 2 percent of land use.

The aquifer system is the source of freshwater for most public and self-supplied domestic water users in the area (Imes and Emmett, 1994). The total ground-water withdrawals for 2000 from the Ozark Plateaus aquifer system were 165 Mgal/d, of which 131 Mgal/d was public supply (table 1).

Piedmont and Blue Ridge Carbonate-Rock Aquifers

The boundaries of the Piedmont and Blue Ridge aquifer system are coincident with the Piedmont and Blue Ridge Physiographic Provinces. These provinces are bounded on the north and west by the Valley and Ridge and New England Physiographic Provinces (Fenneman and Johnson, 1946) and on the south and east by the Coastal Plain Physiographic Province. The Piedmont and Blue Ridge aquifers extend in a band from eastern Alabama through Georgia, South and North Carolina, north to Virginia, West Virginia, Maryland, Pennsylvania, and New Jersey (Trapp and Horn, 1997) (fig. 1). Rocks in the Piedmont and Blue Ridge Provinces are crystalline, carbonate, and sedimentary (Briel, 1997). The principal aquifer in carbonate rock in the Piedmont is the Piedmont and Blue Ridge carbonate-rock aquifer. This report focuses on the ground water sampled from the carbonate aquifers in the Piedmont; therefore, this aquifer is referred to hereafter as the Piedmont aquifer. In northern New Jersey, southeastern Pennsylvania, and eastern Maryland, these Precambrian and lower Paleozoic carbonate rocks form a series of long, narrow blocks interspersed with granite and gneiss.

In the area of the Piedmont aquifer in Pennsylvania and Maryland, the average annual temperature is about 54°F. Precipitation ranges from 38 to more than 48 in/yr (Risser and Siwiec, 1996).

The predominant land use overlying the Piedmont aquifer is agricultural (at over 80 percent), and 15 percent of the remainder is categorized as urban (Lindsey and others, 2006).

Although the carbonate-rock aquifers cover only about 3 percent of the Piedmont and Blue Ridge Provinces, they are a substantial local source of water (Trapp and Horn, 1997). Approximately 30 Mgal/d (table 1) is withdrawn from the Piedmont aquifer, primarily from Pennsylvania, supplying water to about 44 percent of the population in that area (Lindsey and others 2006).

Prairie du Chien of the Cambrian-Ordovician Aquifer System

The Cambrian-Ordovician aquifer system lies within the Central Lowland and the Superior Upland Physiographic Provinces (Fenneman and Johnson, 1946). Cambrian- and Ordovician-age sandstones and carbonates constitute most of the bedrock and subcrop beneath glacial drift in southeastern Minnesota, northeastern Iowa, Wisconsin, northern Illinois, and extreme northwestern Indiana (fig. 1) (Olcott, 1992). The Cambrian-Ordovician aquifer system consists of three aquifers separated by two leaky confining units and capped by a confining unit. The three aquifers are the St. Peter-Prairie du Chien-Jordan, the Ironton-Galesville, and the Mount Simon. The Prairie du Chien Group consists of upper and lower dolomite units with an intervening sandstone unit. The NAWQA Program sampled ground water from the Prairie du Chien aquifer, the middle dolomite unit of Ordovician age. Surface topography is generally smooth with some gently rolling hills and dissected uplands. The climate ranges from cold winters to cool summers; mean annual temperatures range from 44 to 46°F. Average annual precipitation increases from 24 to 44 in. from northwest to southeast. The predominant land uses in the area are agricultural, forest, and urban (Fong and others, 1998).

The St. Peter-Prairie du Chien-Jordan aquifer is a multi-unit aquifer that is a major source of ground water for Iowa and Minnesota. The aquifer in Minnesota is the principal source of water for domestic wells and municipal wells in suburban communities surrounding the Minneapolis-St. Paul metropolitan area (Fong and others, 1997). Total ground water withdrawn from the Cambrian Ordovician aquifer system in Minnesota was 271 Mgal/d, more than 75 percent of which was for public supply (table 1).

The Prairie du Chien aquifer is the only aquifer referred to in this study by a name that is not a principal aquifer, because the sampling was limited to a specific (carbonate-bedrock) part of the principal aquifer that is otherwise mostly noncarbonate bedrock. The specific aquifer name 'Prairie du Chien' is used to describe this area rather than the principal aquifer name 'Cambrian-Ordovician.'

Silurian-Devonian/Upper Carbonate Aquifers

The Silurian-Devonian and Upper carbonate aquifers were sampled in eastern Iowa and southern Minnesota (fig. 1). The Silurian-Devonian aquifer consists of 200–400 ft of limestone, dolomite, sandstone, shale, and evaporite deposits (Olcott, 1992). The boundary between Silurian-Devonian and Upper carbonate aquifers is a facies change in northern Iowa. The Upper carbonate aquifer consists of 250–600 ft of Ordovician- and Devonian-age limestone, dolomite, and shale. Both of these aquifers are primarily unconfined. The Devonian-age carbonate rocks are present in both aquifers, but the Silurian-age units are absent in the Upper carbonate aquifer. The area is characterized by low relief to gently rolling topography.

The continental climate brings hot summers (average of 71°F) and cold winters (average 20°F) to the area. Mean annual temperature is 47°F (Schnoebelen and others, 1999), and precipitation averages about 30 to 36 in/yr (Kalkhoff and others, 2000)

Agriculture is the dominant land use in the area, covering over 90 percent of the area (Savoca and others, 1999).

Water use in 2000 from the Upper carbonate aquifer in Minnesota totaled 9.55 Mgal/d and from the Silurian-Devonian aquifer in Iowa was 49.8 Mgal/d (table 1).

The Silurian-Devonian/Upper carbonate aquifers are two individual principal aquifers, but they were sampled as a single unit and therefore are grouped together for this study.

Valley and Ridge Carbonate-Rock Aquifers

The Valley and Ridge carbonate-rock aquifers are in the Valley and Ridge Physiographic Province. The carbonate aquifer extends from Alabama to New Jersey, including parts of Georgia, Tennessee, West Virginia, Virginia, Maryland, Pennsylvania, and New Jersey (fig. 1). Only the carbonate aquifers in the Valley and Ridge are included in this study; therefore, the aquifer is hereafter referred to as the Valley and Ridge aquifer. The Valley and Ridge consists of a long, narrow belt of folded and faulted Paleozoic rocks. The Valley and Ridge is characterized by a series of sub-parallel northeast-trending ridges. The aquifer is the widest in Pennsylvania and is bounded by the Blue Ridge and Piedmont Provinces to the southeast and by the Appalachian Plateaus to the northwest (Trapp and Horn, 1997). The Great Valley in Pennsylvania is floored with lower Paleozoic carbonate rocks and shale. The most productive Valley and Ridge aquifers are within the limestone and dolomite rocks (of Cambrian and Ordovician age) in the valleys.

The climate varies from north to south; average annual temperatures range from 59°F in Eastern Tennessee (Hampson and others, 2000) to 46°F in northeastern Pennsylvania (Fischer, 1999). Precipitation averages about 40 in/yr, but in areas of higher altitude in the Valley and Ridge, precipitation can be as high as 90 in/yr (Hampson and others, 2000).

For the Valley and Ridge aquifer, forested land makes up 47 percent of the land area, and agricultural land use covers about 27 percent of the land area (Vogelmann and others, 2001). In the northern Great Valley, the percentage of agricultural land use is much greater; 78 percent of the carbonate aquifer in the Great Valley in the Lower Susquehanna River Basin study unit underlies agricultural land (Risser and Siwiec, 1996).

Water use in the Valley and Ridge carbonate aquifer totaled 267 Mgal/d; 177 Mgal/d was for public supply (table 1).

Hydrogeology

The 12 carbonate aquifers selected for study have similar overall lithology (limestone and (or) dolomite) and mineralogy (calcite, dolomite, and trace amounts of other evaporite minerals such as gypsum in some rocks). Some carbonate aquifers are interlayered with sandstones or shales (Mississippian, Piedmont, and Valley and Ridge) or crystalline rocks (Piedmont). However, differences in geology, aquifer properties (such as porosity and transmissivity), extent of karstification, degree of confinement, and climate (precipitation, temperature, and recharge) all are key factors that account for variations among these 12 aquifers in major-ion chemistry, pH, oxidation-reduction (redox) status, and ground-water residence time. Additional factors (lithology, stratigraphy, geomorphology, structural, and tectonic), described by Brahana and others (1988), affect the evolving porosity and permeability of carbonate rocks (and hence water quality) for carbonate aquifers in North America. Differences in pH and redox status in an aquifer can greatly affect the movement and fate of contaminants and trace elements in ground water.

Generalized hydrogeologic properties for the 12 carbonate aquifers are included in table 2, but it is worth noting that there can be a wide range in aquifer properties and confinement conditions within each of these systems. This section describes some of the important hydrogeologic differences

Table 2. Hydrologic properties of the 12 carbonate aquifers or aquifer systems included in study.

Aquifer or aquifer system	Location (states)	Approximate areal extent, square miles	Composition	Depositional age	Thickness, feet
Basin and Range	Nev., Utah, Calif., Ariz., Idaho, Oreg.	50,000	Limestone, dolomite, layers of shale, sandstone, and quartzite	Cambrian-Permian	up to 25,000
Biscayne	Fla.	3,600	Shelly limestone, sand infilling of large voids	Pleistocene-Pliocene	20–250
Castle Hayne	N.C.	11,500	Limestone, calcirudite, calcarenite, sandy marl, fine to coarse calcareous sand in N.C.	Eocene-Oligocene	<10–1,000
Edwards-Trinity	Tex., Okla.	77,000	Limestone, dolomite, evaporite	Cretaceous	[3]300–700
Floridan	Fla., Ga., S.C., Ala.	100,000	Limestone, dolomite	Tertiary (Eocene-Oligocene)	[4]0–2,500
Mississippian	Tenn., Ala., Ky., Ind.	[1]20,000	Limestone	Mississippian	100–400
Ordovician	Tenn., Ky.		Thin-bedded limestones and dolostones (mostly in Tenn.) interbedded with shales	Ordovician, Cambrian-Ordovician	large variations over short distances
Ozark Plateaus	Mo., Ark., Okla.	50,000	Limestone, dolomite; some sandstones	Cambrian-Mississippian	200–400 (Springfield Plateaus); 1,000–3,000 (Ozark aquifer)
Piedmont	Pa., Md.	900	Limestone, dolomite, marble	Precambrian-Ordovician	[3]4,700–8,000
Prairie du Chien	Minn., Wis.	4,000	Limestone, dolomite	Lower Ordovician	0–335
Silurian-Devonian/ Upper carbonate	Iowa, Wis., Ill., Mich., Ind., Ohio	[2]12,400	Limestone, sandstone, small amts gypsum	Silurian-Devonian	200–400
Valley and Ridge	N.J., Pa., Md., W.Va., Va., N.C., Ga., Ala.	15,300	Limestone, dolomite, with interbedded clastics	Cambrian, Ordovician, Silurian, Devonian, Mississippian	[3]8,000

[1] Noncontinuous.

[2] Iowa only.

[3] Formations are folded, faulted or tilted. Formation thickness may not be equal to aquifer thickness.

[4] The maximum potable thickness is about 1,000 feet.

Table 2. Hydrologic properties of the 12 carbonate aquifers or aquifer systems included in study.—Continued

Aquifer or aquifer system	Confinement	Composition of confining material	Areal extent of confinement, percent	Thickness of confining unit, feet	Porosity	Transmissivity, feet squared per day
Basin and Range	Unconfined to confined	Clastic sedimentary, volcanic rocks	Variable	Variable	Secondary dissolution along fractures, and conduits	13–130,000
Biscayne	Unconfined, but overlying sand cover provides storage	Unconfined	None	none	Primary: highly porous shelly material	75,000–300,000
Castle Hayne	Unconfined, but thin confining unit in N.C.	Clay and sandy clay	Variable	Generally less than 50 in N.C.	Secondary	10,000–70,000
Edwards-Trinity	Unconfined to confined	Clay, limestone	60–70	0–2,000	Secondary dissolution along fractures, and conduits	10,000–5,000,000
Floridan	Unconfined to confined	Clay and silt	50–80	0–400	Dual: conduits, porous matrix	10,000–1,000,000
Mississippian	Variable—mostly unconfined	Regolith, clay, silt, chert	Variable	10–100	Secondary: chert gravel and rubble at top of rock, fractures and conduits	30–4,400 (Tenn.)
Ordovician	Unconfined to confined	Shale and shaly limestone	Variable	large variations over short distances	Secondary dissolution along fractures, and conduits	large variations over short distances
Ozark Plateaus	Variable—mostly unconfined	Shale, dolomite	Springfield Plateaus aquifer is variably confined; Ozark aquifer is mostly unconfined	less than 100	Secondary dissolution along fractures, faults, and conduits	highly variable
Piedmont	Unconfined to confined	Shale, crystalline rocks or poorly fractured carbonate rock	Variable		Secondary dissolution along joints, fractures	20–30,000
Prairie du Chien	Unconfined to confined	Glacial and alluvial deposits	Variable	<50–450	Secondary: fractures, vugs, caverns, conduits	12,000
Silurian-Devonian/ Upper carbonate	Mostly unconfined	Shale	25 percent		Secondary dissolution along fractures, bedding plane openings	360,000 (unconfined areas)–1,200 (confined areas)
Valley and Ridge	Unconfined to confined	Shale, clay, poorly fractured limestone	Variable		Secondary dissolution along fractures, and conduits	15–120,000

Table 2. Hydrologic properties of 12 carbonate aquifers or aquifer systems included in study.—Continued

Aquifer or aquifer system	Karst features, types	Approximate age of ground water, years	Water-quality issues	References
Basin and Range	Springs, caverns	1,000s; interbasin movement of ground water with deep circulation	Rapid urban growth	Winograd and Thordarson (1975); Harrill and Prudic (1998); Schaefer and others (2005); Planert and Williams (1995)
Biscayne	None		Urban, saltwater intrusion	Renken and others (2005); Bradner and others (2005); Radell and Katz (1991)
Castle Hayne	Some karst features in outcrop areas or unconfined areas		Saltwater intrusion	Trapp and Meisler (1992); Miller (1999); Winner and Coble (1996)
Edwards-Trinity	Sinkholes, large conduit systems, springs	recent–200 (average residence time)	Urban	Barker and Ardis (1996); Maclay and Small (1983); Maclay and Land (1988); Maclay (1995)
Floridan	Sinkholes, large conduit systems, numerous springs	10–40 unconf.;10,000–30,000 conf.	Urban, agriculture	Miller (1986, 1999); Sprinkle (1989) Marella (2004)
Mississippian	Sinkholes, springs, caverns	<10–35	Agriculture, urban	Kingsbury and others (1999); Kingsbury and Shelton (2002); Plebuch and others (1985)
Ordovician	Sinkholes, caverns, springs	young	Agriculture	Webbers (2003); Miller (1999)
Ozark Plateaus	Sinkholes, springs, large conduit systems, caverns		Agriculture, urban	Adamski and others (1995); Adamski (1997, 2000); Peterson (2002); Imes (1987); Renken (1998)
Piedmont	Sinkholes, springs	0–20	Agriculture, urban	Lindsey and others (2006); Trapp and Horn (1997)
Prairie du Chien	Caverns, conduits	slightly younger in unconfined area, young and old mixtures	Agriculture	Young (1992); Fong and others (1998); Olcott (1992)
Silurian-Devonian/ Upper carbonate	Sinkholes, springs, conduits		Agriculture	Savoca and others (1999); Olcott (1992); Hershey (1969); Tucci and McKay (2006)
Valley and Ridge	Sinkholes, springs, caverns	0–20	Agriculture, urban	Parizek and others (1971); Swain and others (2004)

among these aquifers that can result in ground-water-quality variations. More detailed information about each aquifer system can be obtained from the references provided in table 2. Differences in land-use activities that affect the occurrence of anthropogenic contaminants in these ground-water systems are discussed in subsequent sections. In addition, natural ground-water flow is affected by the amount of pumpage in each aquifer system. The estimated amount of ground water withdrawn from each aquifer system for various uses is presented in table 1.

The rocks that comprise these carbonate aquifers have different depositional and post-depositional histories. Depositional environments determine to a large extent the properties of carbonate aquifers, because they affect texture, fabric, and original porosity and permeability (Brahana and others, 1988). The age of rocks for eight of the aquifers ranges from Precambrian to Paleozoic (Piedmont, Valley and Ridge, Basin and Range, Mississippian, Ordovician, Ozark Plateaus, Prairie du Chien, and Silurian-Devonian/Upper carbonate) to Pleistocene (Biscayne aquifer), with Cretaceous rocks comprising the Edwards-Trinity aquifer system and Tertiary rocks comprising the Floridan aquifer system and the Castle Hayne aquifer (table 2). Primary porosity associated with these aquifer systems ranges from 1 to more than 50 percent, but subsequent diagenetic processes (compaction, cementation, and dolomitization) and dissolution have affected both porosity and permeability. In addition, structural forces associated with tectonic movement have caused deformation (folding, faulting, and fracturing) of rocks in several systems (Edwards-Trinity, Ozark Plateaus, Piedmont, and Valley and Ridge aquifers/aquifer systems). Faults are especially important hydrogeologic features. The extent of the Edwards-Trinity aquifer system is generally coincident with a major fault zone. Aquifers in carbonate rocks of Precambrian to Cretaceous age typically yield water primarily from solution openings. The Silurian-Devonian/Upper carbonate and Ordovician aquifers are in layered limestones and dolomites of Paleozoic age, in which solution openings are locally well developed. Likewise, in the Piedmont and Valley and Ridge carbonate aquifers, dissolution has occurred along structural planes, such as bedding, cleavage, or other joints, and has greatly enhanced permeability by forming interconnected conduit networks.

Aquifers in carbonate rocks of Tertiary and younger age have different porosity and permeability characteristics than aquifers in Cretaceous and older carbonate rocks. The aquifers in Tertiary and younger rocks (Castle Hayne aquifer, Floridan aquifer system, and Biscayne aquifer) contain strata that were deposited in warm marine waters on shallow shelves and are mostly platform carbonate deposits in which intergranular porosity is present as well as large solution openings (Miller, 1999). However, the hydrogeology of these younger systems can be highly complex and variable. For example, the sequence of rocks in the Floridan aquifer system was deposited in different environments that result in wide variations in texture, from coarse coquina that is extremely permeable to micrite that is almost impermeable. Subsequent dolomitization has changed the original texture and mineralogy of the carbonate rocks by increasing the volume of connected pore space in fine-grained limestones and calcite or dolomite overgrowths.

Degree of Confinement

The thickness and type of sediments that overlie the different carbonate aquifers can affect the flux of water from the surface to the carbonate-rock material (Brahana and others, 1988) and hence the development of secondary porosity, permeability, transmissivity, recharge rate, and ground-water residence time. Therefore, the susceptibility of an aquifer to contamination from land-surface activities can be directly related to the degree of confinement. Unfortunately, the definition of confinement is not consistent among study areas. The degree of confinement in this study is defined generally by the presence of lower permeability rocks or unconsolidated material overlying the aquifer or aquifer systems (see table 2).

Variable degrees of confinement occur within all 12 carbonate aquifers (table 2). The Biscayne, Mississippian, Ordovician, Piedmont, and Valley and Ridge aquifers have been classified as unconfined (table 2); however, some confinement by low-permeability material may occur locally in some of these systems. The Mississippian aquifer is overlain by relatively thick regolith or residuum (up to 100 ft in some places). The Basin and Range aquifer is considered to be confined because of the long, deep flowpaths (Susan Thiros, U.S. Geological Survey, written commun., 2007), and the fact that the carbonate aquifer is typically overlain by low-permeability volcanic rocks (Schaefer and others, 2005). The Castle Hayne aquifer is confined or unconfined based on the presence or absence of the Castle Hayne confining unit (Giese and others, 1997). The Edwards-Trinity aquifer system is confined where it is fully saturated and buried (Groschen, 1996) and unconfined otherwise. The Upper Floridan aquifer is considered to be unconfined when it occurs near the surface or is covered by a thin layer of permeable sediments; semiconfined or poorly confined when there is less than 100 ft of lower-permeability sediments overlying the aquifer or if the overlying material is breached by sinkholes; and confined when the thickness of overlying low-permeability sediments exceeds 100 ft. The Prairie du Chien aquifer is considered to be confined where it is overlain by less permeable bedrock units or by at least 10 ft of clay or clay-rich glacial till, and the aquifer is considered to be unconfined where those units are not present (Fong and others, 1998). In the Silurian-Devonian/Upper carbonate aquifer, Savoca and others (1999) considered a well to be ‘protected’ if it was overlain by a confining unit or 100 ft of glacial material. Their description of ‘protected’ wells was considered equivalent to ‘confined’ for this study. Intense folding and thrust faulting followed by erosion of sandstone strata have resulted in near-surface exposure of the limestones that comprise the Valley and Ridge aquifer and generally result in the aquifer being unconfined.

Parts of the Upper Floridan and the Ozark aquifer do not fall into either confinement category and have been categorized as follows. The Upper Floridan aquifer is considered to be semiconfined in areas where the confining unit is less than 100 ft thick or breached (Miller, 1986). For the Ozark aquifer, the term ‘mixed confinement’ was used in cases where a given well had a long open interval and was open to both the upper unconfined aquifer and the lower confined aquifer (Daniel Yeatts, U.S. Geological Survey, written commun., 2007). The shale confining unit for the Ozark aquifer generally is less than 100 ft thick where it is overlain by the Springfield Plateaus aquifer, but the Ozark aquifer is mostly unconfined where it occurs near the surface. The age of ground water, which typically refers to the time since recharge, is related to aquifer confinement (Cook and Böhlke, 2000), ground-water flow patterns, and other aquifer properties (Focazio and others, 1998, 2002). In shallow flow systems that are unconfined, such as in the Biscayne aquifer, ages of ground water can vary from days to tens of years. In deeper aquifer systems, such as in confined parts of the Floridan aquifer system, ground-water age can reach tens of thousands of years along long flowpaths (Plummer and Sprinkle, 2001). However, short-circuiting of water through sinkholes and other solution features can result in mixtures of young and old water in parts of many carbonate aquifer systems (Plummer and others, 1998) and affect the quality of water withdrawn by public supply wells (Katz and others, 2007; Metz and others, 2007).

In this report, differences in geochemistry and contaminant occurrence among the 12 carbonate aquifers are evaluated relative to the degree of confinement. Wells in each aquifer were grouped into three categories (unconfined, semiconfined or mixed confined, and confined) for detailed statistical analysis. The number of samples that were considered as mixed confinement was very small; therefore, they were lumped with the semiconfined category for analysis, as they are neither confined nor unconfined.

Karstification

Considerable variability in permeability within and among each of the carbonate aquifers has resulted from carbonate dissolution along joints, bedding planes, cavities, and faults, which has produced small to large conduits at different depths. Recharge water that contains carbon dioxide (forming carbonic acid) and organic acids can readily dissolve carbonate rocks to depths of about 300 ft where the rocks crop out or are covered by a thin layer of noncarbonate material (Miller, 1999). The end result of extensive carbonate-rock dissolution is expressed at the land surface as karst topography, characterized by sinking streams, sinkholes, caves, and other types of solution openings and by internal surface-water drainage systems. Almost all carbonate terranes are underlain by one or more karst aquifers (Quinlan and others, 1991); however, these authors state that the degree of karstification can vary considerably, and the “absence or unrecognized presence of sinkholes, and other karst features does not mean that a karst aquifer is not present.”

In karst terranes, water typically enters the carbonate-rock aquifers rapidly through large openings (solutionally enlarged fractures), and contaminants in the water can be transported though pipe-like or channel-like openings called conduits, rapidly spreading through the aquifers. The length and depth of caves and fissures vary widely across the study areas and are related to topographic relief, thickness of soluble rock, geologic structure, and position of the water table. Quinlan and others (1991) grouped karst aquifers into a continuum of three categories—hypersensitive karst aquifers, moderately sensitive karst aquifers, and slightly sensitive (non-karst) aquifers—on the basis of the sensitivity of their response to variations in recharge, storage, and flow and the relative vulnerability to point and nonpoint sources of contamination at the land surface. It is beyond the scope of this study to characterize in detail the degree of sensitivity of each aquifer system with respect to its response to fluctuations in recharge, storage, and flow. However, it is worth mentioning prominent karst features that have been noted for some of the aquifers. In the Edwards-Trinity aquifer system, large caves and fissures are present to a depth of 600 ft, and fissure systems and passages of single caves commonly extend for more than 1 mi (Davies and others, 1984). In the Ozark Plateaus, caves with passages 1,000 ft or more long are common, and most cave passages extend to depths of less than 100 ft (Davies and others, 1984). In parts of the Upper Floridan aquifer in northern Florida, cave passages of several miles recently have been mapped by cave divers (Florida Department of Environmental Protection, 2007).

This study used the generalized location of karst areas in the United States shown on a national atlas karst map (Davies and others, 1984). The map by Davies and others (1984) eventually will be replaced by a new national karst map (Weary, 2006). This new geographic information system-based, soluble-rock map will better display surficial karstic features from various data sources including state geologic maps and will include the distribution and density of caves, sinkholes, and other karst features. This new map is considered a work in progress because issues still need to be resolved about the lack of consistency in spatial precision and lithologic classification, and the difficulties in obtaining statewide and regional information on cave locations and other solution features.

Springs

In most karstic aquifer systems, springs are important ground-water-discharge features (Meinzer, 1927). As one might expect from variations in topography, hydraulic gradient, recharge, and degree of karstification among these carbonate aquifers, there is a large variation in the number of springs and the volume of water that they discharge. Spring-water chemistry can reveal important information about aquifer water quality, because a spring integrates ground water spatially, vertically, and temporally from an aquifer (Rosenau and others, 1977). Spring flow is controlled by the size of the ground-water contributing area, hydraulic gradient, the amount of recharge, and the size of the openings through which the springs discharge (Meinzer, 1927). Springs in unconfined and poorly confined parts of an aquifer generally can have large seasonal fluctuations in flow. Large volumes of water move quickly in and out of the aquifer, and concentrations of dissolved solids tend to be lower than in areas of slower flow through small pores in the carbonate matrix.

Few if any springs are present in the Biscayne aquifer; in contrast, the Floridan aquifer system contains 33 first-magnitude springs, each of which discharge more than 100 ft^3/s (greater than 62 Mgal/d). Most of the springs that discharge water from the Floridan aquifer system are in areas where the aquifer is exposed at the land surface or is covered by less than 100 ft of clayey confining material. A smaller number of large-volume springs also are associated with the Edwards-Trinity aquifer system and the Basin and Range aquifer. Smaller-volume springs or seeps are found in the Mississippian aquifer, Valley and Ridge aquifer, and the Ozark Plateaus aquifer system. Spring-water samples were collected from six aquifers or aquifer systems—Edwards-Trinity, Floridan, Mississippian, Valley and Ridge, Basin and Range, and Ozark Plateaus.

Berndt and others (2005) compared water chemistry in samples from 226 wells and 176 springs in selected carbonate aquifers to determine if water from springs and wells has similar concentrations of selected properties and constituents such as dissolved solids, dissolved oxygen, nitrate, and calcite and dolomite saturation index (S.I.). Samples were collected in seven carbonate aquifers/aquifer systems—Edwards-Trinity, Floridan, Mississippian, Basin and Range, Valley and Ridge, Springfield Plateau, and Ozark (samples from the Springfield Plateau and Ozark aquifers were combined into the Ozark Plateaus aquifer system in the current study). Although concentrations of nitrate were only significantly different between spring and well samples in one of the seven aquifers, concentrations of dissolved oxygen were significantly different between well and spring samples in four of the seven aquifers. Median calcite and dolomite S.I. values were significantly different between well and spring samples in three of the seven aquifers. Springs probably represent mixtures of younger water from shallower parts of the aquifer flow systems and thus may receive water from those parts of the flow system that are most susceptible to contamination from land-use practices. The collection of water from springs is critical to adequately characterize water quality and vulnerability to contamination in carbonate aquifers (Adamski and Pugh, 1996; Adamski, 2000; Berndt and others, 2005). Because the differences in concentrations of anthropogenic contaminants in wells and springs were generally not significant, water-quality data from springs are analyzed along with data from wells from the studied aquifers in this report.

Recharge

The 12 carbonate aquifers are in areas of the United States where there is a large variability in climate, which in turn affects the amount of rainfall and estimated recharge to each aquifer. Annual average precipitation is low in Nevada where the Basin and Range aquifer is present (5–16 in. in the valleys but ranges from 8 to more than 60 in. over the mountains where most recharge occurs) (Schaefer and others, 2005), but ranges to more 60 in. over parts of Florida where the Floridan aquifer system is unconfined. However, the actual amount of recharge to each aquifer varies substantially within each study unit and among the aquifers due to soil type, topography, streamflow characteristics, faults and fractures, solution openings, distribution of precipitation, and pumpage patterns. Recharge estimates are included in this report as a possible factor affecting water quality in carbonate aquifers.

Sampling-Network Characteristics

The following description of the sampling-site networks provides a basic overview of the study types, water use, characteristics of sampling sites, the land use, and potential contaminant sources in the area around the sampling sites and the potential factors affecting transport of contaminants to the sampling sites. These ancillary data sets will be used in the analysis of the water quality in the 12 carbonate aquifers.

Sampling for this study was conducted as a part of a USGS national program, and therefore, the networks have similar characteristics (Koterba and others, 1995). All 1,042 samples were collected as a part of 1 of 5 basic types of ground-water studies. Each study type had different objectives; however, they were components of an overall program objective of characterizing ground-water resources in these aquifers. The major-aquifer study was a broad characterization of water quality in the aquifer, typically from domestic-supply wells. The land-use study focused on a specific land use (agricultural or urban) and typically included domestic-supply wells for agricultural land-use studies. In the urban land-use studies, monitoring wells were drilled, and in some cases, older abandoned wells were sampled. Some land-use-study networks had a companion network with a small number of reference wells (two to three wells) that were from areas where land use was not expected to affect water quality. The ‘spring’ study type was made up entirely of springs. Springs were included in some of the other networks study types, but the network maintained the name of the primary sampling objective. The fourth type of study was the source-water-quality assessments that were focused on water quality in public-supply wells. The last type of study was a flowpath study. These were typically wells installed along a flowpath in a small area and were only included in this analysis in one case where the wells were spread out over a large area. The sampling sites included 865 wells and 177 springs. If a site was sampled multiple times, only the most recent sample was

Table 3. Summary of network names, National Water-Quality Assessment (NAWQA) study types, numbers of wells and springs sampled, and sampling time period in the 12 carbonate aquifers or aquifer systems included in study.

Aquifer or aquifer sytem	Network name	Study type	Site type	Number of sampling sites	Sample collection period
Basin and Range	nvbrsus4	Major-Aquifer Study	Wells	12	2003
	nvbrsus4	Major-Aquifer Study	Springs	12	2003
Biscayne	sofllusot1	Reference Wells	Wells	3	1996–97
	sofllusrc1a	Urban Land-Use Study	Wells	30	1996–97
	sofllusrc1b	Urban Land-Use Study	Wells	2	1996
	soflsus1	Major-Aquifer Study	Wells	30	1998
Castle Hayne	albesus5	Major-Aquifer Study	Wells	2	1994
	albesus7	Major-Aquifer Study	Wells	30	2002–04
Edwards-Trinity	sctxlusrc1	Urban Land-Use Study	Wells	30	1998
	sctxrefre1	Reference Wells	Wells	1	2000
	sctxspr2	Spring Study	Springs	6	1997
	sctxsus1	Major-Aquifer Study	Wells	28	1996
	sctxsus2	Major-Aquifer Study	Wells	30	1996
	sctxsus3	Major-Aquifer Study	Wells	30	1997
Floridan	acfbsus1	Major-Aquifer Study	Wells	33	1995–2002
	acfbsus2	Spring Study	Springs	22	1995
	gafldwgs1	Source Water-Quality Assessment	Wells	15	2002–04
	gafldwgs2	Source Water-Quality Assessment	Wells	15	2002–03
	gafllusrc1b	Urban Land-Use Study	Wells	16	2002
	gaflrefot1	Reference Wells	Wells	2	2002
	gaflsus2	Major-Aquifer Study	Wells	30	2002–03
	gaflsus3	Major-Aquifer Study	Wells	30	2002
	gaflsus4	Major-Aquifer Study	Wells	30	2005
	santsus2	Major-Aquifer Study	Wells	30	1998
Mississippian	ltenlusag1	Agricultural Land-Use Study	Wells	32	2000–01
	ltenreffo1	Reference Wells	Wells	1	2000
	ltenspr1	Spring Study	Springs	2	1999
	ltenspr2	Spring Study	Springs	1	2000
	ltensus1	Major-Aquifer Study	Wells	30	1999
Ordovician	ltenspr2	Spring Study	Springs	9	2000
	ltensus2	Major-Aquifer Study	Wells	31	2000
Ozark Plateaus	ozrklusag1a	Agricultural Land-Use Study	Wells	20	1994
	ozrklusag1b	Spring Study	Springs	22	1993–94
	ozrklusag2a	Agricultural Land-Use Study	Wells	20	1995
	ozrklusag2b	Spring Study	Springs	20	1993–95
	ozrksus1	Major-Aquifer Study	Wells	12	1993–94
	ozrksus2a	Major-Aquifer Study	Wells	30	1993
	ozrksus2b	Spring Study	Springs	30	1993
	ozrksus3a	Major-Aquifer Study	Wells	16	1993
	ozrksus3b	Spring Study	Springs	18	1993
Piedmont	lsuslusag1	Agricultural Land-Use Study	Wells	30	1993
Prairie du Chien	umissus3	Major-Aquifer Study	Wells	12	1996
	umissus4	Major-Aquifer Study	Wells	18	1996
Silurian-Devonian/Upper carbonate	eiwasus1	Major-Aquifer Study	Wells	33	1996

Table 3. Summary of network names, National Water-Quality Assessment (NAWQA) study types, numbers of wells and springs sampled, and sampling time period in the 12 carbonate aquifers or aquifer systems included in study.—Continued

Aquifer or aquifer sytem	Network name	Study type	Site type	Number of sampling sites	Sample collection period
Valley and Ridge	lsuslusag2	Agricultural Land-Use Study	Wells	30	1994
	lsuslusag3	Agricultural Land-Use Study	Wells	30	1995
	lsuslusur1	Urban Land-Use Study	Wells	20	1995
	podlreffo1	Reference wells	Wells	2	2002
	potofpsag2	Agricultural Flowpath Study	Wells	10	1995
	potolusag1	Agricultural Land-Use Study	Wells	29	1993–2002
	utenspr1	Spring Study	Springs	35	1997
	utensus1	Major-Aquifer Study	Wells	30	1998–99

used in this study. The breakdown of samples by study type is 539 from major-aquifer studies, 191 from agricultural land-use studies, 98 from urban land-use studies, 10 from an agricultural flowpath study, 9 from reference sites, 165 from spring studies, and 30 from source-water-quality assessments. The sampling-site networks, type of study, the number of springs and wells associated with each network, and the sampling time period are given in table 3. The current study was conducted by compiling all NAWQA studies that had been conducted in carbonate aquifers. Thus, this does not represent a random sampling design that represents all aquifers and land-use types equally.

The water use associated with the sampling sites in the various study types is given in table 4. Domestic water use from private wells was predominant overall. The second most frequent water use was “unused,” which, except in the case of springs, indicates a monitoring well or an abandoned domestic well. Public water use from production wells characterized the source-water-quality assessment networks, as well as a large number of the wells from major-aquifer studies. A variety of miscellaneous water uses characterize the rest of the sites. The water use has some effect on potential water-quality issues. Public-supply wells are typically deeper, are pumped more heavily, and have better well-construction characteristics than most of the other well types. The unused springs and wells may be the least protected, because they are not designed to produce water for human consumption. Overall, the variety of water use, study type, and site type represents various parts of the aquifer systems; shallow monitoring wells represent recently recharged water, deeper domestic and public supply wells represent the deeper system, and springs represent the discharge points of the system.

A summary of the characteristics of the sampling sites is included in table 5. The Biscayne and Castle Hayne aquifers had the shallowest median depth to water, and the Basin and Range aquifer and the Edwards-Trinity aquifer system had the deepest median depths to water. Shallowest median well depths were in the Biscayne and Mississippian aquifers, and the Basin and Range aquifer and the Edwards-Trinity aquifer system had the deepest median well depth. The depth to the top of the open interval is the shallowest point at which water can flow into a well. In most cases, this is given as the bottom of the casing or the depth to a well screen; however, if information on specific water-bearing zones is available, this is the distance to the shallowest water-bearing zone. The median depth to the top of the open interval was smallest in the Biscayne and Ordovician aquifers. The median depth to the top of the open interval was also largest in the Basin and Range aquifer and the Edwards-Trinity aquifer system. The well-construction data are indicative of the variety in the aquifer characteristics. Some aquifers are shallow with a high water table, and others are deep with a lower water table. These factors could be important in determining the presence of contaminants in wells; however, because of the nature of carbonate aquifers, contaminants can travel rapidly to deep parts of these aquifers.

Source Factors

Several potential sources of contamination were compiled for use as variables to explain water-quality results. These included information on land use, population density, nitrogen sources, and underground storage tanks. In most cases, these data were compiled for the NAWQA Program for a 1,640-ft (500-m) radius around the sampling sites. The arbitrary 1,640-ft radius area is not assumed to be the actual contributing area to the sampling site, but the data compiled for this area are considered to be representative of land-surface activities in the area near the sampling site.

The land-use data are from the National Land Cover Data (NLCDE) data sets (U.S. Geological Survey, 1999; Price and others, 2007), which are enhanced by the GIRAS data sets to include the addition of categories for orchards, tundra, residential with forest, and residential without forest (Price and others, 2007). This data set represents land use in the early 1990s. For much of the data analysis, the NLCDE codes were lumped

Table 4. Summary of water use by National Water-Quality Assessment (NAWQA) study type in the 12 carbonate aquifers or aquifer systems included in study.

Study type	Sub-type	Water use	Number of sites
Major-Aquifer Study		Domestic	339
		Other[1]	53
		Public Supply	78
		Unused	69
Land-Use Study	Urban	Domestic	7
		Other[1]	7
		Public Supply	2
		Unused	82
	Agricultural	Domestic	155
		Other[1]	4
		Unused	32
Reference Wells		Domestic	1
		Other[1]	1
		Unused	7
Spring Study		Domestic	43
		Other[1]	35
		Public Supply	6
		Unused	81
Source-Water-Quality Assessment		Public Supply	30
Agricultural Flowpath Study		Domestic	10

[1] "Other" category includes aquaculture, commercial, dewatering, industrial, industrial cooling, institutional, irrigation, other, power, recreation, stock.

Table 5. Summary of site characteristics for wells and springs in the 12 carbonate aquifers or aquifer systems included in study.

Aquifer or aquifer system	Numbers of sites			Water levels, depth to water, feet below land surface				Total depth, feet below land surface				Depth to top of open interval, feet below land surface			
	Total number of sites	Number of springs	Number of wells	Number of sites	Minimum	Median	Maximum	Number of sites	Mimimum	Median	Maximum	Number of sites	Mimimum	Median	Maximum
Basin and Range	24	12	12	[1]14	[2]-185	3	760	12	278	890	1,979	12	122	455	1,197
Biscayne	65	0	65	63	1	5	28.6	64	10	45	165	63	5	24	165
Castle Hayne	32	0	32	25	3.67	10.32	32.18	32	22	94	350	30	12	71	350
Edwards-Trinity	125	6	119	69	5	178	447	104	80	385	2,700	91	0	201	2,700
Floridan	224	22	202	128	.82	28.54	179.53	201	33	170	840	180	20	88.5	800
Mississippian	66	3	63	62	1	22.22	72.66	63	14	53	157	61	6	33	157
Ordovician	40	9	31	70	5.18	27.02	106.2	31	22	125	300	30	6	20	300
Ozark Plateaus	188	90	98	48	.3	47.9	194	92	32	183	1,769	44	10	83	1,769
Piedmont	30	0	30	30	6.8	31.13	84.44	30	75	160	200	30	41	98	175
Prairie du Chien	30	0	30	30	13.38	78.96	239	30	66	177	380	30	12	144	380
Silurian-Devonian/Upper carbonate	33	0	33	25	11.45	58.58	222.4	33	32	225	750	20	18	143.5	507
Valley and Ridge	186	35	151	150	0	50.79	262	151	30	158	670	125	11	84	670

[1] Some improved springs have reported water levels.

[2] Negative water level is estimate of hydraulic head from a flowing well.

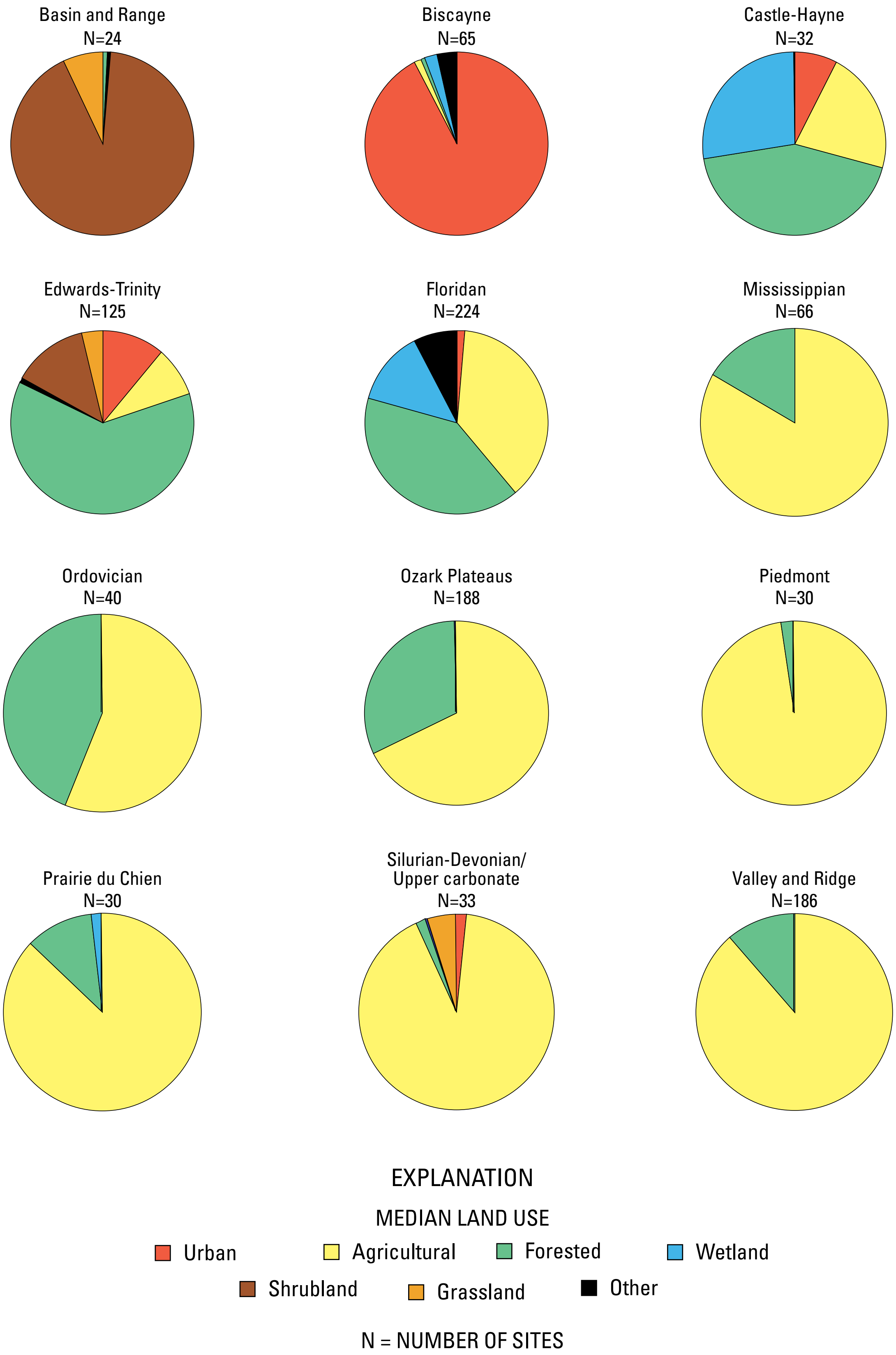


Figure 3. Median percentages of land use in a 1,640-foot radius around sampling sites for each of the 12 carbonate aquifers or aquifer systems (U.S. Geological Survey, 1999; Price and others, 2007).

into categories of agricultural, urban, forested, shrubland, or wetlands. The land-use data sets were processed to summarize the data for the 1,640-ft radius around each sampling site. Figure 3 illustrates the median value from a summary land use surrounding individual wells in each of the aquifers.

The mix of land-use types is an indication of potential sources of contamination in these aquifers. All but two of the aquifers are dominated by a mixture of agricultural and forested land use. The Biscayne aquifer is largely overlain by urban areas, and the Basin and Range aquifer is overlain largely by shrub land. The Mississippian, Silurian-Devonian/Upper carbonate, Ozark Plateaus, Piedmont, Prairie du Chien, and Valley and Ridge aquifers/aquifer systems are dominated by agricultural land use. For some data-analysis purposes, individual sampling sites were assigned a predominant land use using one of four general land-use designations (agricultural, urban, mixed land use, and undeveloped) used by Gilliom and others (2006). A sampling site with greater than 50 percent agricultural land use and less than 5 percent urban land use was determined to be predominantly agricultural. A sampling site with greater than 25 percent urban land use and less than 25 percent agricultural land use was determined to be predominantly urban. A sampling site with less than 25 percent agricultural and less than 5 percent urban land use was determined to be predominantly undeveloped. Any sampling site not meeting those three definitions was determined to have predominantly mixed land use, typically meaning a combination of both urban and agricultural land use with neither one dominant.

Population density is another factor considered as a possible indicator of contaminant sources. Population characteristics were also processed for the 1,640-ft radius for the 1990 census (U.S. Bureau of Census, 1990, 1991) and the 2000 census (GeoLytics, 2001; U.S. Bureau of Census, 2001) The Biscayne aquifer underlies areas with the highest median population density, followed by the Piedmont aquifer (fig. 4). The high population density of land overlying the Piedmont aquifer is interesting, because the Piedmont also has the highest median percentage of agricultural land, so it is a densely populated agricultural area. The area around the sampling sites in the Basin and Range aquifer is largely unpopulated.

The density of storage tanks can be a factor affecting the presence of VOCs. The density of the various categories of storage tanks is greatest in the Biscayne aquifer (table 6) (Vista Information Solutions, 1999). The median density of storage tanks in the other aquifers is zero. The maximum density value however for the storage tanks is much larger in most of the aquifers. The implications of this distribution are that most wells probably have little or no exposure to VOC contamination from storage-tank leaks, but a few sampling sites in most of the aquifers have a large number of storage tanks as potential sources of VOC contamination.

Another potential source of contamination is the estimated nitrogen input from various sources. These variables have been compiled for the 1,640-ft radius around sampling sites for atmospheric deposition of nitrogen and nitrogen from manure and fertilizer (Ruddy and others, 2006). Estimates of nitrogen from septic systems were made by using census data and equation (1).

$$\text{N-Septic} = \text{POPDENS} \times (\text{SEWSEP}/100) \times 0.785 \times 6.72 \text{ lb/yr-person} \times 0.454 \text{ kg/lb} \qquad (1)$$

where

N-Septic is the nitrogen input from septic systems, in kilograms per year,

POPDENS is the population density in the 1,640-ft radius, in persons per square kilometer (U.S. Bureau of Census, 1990, 1991),

SEWSEP is the percent of the housing units on septic systems (U.S. Bureau of Census, 1992)

0.785 is a conversion of the area of the 1,640-ft (500-m) radius to square kilometers,

6.72 lb/yr is an estimate for nitrogen production per person for human septic effluent (U.S. Environmental Protection Agency, 2002), and

0.454 is a conversion from pounds to kilograms.

Equation 1 probably results in a slight overestimation, because it assumes equal distribution of the population among areas with public sewer and septic systems; however, for the small area in the 1,640-ft radius, the overestimation can be ignored. The sum of nitrogen from atmospheric deposition, fertilizer, manure, and septic systems is used as the total nitrogen input in the buffer area. The median values for nitrogen sources and the distribution of the sources of nitrogen are given on figure 5. It is important to note that although the value of nitrogen from septic systems is relatively small, it is discharged beneath the ground, unlike the other sources, particularly fertilizer and manure, which are applied to the land surface and are subject to plant uptake. Septic systems typically are located in relatively close proximity to domestic wells, increasing the probability of a direct connection between the septic system and the well, especially in karst areas.

The estimated agricultural application rate of pesticides is shown for atrazine, simazine, and metolachlor (fig. 6). These herbicides are the three most frequently occurring compounds analyzed by the NAWQA Program (Gilliom and others, 2006) that have application-rate information available (Nakagaki and Wolock, 2005). The application estimates are based on agricultural uses only and do not account for nonagricultural applications. The application rates for atrazine are highest in the Silurian-Devonian/Upper carbonate and the Piedmont aquifers. For most aquifers, atrazine has the highest application rate of the three pesticides. Simazine application is typically much lower than the rate for the other two pesticides; the Piedmont and Prairie du Chien aquifers have the highest median simazine application rates. Metolachlor application rates are highest in the Silurian-Devonian/Upper carbonate and the Piedmont aquifer.

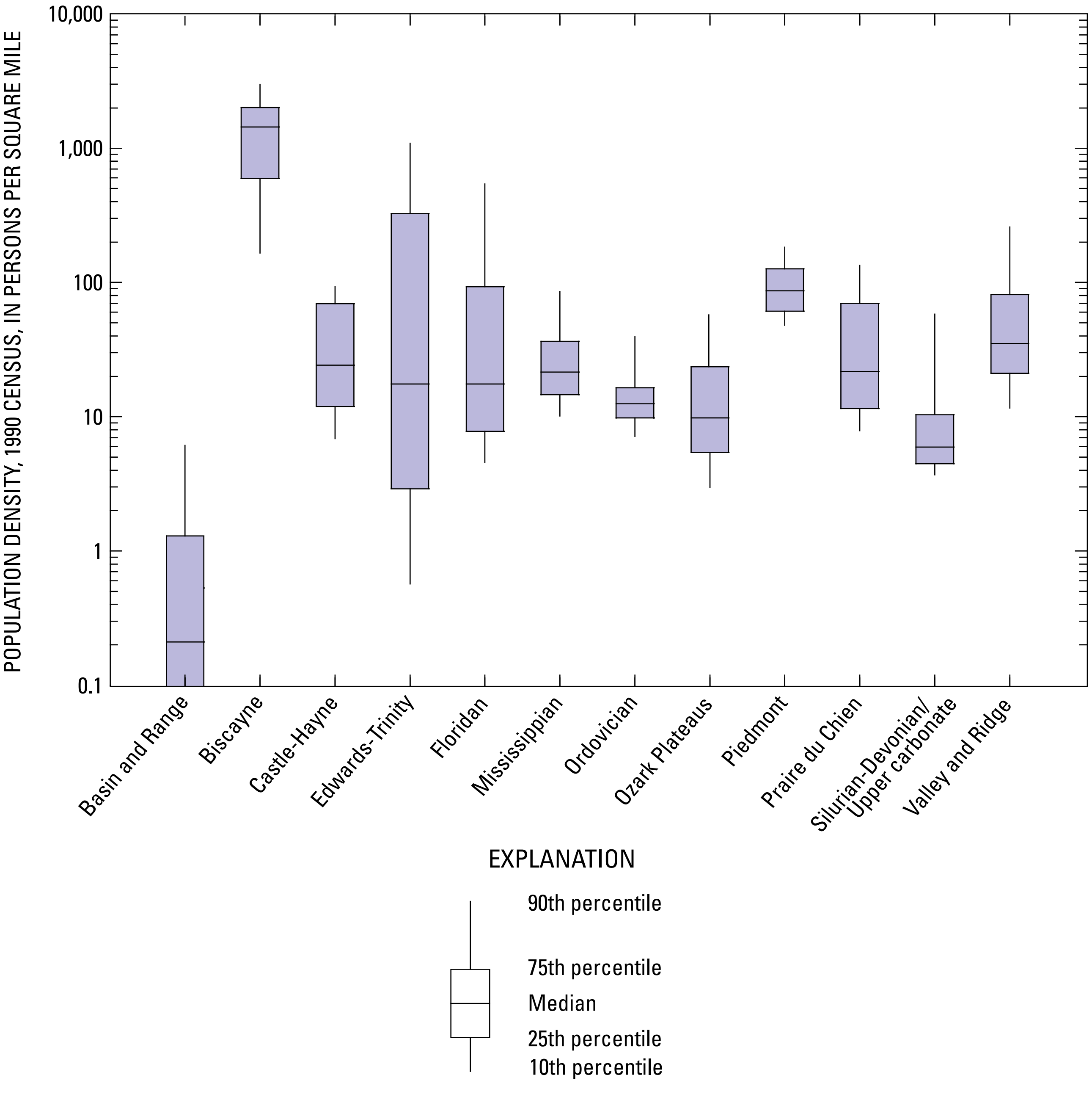


Figure 4. Median population density from 1990 census in 1,640-foot radius around sampling sites in the 12 carbonate aquifers or aquifer systems (U.S. Bureau of Census, 1990, 1991).

Table 6. Summary of underground storage tanks in 3,280-foot radius around sampling sites in the 12 carbonate aquifers or aquifer systems included in study.

[Storage tank data from Vista Information Solutions (1999); Total storage tanks does not equal the sum of the other columns; each column is calculated individually]

Aquifer or aquifer system	Number of sites	Statistic	Storage tanks in 3,280-foot radius			
			Underground	Leaking-underground	Above ground	Total storage tanks
Basin and Range	24	Minimum	0	0	0	0
		Median	0	0	0	0
		Maximum	0	0	0	0
Biscayne	65	Minimum	0	0	0	0
		Median	5	2	2	9
		Maximum	33	26	16	65
Castle Hayne	32	Minimum	0	0	0	0
		Median	0	0	0	0
		Maximum	7	4	0	11
Edwards-Trinity	125	Minimum	0	0	0	0
		Median	0	0	0	0
		Maximum	57	23	16	91
Floridan	224	Minimum	0	0	0	0
		Median	0	0	0	0
		Maximum	54	19	46	119
Mississippian	66	Minimum	0	0	0	0
		Median	0	0	0	0
		Maximum	18	4	1	23
Ordovician	40	Minimum	0	0	0	0
		Median	0	0	0	0
		Maximum	3	1	0	4
Ozark Plateaus	188	Minimum	0	0	0	0
		Median	0	0	0	0
		Maximum	25	10	2	35
Piedmont	30	Minimum	0	0	0	0
		Median	0	0	0	0
		Maximum	0	1	1	1
Prairie du Chien	30	Minimum	0	0	0	0
		Median	0	0	0	0
		Maximum	14	4	3	15
Silurian-Devonian/Upper carbonate	33	Minimum	0	0	0	0
		Median	0	0	0	0
		Maximum	3	2	0	5
Valley and Ridge	186	Minimum	0	0	0	0
		Median	0	0	0	0
		Maximum	24	27	12	63

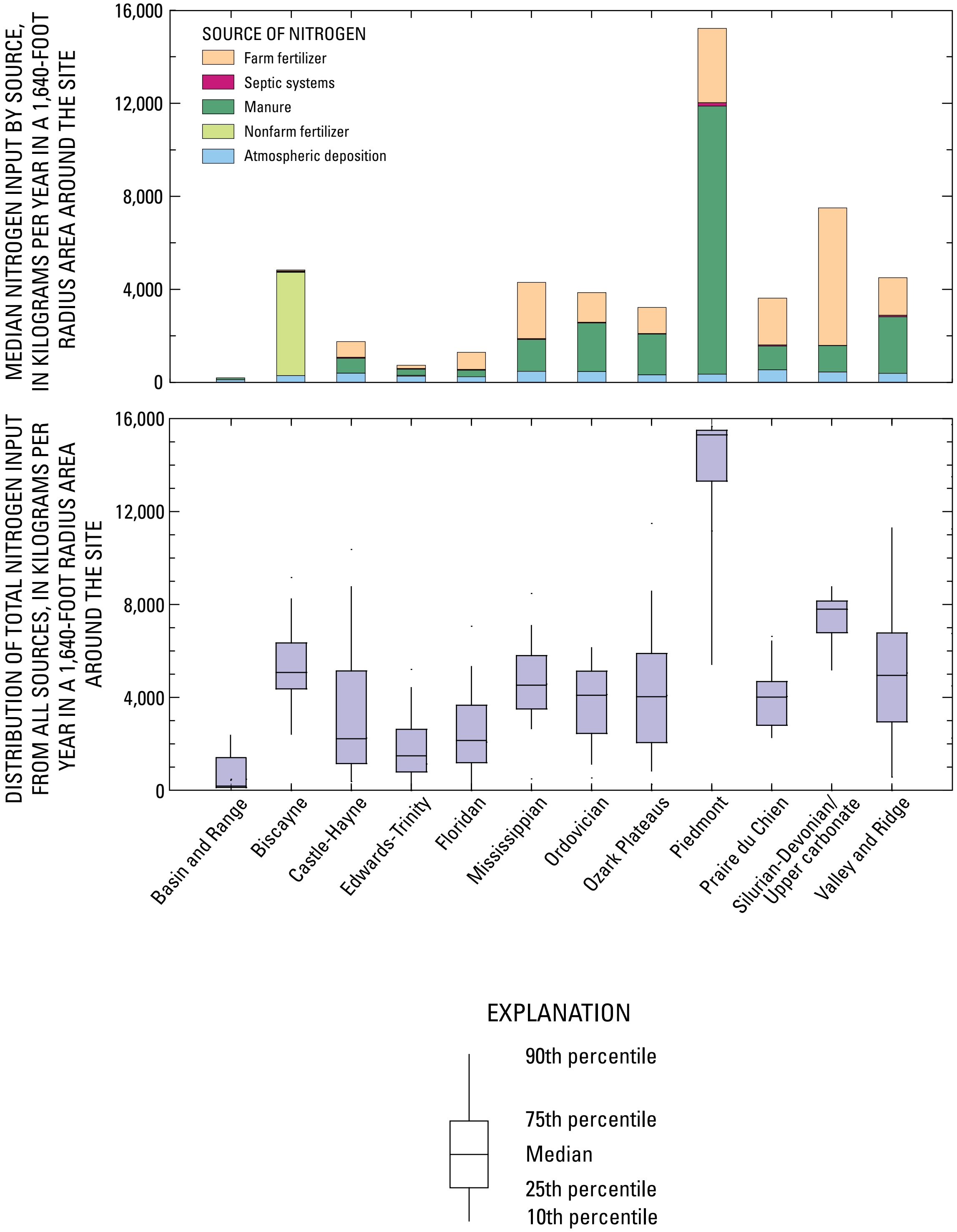


Figure 5. Median values for nitrogen from septic systems, manure, fertilizer, and atmospheric deposition, and distribution of total nitrogen input from all sources for the 1,640-foot radius around sampling sites in the 12 carbonate aquifers or aquifer systems.

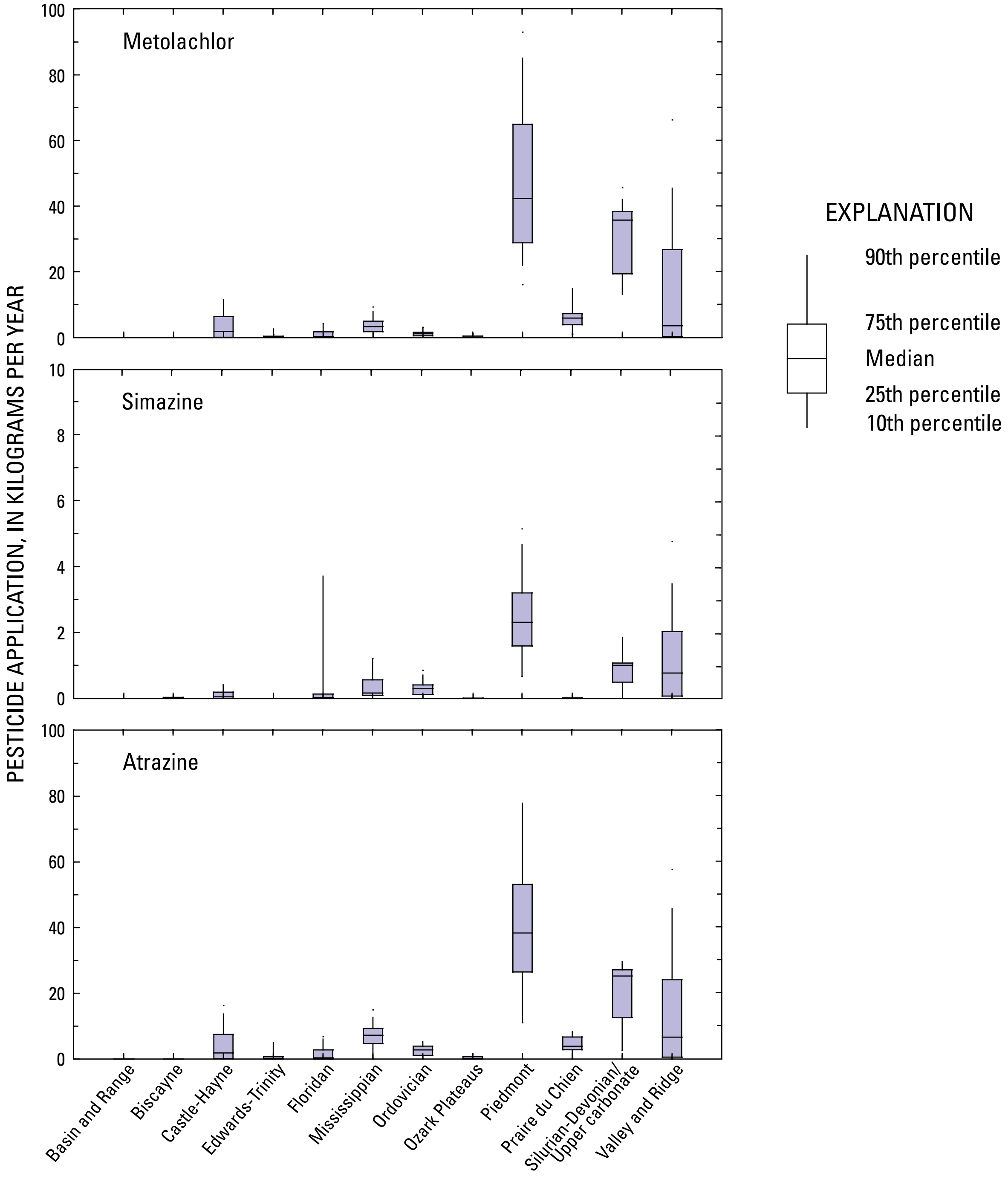


Figure 6. Median application rates of selected pesticides for the 1,640-foot radius around sampling sites in the 12 carbonate aquifers or aquifer systems (data for 1997 agricultural use only, Nakagaki and Wolock, 2005).

Fate and Transport Factors

In addition to potential sources of contaminants, data potentially related to movement of contaminants through the aquifer were compiled for each site. As with the source factors, the 1,640-ft radius was used, not necessarily as an indicator of the contributing area to the sampling site but as a representation of the conditions in the area. Transport factors relate to the physical movement of the water and contaminants. Fate factors are related to the potential transformation or degradation of the contaminant as it travels through the ground-water system.

Four hydrologic variables, Dunne overland flow, Horton overland flow, recharge, and runoff, are used as indicators of the predominant pathway for movement of water through the hydrologic system. These variables have been compiled as national data sets and are summarized in table 7. The overland-flow variables represent two mechanisms for generation of surface runoff. Dunne overland flow (Wolock, 2003a) is caused by saturation of surface areas. Horton overland flow (Wolock, 2003b) is a result of precipitation rates that exceed infiltration rates. Runoff (Gebert and others, 1987) is long-term average streamflow. Recharge was calculated by Wolock (2003c). The hydrologic variables illustrate the variation in climate; Dunne overland flow is highest in the humid southeast and lowest in the Basin and Range. The data set also illustrates the pathways that the water travels; Horton overland flow is highest in the Edwards-Trinity aquifer system, and recharge is greatest in the Mississippian, Piedmont, and Valley and Ridge aquifers. All of the hydrologic characteristics are considered transport factors.

Soils characteristics also are considered to be potential indicators of fate and transport of contaminants. Soils data from State Soil Geographic Data (STATSGO, U.S. Department of Agriculture, Natural Resources Conservation Service, 1994; Wolock, 1997) were compiled for the 1,640-ft radius. This data set includes characteristics such as permeability, soil thickness, organic-matter content, particle size, and hydrologic groupings (table 8). Particle size can have an effect on transport of contaminants. Smaller particle sizes, such as clay, are associated with slow infiltration rates; however, macropore flow and karst features allow bypassing of the soil profile in some cases. Hydrologic groups are ordered from A to D with group A having the lowest runoff potential and D having the highest runoff potential (U.S. Department of Agriculture, 2007). Soils overlying the Biscayne aquifer, Castle Hayne aquifer, and Floridan aquifer system are dominated by the sand fraction, whereas silt and clay are more prevalent for most of the other aquifers. Hydrologic group B, with moderate infiltration rates, was the predominant hydrologic group with the exception of the Basin and Range, Castle Hayne aquifers, and the Edwards-Trinity aquifer system, which were dominated by soil hydrologic group D. Organic matter was highest in the Biscayne aquifer, and slightly higher in the Silurian-Devonian/Upper carbonate and Prairie du Chien aquifers than in the rest of the aquifers. Organic matter is a factor that can affect the fate and transport of contaminants, whereas all the other soils characteristics are considered transport factors.

Table 7. Summary of median hydrologic characteristics for the 1,640-foot radius around sampling sites in the 12 carbonate aquifers or aquifer systems included in study.

[Dunne overland flow, Wolock (2003a); Horton overland flow, Wolock (2003b); Runoff, Gebert and others (1987); Recharge, Wolock (2003c)]

Aquifer or aquifer system	Dunne Overland Flow (percent)	Horton overland flow (percent)	Recharge (inches per year)	Runoff (inches per year)
Basin and Range	0.0	0.0	0.0	0.8
Biscayne	6.0	1.0	3.0	8.2
Castle Hayne	5.0	4.0	8.0	18.8
Edwards-Trinity	1.0	26.0	1.0	2.7
Floridan	6.0	2.0	5.0	11.3
Mississippian	5.0	7.0	9.0	25.8
Ordovician	4.0	4.2	8.0	25.3
Ozark Plateaus	3.6	6.0	4.0	11.3
Piedmont	2.7	4.0	9.0	18.0
Prairie du Chien	2.0	2.0	3.0	5.8
Silurian-Devonian/Upper carbonate	2.0	4.0	3.0	7.3
Valley and Ridge	3.0	3.2	9.0	19.1

Table 8. Summary of median soil characteristics for the 1,640-foot radius around sampling sites in the 12 carbonate aquifers or aquifer systems included in study.

[Soils data from U.S. Department of Agriculture, Natural Resources Conservation Service (1994); Wolock (1997); Soils drainage class compiled by Schwarz and Alexander (1995)]

Aquifer or aquifer system	Median particle size, percent			Hydrologic group, percent				Other soil properties							
	Sand	Silt	Clay	A (High infiltration)	B (Moderate infiltration)	C (Poor infiltration)	D (Very poor infiltration)	Organic matter (Percent)	Available water capacity (fraction)	Depth to seasonally high water table (feet)	Thickness of soil examined (inches)	Permeability (inches per hour)	Bulk density (grams per cubic centimeter)	Drainage class[1]	Slope (percent)
Basin and Range	39	42	16	3	44	4	30	0.5	0.1	6.0	60.0	3.9	1.4	3.0	6.0
Biscayne	91	6	3	0	74	0	10	3	.1	.5	22.9	12.6	1.5	6.0	.9
Castle Hayne	61	21	18	8	7	7	29	1	.1	1.3	60.0	6.9	1.4	5.5	1.2
Edwards-Trinity	12	45	45	0	3	28	61	1	.1	6.0	36.2	.8	1.4	3.0	4.8
Floridan	70	13	16	26	11	12	9	0	.1	3.3	60.0	6.9	1.5	4.4	1.9
Mississippian	12	48	37	0	75	19	6	0	.2	4.5	60.0	1.3	1.4	3.3	4.1
Ordovician	13	48	35	0	66	27	7	1	.1	5.8	53.6	1.7	1.4	3.1	6.9
Ozark Plateaus	20	42	39	0	58	30	4	1	.1	5.5	57.7	1.6	1.4	3.1	12.3
Piedmont	9	54	36	0	84	14	0	1	.2	5.3	69.6	1.4	1.4	3.2	6.1
Prairie du Chien	32	42	15	2	70	8	0	2	.2	4.7	60.0	3.1	1.5	3.5	5.5
Silurian-Devonian/Upper carbonate	29	44	25	0	73	2	0	2	.2	4.1	60.0	1.8	1.5	4.4	2.7
Valley and Ridge	13	50	36	0	84	14	0	1	.2	5.3	60.0	1.4	1.4	3.2	8.2

[1] Drainage class: 1= excessive, 2 = somewhat excessive, 3 = well drained, 4 = moderately drained, 5 = somewhat poorly drained, 6 = poorly drained, 7 = very poorly drained.

Methods

The following sections describe the methods used to collect data for this project. Results of the quality-assurance program are analyzed. Treatment of nondetections specific to this report and statistical methods used to analyze data are described. The programs used for analysis of geochemical data are described, and methods used to determine potential health affects of water-quality analyses are explained.

Sample Collection and Processing

The NAWQA Program has rigorous protocols to ensure that the data collected are of known and good quality. Water samples were collected using established USGS protocols and procedures to obtain a representative sample and avoid contamination (Koterba and others, 1995). All the networks were designed using a similar approach to well selection in order to ensure geographic coverage and random distribution of the sample locations. Water-quality samples were analyzed at the USGS National Water Quality Laboratory in Denver, Colo. The quality of the environmental data was determined by analysis of blanks and spikes that were collected as part of each study. Blanks were collected to quantify the probability of cross contamination from sample to sample. Contaminated blanks would indicate an increased possibility of a false-positive result, that is, a reported concentration for a contaminant where none is present, or the contaminant concentrations are greater than the true concentration. Spikes indicate the accuracy of the reported results. A spiked sample is prepared by adding a known quantity of a target analyte to a known volume of water collected from the aquifer. These differ from laboratory-control samples in that they are prepared in natural water and can indicate the effects of matrix interference and sample handling on recovery of the analyte.

Quality-Assurance Methods and Results

A summary of the results of the quality-assurance methods is provided to illustrate potential issues related to data quality. Blank samples indicate the ability to obtain samples that are not influenced by contamination from a previous site or other sources. Spikes indicate the ability to correctly quantify concentrations in environmental samples.

Nitrate Blank Sample Results

Nitrate was detected at a concentration of greater than 0.06 mg/L in 11 percent of the 130 blank samples; the maximum concentration detected in a blank was 0.21 mg/L. The contamination is likely because of the ubiquitous nature of nitrate in water samples and in the environment. Nitrate was detected in 76 percent of the 1,037 environmental samples. A ratio of environmental detection frequency to blank detection frequency of five or less is used as an indication that contamination should be considered in the interpretation of the environmental data (Martin and others, 1998). The ratio of contamination in blanks to the rate of detection in environmental samples was greater than five. When comparing the environmental concentrations to the maximum blank concentration, 86 percent of the samples with reported concentrations of nitrate were greater than the maximum concentration detected in any blank sample. A small number of environmental samples may be affected by low levels of contamination; this may have a minimal affect on the statistical analysis of the data.

Pesticide Blank and Spike Recovery Analysis

Pesticide contamination in blank samples was evaluated by using all the ground-water blanks from the 14 study units that were included in this study if the blank samples were collected during the year of sampling and in the carbonate network. The results of the blank samples also were compared to a national summary of field blanks conducted by the NAWQA Program (Martin and others, 1998). The number of blank samples for the study ranged from 97 to 102 for the 5 pesticides that were most frequently detected. The analysis of the blank data indicates a low percentage of samples affected by contamination and low concentrations in those samples. The overall number of samples with contaminated blanks was low (0 to 4 percent) and similar to the national level for all five of the pesticides analyzed. The number of detections of pesticides in blanks is higher for pesticides that are widely used and frequently detected (Martin and others, 1998).

The effect of contamination on the analysis of the environmental data depends on the relative frequency of detection of pesticides in blanks and environmental samples and the concentrations in blanks compared to the typical concentrations in environmental samples. Most blank samples did not have detectable concentrations of pesticides. The highest frequency of detection in blank samples was metolachlor, at 4 percent. For all the pesticides selected for detailed study except for metolachlor, the detection frequency of the pesticide in environmental samples was an order of magnitude greater than the detection frequency in blank samples, hence, these detection frequencies are higher than the ratio of five used by Martin and others (1998) as an indication that contamination should be considered in the interpretation of the environmental data for pesticides. Metolachlor, with a ratio of four, is slightly lower than the ratio of five suggested by Martin and others as an indicator that contamination may need to be considered when interpreting results. One other way to evaluate the blank data is to compare the highest concentration in the blanks to all detections in environmental samples. When comparing the highest concentrations detected in blank samples to the concentrations in environmental samples, between 68 and 100 percent of the detections in environmental samples had concentrations greater than the highest concentration detected in any blank. The highest concentrations in blanks were typically an order of magnitude lower than the concentrations detected in environmental samples. The combination of the detection-frequency ratios and the comparison of concentration ranges indicates that contamination is not a major factor to consider in the analysis of the environmental data for four of the five pesticides, and may be a factor affecting analysis of data for metolachlor.

Spiked samples were submitted to determine the ability of the sampling program to detect a pesticide when it is present and to determine the accuracy of that finding. The spike program consisted of adding 0.1 µg of a pesticide to a 1 L water sample to create a 0.1 µg/L solution. Because the spike was added to an environmental sample that may have already contained pesticides, the evaluation of spike recovery has to consider the measured concentration of pesticides in the unspiked environmental sample. For each spiked sample, there was a corresponding environmental sample. If a pesticide was detected in the environmental sample, the concentration from the environmental sample was subtracted from the value in the spiked sample, prior to comparing the measured value for the spike to the expected value for the spike (eq. 2). For a sample in which no pesticide was detected in the corresponding environmental sample, no such adjustment was necessary. The data were evaluated to determine false negatives (no pesticide detected when a known concentration was added to the sample) and the average recovery of the spike from the samples.

$$\text{Percent recovery} = 100 \times (C_{Spiked} - C_{Sample}) / C_{theoretical} \quad (2)$$

The analysis of the pesticide spike data indicates no false negatives; that is, the pesticides were detected in all the spiked samples. When calculating the percent recovery, the four of the five pesticides selected for the study were found to have recovery percentages (94 to 100 percent) that were similar to the recoveries in the rest of the NAWQA Program as summarized by Martin (1999). It is worth noting that deethylatrazine has a low percent recovery [52 percent in the current study, 31 percent in Martin (1999)]. The USGS National Laboratory reports all values for deethylatrazine as 'estimated' values because of this known poor recovery. Therefore, the concentrations of deethylatrazine used in this study are likely to be biased low. No attempt was made to adjust the concentrations of deethylatrazine during data analysis to account for this low recovery rate.

Volatile Organic Compound Computational and Blank Analysis

The minimum laboratory reporting levels (LRLs) for VOCs varied greatly between compounds and over time. Prior to April 1996, the minimum LRL was 0.2 µg/L for all VOCs except DBCP, which had a minimum LRL of 1.0 µg/L (Carter and others, 2008). Of the 793 samples analyzed for VOCs, 154 samples (19 percent) were collected prior to April 1996, including data from 5 of the aquifers/aquifer systems—53 samples in the Valley and Ridge, 49 samples in the Ozark Plateaus, 30 samples in the Piedmont, 20 samples in the Floridan, and 2 samples in the Castle Hayne. For the Ozark Plateaus and Piedmont, all of the VOC data were collected prior to April 1996, and for the Valley and Ridge, 45 percent of the data were collected prior to April 1996. In order to compare samples at concentrations less than 0.2 µg/L, a subset of samples would have to be used and comparisons could only be made between 10 aquifers. Also, the reporting levels varied among individual compounds after April 1996. The use of 0.2 µg/L as an assessment level for calculation of detection frequencies for VOCs allowed the comparison of VOC compounds for all 793 samples and among all 12 aquifers.

The detection of some VOCs in equipment and field blank samples indicated potential for contamination of environmental samples during the sample-collection process. VOCs with the highest detection frequencies in blank samples at the 0.2 µg/L assessment level were acetone (19 percent of samples), ethylmethylketone (8 percent), toluene (6 percent), carbon disulfide (6 percent), tetrahydrofuran (5 percent), tetrachloroethene (4 percent) and 1,2,4-trimethylbenzene (4 percent) and chloroform (2 percent). At the 0.2 µg/L assessment level, however, these VOCs were found to have a low probability (less than 0.1 percent) of remaining contamination after the native water rinsing that followed field-blank collection and preceded the collection of each environmental sample (John Zogorski, U.S. Geological Survey, written commun., 2008). This native water rinsing has been shown to be highly effective in reducing the potential carryover of contaminants from equipment and sample lines to ground-water samples (Taglioli and others, 2001). Thus, the high frequency of detection of some VOCs in blank samples overestimates the potential occurrence of cross-contamination of environmental samples.

Statistical Methods Used to Analyze Water-Quality Data

Interpretation of the water-quality data included use of several statistical methods. Descriptive and nonparametric statistics were used in this report to summarize and compare the concentrations of field characteristics, major and trace inorganic constituents, nutrients, pesticides, VOCs, and dissolved organic carbon. Methods included comparisons of water quality among groupings using the Wilcoxon rank-sum test and the nonparametric Tukey's test, comparisons of groupings where both variables were categorical using contingency tables, comparison of water quality to continuous explanatory variables using the Spearman's rank correlation, and comparison of water quality to explanatory variables using discrete categories using logistic regression. For all statistical tests, an alpha value of 0.05 was used. An alpha value of 0.05 indicates a 95-percent probability that the statistical result is not due to random chance. Thus, a probability or p-value less than or equal to 0.05 indicates a statistically significant result.

Assessment Levels

Data-analysis methods were chosen to account for the fact that, in some cases, a large percentage of the data had concentrations less than the LRL. The term ‘laboratory reporting level’ used herein refers to the value that differentiates a nondetection from any reported quantified value by use of a less than ‘<’ remark. An estimated or ‘E’ value refers to values that are reported where the compound was definitively detected in a sample, but the value has a greater degree of uncertainty because it is approaching the lower analytical capability of the instrumentation. ‘E’ values are typically less than the LRL. The term ‘assessment level’ refers to assigning a common level for analyzing data for a constituent or a group of constituents. An assessment level is used to make consistent comparisons among constituents or studies using multiple reporting levels.

For some constituents, LRLs were constant; therefore, nonparametric statistical analyses using ranks accounted for the nondetects by setting the concentration of all nondetects to a single value below the LRL prior to ranking. In cases where there were multiple LRLs throughout the study period, other considerations had to be taken into account. For example, in a ranking scheme, a value of < 0.2 µg/L cannot be compared to a value of < 0.001 µg/L. The only conclusion that can be made about these two values is that both are < 0.2 µg/L. Therefore, in a data set in which there were two or more LRLs, all data, including quantified detections at values less than the highest LRL, were analyzed using an assessment level based on the higher reporting limit. In the previous example, the higher LRL of 0.2 µg/L would be used as the assessment level. VOCs were handled in this way. The other option in analyzing these data is to analyze the subset of data that has the lower reporting limit and not use the data with the higher reporting limit. In some cases, the assessment level of ‘all detections’ is used. This allows the most data to be retained but creates a bias in that areas with the higher reporting limit appear to have fewer detections, which may or may not be the case.

For analysis of pesticides, the handling of values below the LRL was different and is based on the method used by Gilliom and others (2006). Each pesticide sample includes a result and a remark code. If the remark field is empty, the value in the result field is a quantified detection at a concentration greater than the LRL. If the remark field is a less than (“<”), the value is less than the LRL, indicating that there was no definitive analytical evidence for the occurrence of the compound at a measurable concentration. If the remark field is an ‘E,’ the value is an estimated value, as previously defined. The value associated with a sample having a “<” remark is the LRL for that pesticide. LRLs varied during the period of 1993–2005; however, for a given year, each pesticide typically had a common LRL. If a sample had a “<” remark, and a value greater than the common LRL, this indicates the reporting limit was intentionally raised for that particular sample because of issues such as sample dilution prior to analysis. Cases with a raised LRL were not included in the data analysis. When ranking pesticides for a statistical test, all nondetects are assigned a rank lower than the lowest reported or ‘E’ value, and results with ‘E’ values and quantified detections are assigned ranks on the basis of their reported value, a method used in other national assessments of pesticides (Gilliom and others, 2006).

Wilcoxon Rank-Sum, Kruskal-Wallis, and Nonparametric Tukey’s Test

The Wilcoxon rank-sum test was used to test for differences in values or concentrations between two groups of data (SAS Institute, Inc., 1989a, 1989b; Helsel and Hirsch, 2002, p. 118). A probability, or p-value, of less than 0.05 was used as an indicator of a significant difference.

When comparing differences in the values or concentrations of several independent groups, the Kruskal-Wallis test was used (SAS Institute, Inc., 1989a, 1989b; Helsel and Hirsch, 2002, p. 159). If the Kruskal-Wallis test indicated differences among the groups, the nonparametric Tukey’s test (SAS Institute, Inc., 1989a, 1989b; Helsel and Hirsch, 2002, p. 200) was used to determine the ordering of the groups. This test assigns a common letter to groups that are not statistically different. A p-value of 0.05 was used as an indicator of significant differences for this test as well. Because the data are not normally distributed, the Tukey’s test was performed on the ranks of the values rather than the values themselves and the results refer to mean ranks rather than medians.

Contingency Tables

When analyzing data where both the explanatory and response variables are categorical, contingency tables are used. An example of this would be when a compound is either detected or not detected, and the comparison category is a grouping variable. This test can determine whether the number of detections of the compound is related to the comparison group (Helsel and Hirsch, 2002, p. 378). A matrix analysis is conducted to determine whether or not the distribution of detections differs among groups. P-values of less than 0.05 indicate a 95-percent probability that the differences among groups are not due to random chance.

Spearman’s Rank Correlation

In cases where there is a continuous explanatory variable and a continuous response variable, a Spearman’s rank correlation test (Helsel and Hirsch, 2002, p. 217) was conducted. A continuous variable can have any value within a certain range. An example of this type of comparison is the comparison of the application rate of fertilizer (continuous explanatory variable) to the concentration of nitrate (continuous response variable). The Spearman’s rank correlation method uses ranks of data to determine a monotonic relation between the explanatory variable and the response variable. The statistics produced by the Spearman’s rank correlation are the Spearman’s rho coefficient and the p-value. P-values of less than 0.05 indicate a 95-percent confidence that a monotonic relation exists between the explanatory variable and the response variable. That is, an increase in the explanatory variable is correlated to an increase in the response variable. The values of Spearman's rho range from -1 to 1; larger absolute values indicate a stronger relation. The sign of Spearman's rho is an indicator of whether the relation has a positive or negative slope. Negative values of Spearman's rho are referred to as inverse correlations in this report. The Spearman's rank correlation was used for interpreting concentrations of nitrate and pesticides.

Logistic Regression

A discrete variable has values that are limited to specific categories, such as greater than or less than a specified threshold. In cases where the response variable is discrete, logistic regression can be used to determine the probability of the response variable exceeding a threshold. An example of this would be testing whether increases in pesticide application rate causes an increased probability of that pesticide exceeding the detection limit. The probability of an event occurring is defined by equation 3:

$$p = \frac{e^{(\beta_0 + \beta_1 x_1 + \beta_2 x_2 + ... + \beta_i x_i)}}{1 + e^{(\beta_0 + \beta_1 x_1 + \beta_2 x_2 + ... + \beta_i x_i)}} \quad (3)$$

where β_0 is the intercept, x_1 is explanatory variable 1, β_1 is the slope coefficient of x_1, x_2 is explanatory variable 2, β_2 is the slope coefficient of x_2, x_i is explanatory variable i, β_i is the slope coefficient of *xi* (Helsel and Hirsch, 2002, p. 396). Analyzing the results of logistic regression is more complicated than analyzing the results of linear regression. Statistics that are important are 1) the overall significance of the model, 2) the value of explanatory variables and corresponding p-value, 3) the Hosmer-Lemeshow results, 4) the generalized r-square, 5) the maximum rescaled r-square, and 6) the percent concordance.

The overall significance of the model, indicated by p-values less than 0.05, indicates that the model with explanatory variables is better at predicting the probability of an event occurring than an intercept-only model. The significance of the explanatory variables, indicated by p-values less than 0.05, indicates that a specific explanatory variable improves the model in its ability to predict the probability of an event occurring. The Hosmer-Lemeshow Goodness-of-Fit statistic (Hosmer and Lemeshow, 1989) tests whether or not the outcomes predicted by the model are significantly different than the outcomes from the original data. P-values of a Hosmer-Lemeshow test that are less than 0.05 indicate the model predictions and the data are significantly different; however, the model predictions should fit the data. Therefore, p-values less than 0.05 indicate a poor model fit. There is no r-square value that can be produced by the logistic regression model that is identical to the r-square value from linear regression; however, some substitutes for the r-square value have been calculated. The generalized r-square value (Cox and Snell, 1989) is based on maximizing the log-likelihood and is a generalized method of estimating an r-square value. The maximum-rescaled r-square value (Nagelkerke, 1991) is another method that approximates the linear-regression r-square. Although neither of these statistics can be interpreted as the percentage of variance explained by the model, they can be used as comparisons of one model to another.

The terms concordance and discordance also are used in describing results of logistic regression. These statistics are calculated by comparing every possible combination of data points where one event is equal to '1' and the other event is equal to '0.' If the predicted probability for the case with event equal to '1' is higher than the predicted probability for the case with the event equal to '0,' that pair is concordant. The opposite case would be discordant, and ties are counted; however, concordance is the primary statistic used in this report.

Analysis of Geochemical Data

The geochemical program Aquachem was used to construct Piper diagrams and determine major-ion water types using concentrations of major ions (Waterloo Hydrogeologic Inc., 2005). The program PHREEQCI was used to determine calcite and dolomite S.I. (Charlton and Parkhurst, 2002; Parkhurst and Appelo, 1999).

Drinking-Water Standards and Health-Based Screening Levels

Concentrations of contaminants are compared to Maximum Contaminant Levels (MCLs) or Secondary Maximum Contaminant Levels (SMCLs) for regulated compounds (U.S. Environmental Protection Agency, 2006) and to USGS Health-Based Screening Level (HBSL) concentrations for unregulated compounds. MCLs are enforceable standards determined on the basis of potential human-health effects, and represent the highest level of a contaminant that is allowed in drinking water used for public supply. SMCLs are non-enforceable Federal guidelines regarding cosmetic effects (such as tooth or skin discoloration) or aesthetic effects (such as taste, odor, or color) of drinking water. HBSLs are estimates of benchmark concentrations used to evaluate water-quality data in a human-health context. They were developed collaboratively by the USGS, U.S. Environmental Protection Agency, New Jersey Department of Environmental Protection, and Oregon Health & Science University (Toccalino and others, 2004). HBSLs are not regulatory standards and are not enforceable; however, HBSLs can be used as management tools to help prioritize contaminants that may merit further study or monitoring and to provide an early indication of contaminant concentrations of potential human-health concern in water resources (Toccalino and others, 2006).

Water-Rock Interactions and Ground-Water Geochemistry

In carbonate aquifers, the dissolution of aquifer minerals, such as calcite and dolomite, is an important geochemical process that controls the major-ion composition and pH of ground water. Assessment of dominant-ion water types and ion ratios can provide quantitative information about mineral-water interactions. In addition, the determination of saturation indices with respect to certain minerals (calcite, dolomite, and gypsum) using thermodynamic models is useful to gain an improved understanding of the factors that influence ground-water geochemistry (Stumm and Morgan, 1981). Analysis of concentrations of dissolved oxygen in ground water aid in determining the oxidation and reduction reactions that play an important role in controlling many chemical processes in ground water, such as the speciation of various naturally occurring elements and the transformation and biodegradation of anthropogenic compounds such as nitrate, pesticides, and VOCs. Examination of concentrations of major ions, pH, and dissolved solids with depth in the aquifer can provide a means to assess the importance of ground-water residence time as a controlling factor on major-ion geochemistry.

Major Ions, Dissolved Solids, pH, and Mineral Saturation Indices

Previous studies of carbonate aquifers have shown that dissolution of aquifer minerals is a major geochemical process that controls the major-ion composition and pH of ground water (Sprinkle, 1989; Thomas and others, 1996; Adamski, 2000). However, water from the 12 carbonate aquifers showed considerable variability in pH, major-ion composition, and concentrations of dissolved solids (table 9). The median pH value for all samples was 7.1, and medians ranged from 6.54 in the Mississippian aquifer to 7.4 in the Floridan aquifer system and the Prairie du Chien aquifer (medians were 7.3 and 7.35 in the Basin and Range and Castle Hayne aquifers). The median bicarbonate concentration in all samples was 249 mg/L—the lowest median bicarbonate concentration was 121 mg/L in the Mississippian aquifer, and the highest median concentration was 336 mg/L in the Silurian-Devonian/Upper carbonate aquifer (table 10). Median concentrations of calcium and magnesium in all samples were 63.7 and 10.4 mg/L, respectively. Median concentrations of calcium ranged from 27.8 mg/L in the Mississippian aquifer to about 99.8 mg/L in the Biscayne aquifer, and median magnesium concentrations ranged from 2.2 mg/L in the Castle Hayne aquifer to 25 mg/L in the Silurian-Devonian/Upper carbonate aquifers and 25.5 mg/L in the Prairie du Chien aquifers (table 10). The median concentration of sulfate for all samples was 9.4 mg/L, and median concentrations in individual aquifers ranged from 0.3 mg/L in the Castle Hayne aquifer to 54.8 mg/L in the Basin and Range aquifer. Concentrations of dissolved solids ranged from 7 to 5,370 mg/L; the median concentration was 269 mg/L (table 10). Median concentrations of dissolved solids in individual aquifers ranged from 139 mg/L in the Mississippian aquifer to 391.5 mg/L in the Piedmont and 417.8 mg/L in the Basin and Range aquifers (table 10).

Comparison of major-ion concentrations and pH values to MCLs or SMCLs (U.S. Environmental Protection Agency, 2006) indicated that few samples exceeded MCLs or SMCLs for pH, chloride, fluoride, sulfate or dissolved solids. Comparisons were made for data from all wells and for data from drinking-water wells (domestic and public supply wells). Fluoride was the only major ion or water property for which an MCL has been established, and less than 1 percent of wells (all wells or drinking-water wells) exceeded the MCL of 4 mg/L (table 11). About 13 percent of all wells and nearly 16 percent of drinking-water wells had fluoride concentrations within 10 percent of the MCL. Dissolved solids concentrations exceeded the SMCL of 500 mg/L in about 7 percent of wells and nearly 8 percent of drinking-water wells. For pH, about 6 percent of samples from all wells and about 4 percent of drinking-water wells had values outside the SMCL range of 6.5–8.5. SMCLs for chloride (250 mg/L), fluoride (4 mg/L), and sulfate (250 mg/L) were exceeded in less than 3 percent of wells (all wells or drinking-water wells).

As one would expect from the dissolution of calcite and dolomite in the selected carbonate aquifers, most water samples contained calcium, bicarbonate, and magnesium as dominant ions (fig. 7). The most commonly occurring major-ion water types among all samples were calcium-bicarbonate (42 percent of the samples) and calcium-magnesium-bicarbonate (40 percent). About 18 percent of samples were classified as a mixed water type, indicating more than one cation or anion was dominant with the exception of Ca-Mg-HCO_3 and Ca-Mg-SO_4. One percent of samples had sodium-bicarbonate as dominant ions and 0.2 percent had sodium-chloride as dominant ions.

Calcium-bicarbonate was the dominant major-ion water type in water from the Biscayne (71 percent of 62 samples), Castle Hayne (72 percent of 30 samples), and Floridan (61 percent of 204 samples) aquifers/aquifer systems (fig. 8). Calcium-magnesium-bicarbonate was the dominant major-ion water type in the Piedmont (63 percent of 30 samples), Prairie du Chien (100 percent of 29 samples), Silurian-Devonian/Upper carbonate (64 percent of 33 samples), and Valley and Ridge aquifers (63 percent of 186 samples), reflecting the presence of dolomite in these aquifer systems. Water samples from the Edwards-Trinity, Mississippian, Ordovician, and Ozark Plateaus aquifers/aquifer systems did not have one dominant water type, but three water types were noted in similar amounts—calcium-bicarbonate, calcium-magnesium-bicarbonate, and mixed water types, reflecting the diverse mineralogy and hydrogeology present in these systems. The Basin and Range aquifer samples were the only samples where the dominant water type was not calcium-bicarbonate or calcium-magnesium-bicarbonate—75 percent of 24 samples were classified as mixed water type.

Table 9. Descriptive statistics for well depths and selected inorganic constituents in 12 carbonate aquifers or aquifer systems, 1993–2005.

[Concentrations are expressed as milligrams per liter, except as noted; µg/L, micrograms per liter; S.I., saturation index]

Variable	Number of observations	Median	25th percentile	75th percentile	Maximum
Well depth, feet	842	160	98.0	270.0	2,700
Temperature, degrees Celsius	1,033	17.4	14.1	23.1	53.3
Specific conductance, microsiemens per centimeter	1,023	469	309	610	9,180
Dissolved solids	1,027	269	183	357	5,370
Dissolved oxygen	1,029	4.3	.3	7.1	20.5
pH, standard units	1,034	7.1	6.9	7.4	9.0
Bicarbonate	980	248.7	166.5	315.2	690.0
Calcium	1,030	63.7	44.0	85.0	550.0
Magnesium	1,030	10.4	3.3	21.0	270.0
Sodium	1,030	5.4	2.6	11.7	1,763
Potassium	1,030	1.2	.7	2.1	117.2
Sulfate	1,027	9.4	3	23	2,100
Chloride	1,027	8.0	3.7	17	2,747
Silica	1,030	9.8	8.1	12.3	68.9
Fluoride	1,027	.1	.1	.2	5.5
Strontium, µg/L	425	220.0	92.3	606.1	43,950
Barium, µg/L	603	25.0	10.2	42.2	1,000
Boron, µg/L	217	13.9	9.5	22.4	1,388
Bromide	992	.04	.02	.08	9.50
Nitrate as nitrogen	1,037	.9	.06	2.6	25.0
Organic carbon	1,006	.4	.3	.9	36.0
Radon, picocuries per liter	735	360.0	160.0	630.0	5,994
S.I.-Calcite	973	-.07	-.26	.06	.65
S.I.-Dolomite	973	-.74	-1.39	-.24	1.29
S.I.-Gypsum	1,025	-2.63	-3.26	-2.19	-.06
Calcium to magnesium molar ratio	1,029	3.20	1.50	10.60	80.04
Charge balance error, percent	978	-8.15	-10.01	-6.00	56.15

Table 10. Numbers of samples and median values for well depths and selected inorganic constituents by aquifer, in 12 carbonate aquifers or aquifer systems, 1993–2005.

[Concentrations are expressed as milligrams per liter, except as noted; µS/cm, microsiemens per centimeter; µg/L, micrograms per liter; S.I., saturation index; –, no data]

Constituent	Basin and Range	Biscayne	Castle-Hayne	Edwards-Trinity	Floridan	Mississippian	Ordovician	Ozark Plateaus	Piedmont	Prairie du Chien	Silurian-Devonian/ Upper carbonate	Valley and Ridge
Number of samples	24	65	32	125	215	66	40	185	30	30	33	186
Well depth, feet	890	45	94	385	170	53	125	183	160	177	225	158
Temperature, degrees Celsius	27.5	25.2	18.2	23.4	22.8	17.7	16.3	15.0	13.1	12.3	12.1	13.5
Specific conductance, µS/cm	679.5	624.0	406.5	556.0	305.0	235.0	514.5	391.0	654.0	555.5	589.0	526.0
Dissolved solids	417.8	379.0	264.8	323.0	189.0	139.0	306.0	218.0	391.5	300	341.0	295.1
Dissolved oxygen	2.65	.14	.13	5.95	.7	5.20	1.90	6.65	5.95	.92	.10	7.10
pH, standard units	7.30	6.80	7.35	6.98	7.4	6.54	6.95	7.12	7.30	7.38	7.15	7.20
Bicarbonate	258.0	303.5	245.0	301.8	160.4	121.0	279.5	229.0	257.0	300.7	336.0	271.5
Calcium	53.8	99.8	69.5	81.0	47.0	27.8	69.7	56.0	74.5	66.5	75.0	68.2
Magnesium	20.6	3.9	2.2	15.0	3.8	3.3	8.1	8.1	24.5	25.5	25.0	18.0
Sodium	42.4	21.4	7.3	8.5	4.6	2.1	5.0	3.6	5.7	4.3	8.6	3.8
Potassium	8.0	2.4	1.5	1.1	.6	.5	1.6	1.0	2.0	1.35	2.1	1.5
Sulfate	54.8	17.0	.3	16.9	3.5	2.7	25.6	5.6	37.5	16	24.0	14.0
Chloride	39.6	32.8	8.0	14.0	6.1	3.4	5.6	5.4	18.5	2.95	2.3	9.0
Silica	22.2	6.8	23.1	12.0	12.2	8.5	8.0	9.6	9.4	19	12.0	8.6
Fluoride	.69	.24	.17	.20	.2	.10	.21	.10	.10	.2	.50	.10
Strontium, µg/L	606.3	911.5	209.4	316.2	95.7	–	–	–	–	–	–	200.0
Barium, µg/L	67.0	20.0	11.4	38.0	7.0	19.0	22.8	41.0	–	46.0	–	63.3
Boron, µg/L	230.1	–	16.0	50.2	13.2	–	–	–	–	–	–	7.0
Bromide	.11	.07	.05	.10	.03	.02	.02	.04	.03	.04	.04	.03
Nitrate as ntirogen	.31	.05	.06	1.23	.06	1.35	.44	1.10	11.00	.12	.05	3.50
Organic carbon	.30	11.00	2.51	.40	.42	.40	.83	.40	.30	.60	1.20	.30
Radon, picocuries per liter	482	440	104	168	184	579	222	280	710	410	290	481
S.I.-Calcite	.08	-.15	.08	-.07	-.01	-1.19	-.29	-.23	.10	.21	-.08	-.06
S.I.-Dolomite	.14	-1.34	-1.07	-.56	-.82	-3.01	-1.11	-1.38	-.23	.23	-.46	-.66
S.I.-Gypsum	-2.03	-2.25	-4.21	-2.33	-3.26	-3.39	-2.23	-2.89	-2.00	-2.42	-2.16	-2.39
Calcium-magnesium molar ratio	1.51	14.49	20.55	3.03	7.96	3.19	2.94	3.85	1.78	2.48	1.72	1.87
Charge balance error, percent	-6.54	-8.59	27.92	-8.78	-6.81	-8.63	-8.97	-10.29	-6.99	-4.89	-7.85	-8.42

Table 11. Comparison of water properties and concentrations of major ions in wells with human-health benchmarks and non-health guidelines for drinking water, in 12 carbonate aquifers or aquifer systems, 1993–2005.

[mg/L, milligrams per liter; –, not applicable; drinking-water wells includes domestic and public supply well types]

Property or major ion	Number of wells	Type of drinking-water regulation		Wells exceeding drinking-water regulation					
		Maximum contaminant level[1]	Secondary maximum contaminant level[2]	Maximum contaminant level		Ten percent of maximum contaminant level		Secondary maximum contaminant level	
				Number	Percent	Number	Percent	Number	Percent
Water Properties									
pH, in standard units	1,041	–	6.5 - 8.5[3]	–	–	–	–	64	6.1
(pH in drinking-water wells)	665							27	4.1
Major Ions, in mg/L									
Chloride	1,033	–	250	–	–	–	–	9	.9
(Chloride in drinking-water wells)	662							4	.6
Fluoride	1,033	4	2	3	0.3	138	13.4	22	2.1
(Fluoride in drinking-water wells)	662			3	.5	103	15.6	17	2.6
Sulfate	1,033	–	250	–	–	–	–	21	2.0
(Sulfate in drinking-water wells)	662							15	2.3
Dissolved solids (DS)	1,033	–	500	–	–	–	–	74	7.2
(DS in drinking-water wells)	662							51	7.7

[1] Maximum contaminant levels are National Primary Drinking Water Regulations (NPDWRs or primary standards) established by the U.S. Environmental Protection Agency (USEPA) that are legally enforceable standards that apply to public water systems. Primary standards protect public health by limiting the levels of contaminants in drinking water (U.S. Environmental Protection Agency, 2006).

[2] Secondary maximum contaminant levels are National Secondary Drinking Water Regulations (NSDWRs or secondary standards) established by USEPA that are non-enforceable guidelines regulating contaminants that may cause cosmetic effects (such as skin or tooth discoloration) or aesthetic effects (such as taste, odor, or color) in drinking water. USEPA recommends secondary standards to water systems but does not require systems to comply (U.S. Environmental Protection Agency, 2006).

[3] Samples with pH less than 6.5 or pH greater than 8.5 exceed the SMCL

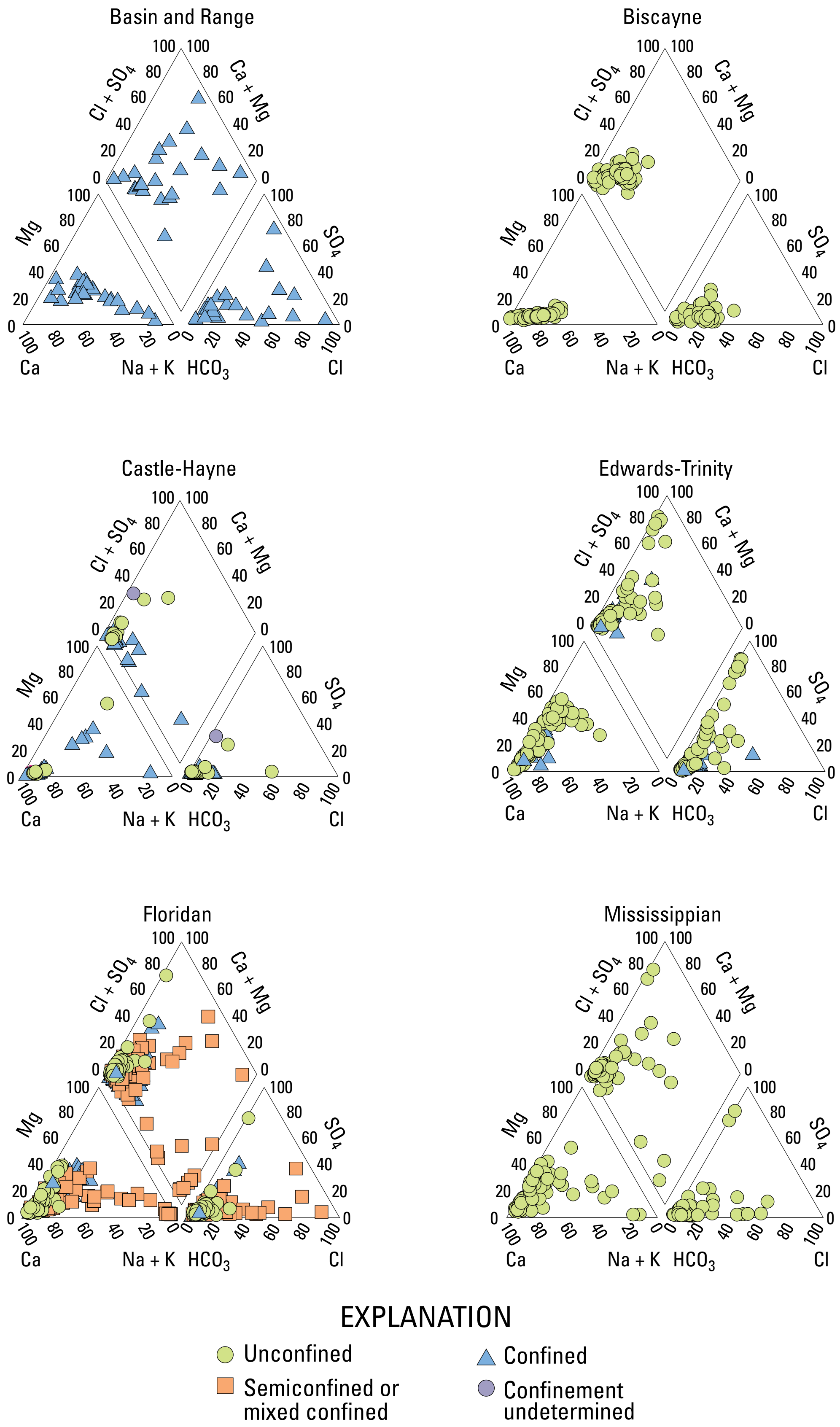


Figure 7. Piper diagrams for 12 carbonate aquifers or aquifer systems, 1993–2005.

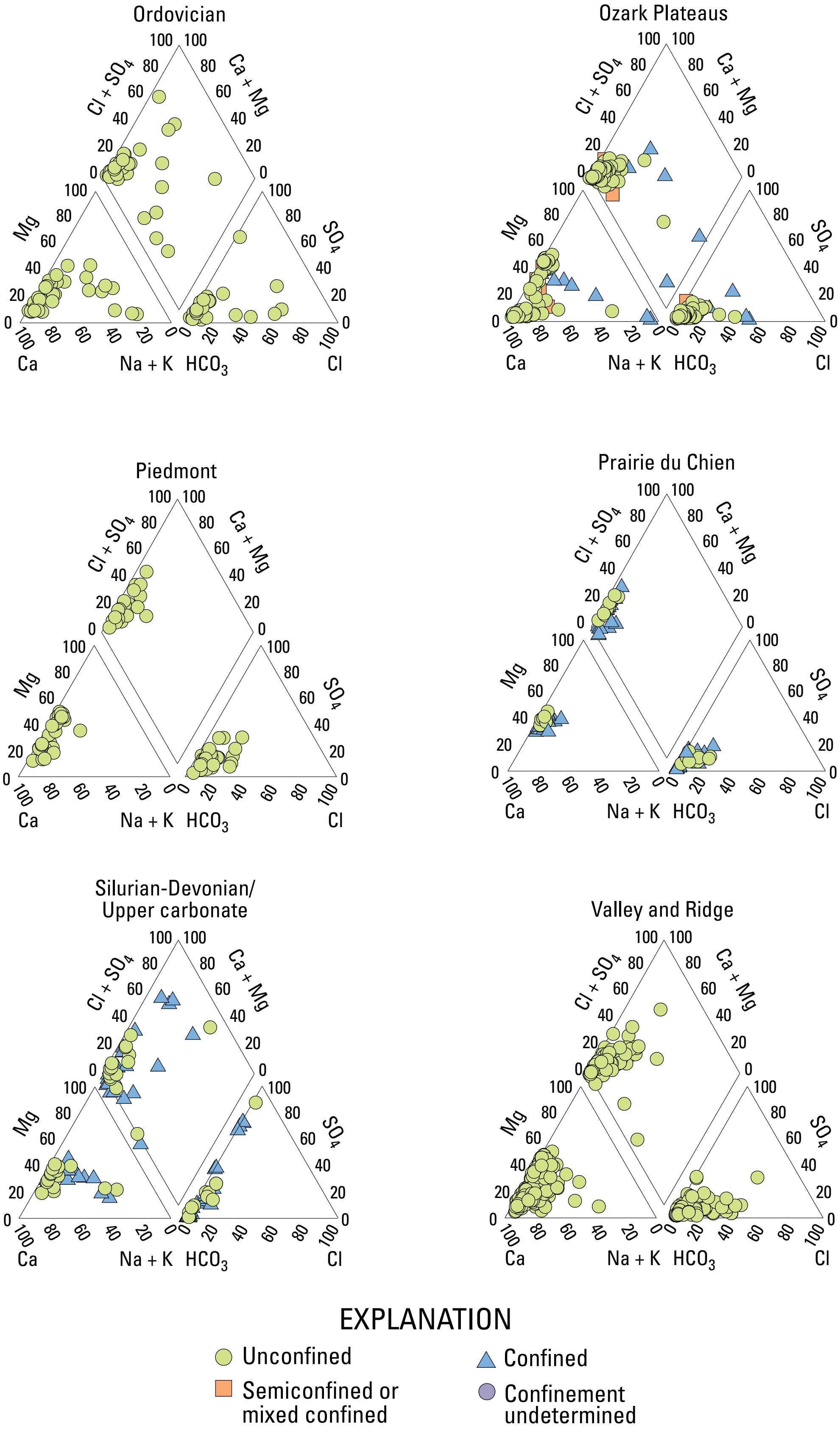


Figure 7. Piper diagrams for 12 carbonate aquifers or aquifer systems, 1993–2005.—Continued

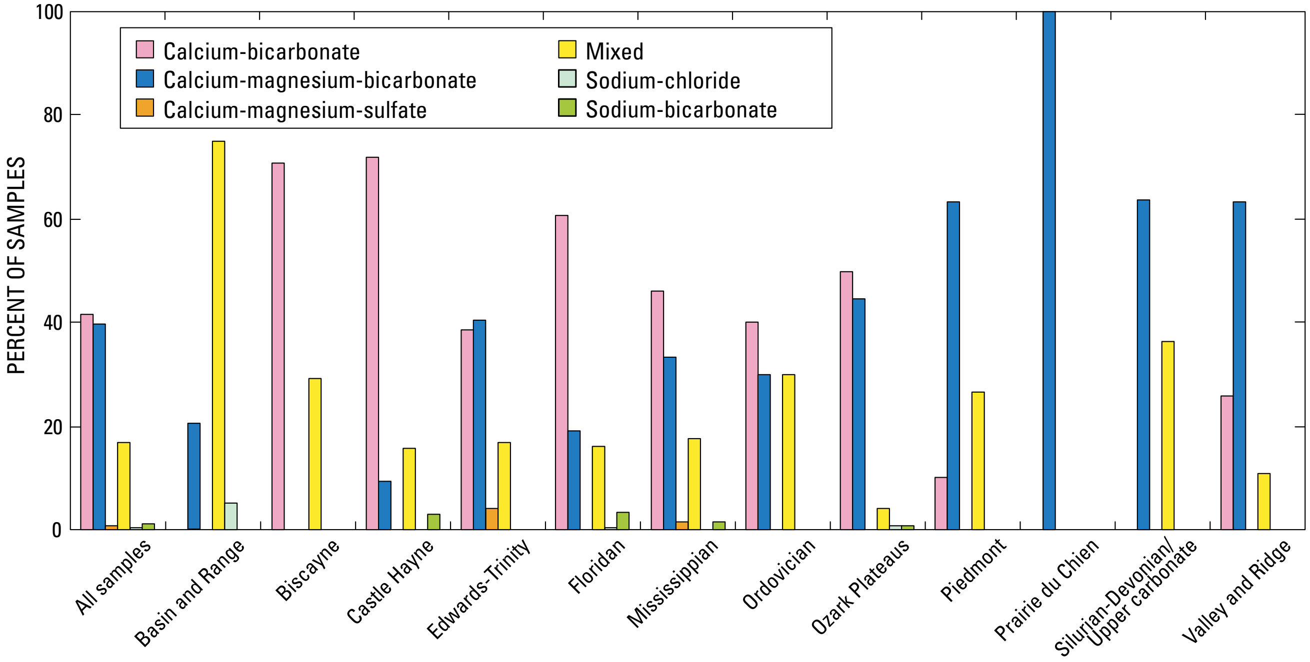


Figure 8. Dominant-ion water types in 12 carbonate aquifers or aquifer systems, 1993–2005.

Water from certain carbonate aquifers showed considerable variability in the composition of major ions (fig. 8). The most variability within aquifers or aquifer systems was seen in the Basin and Range (24 samples), Castle Hayne (32 samples), Floridan (224 samples), Mississippian (66 samples), and Ordovician (40 samples) (fig. 8). In areas where the Floridan aquifer system is poorly confined and confined, sodium-bicarbonate was the water type in 8 of 30 samples (in South Carolina) and sodium is a major cation for 30 percent of samples. Katz (1992) and Sprinkle (1989, p. 31) hypothesized that cation exchange is the likely geochemical process that accounts for this water type in the Upper Floridan aquifer.

Additional evidence for calcite and dolomite dissolution as the major geochemical process that controls the major-ion composition can be gleaned from the relation between molar concentrations of calcium plus magnesium and bicarbonate. The molar concentration of bicarbonate (in millimoles per liter) would be two times the sum of the molar concentrations of calcium and magnesium if calcite and dolomite mineral dissolution was the dominant process. Most water samples plot along a line with a 2:1 slope (bicarbonate to calcium plus magnesium), except for water from the Piedmont aquifer and selected samples in the Basin and Range, Edwards-Trinity, and Silurian-Devonian/Upper carbonate aquifers/aquifer systems, all of which show excess amounts of calcium plus magnesium (fig. 9). These aquifers had median concentrations of sulfate ranging from 17 to 42 mg/L, which were greater than 9.6 mg/L, the median for all samples. In the Edwards-Trinity aquifer system, the excess amount of calcium possibly is related to the presence of gypsum in the aquifer materials, because several of these samples are calcium-sulfate type waters (fig. 9). In the Basin and Range and Silurian-Devonian/Upper carbonate aquifers, the excess calcium may reflect longer residence times of ground water because the median concentrations of dissolved solids in these two aquifers (418 and 341 mg/L, respectively) were higher than most other aquifers (table 10). The Ordovician aquifer also had a median concentration of sulfate in this range at 25.6 mg/L, but this does not appear to be related to concentrations of calcium and magnesium (or gypsum).

Water types and ion ratios provide important information about mineral-water interactions; however, they do not disclose how the chemical composition of water changes as it moves through the various carbonate-aquifer systems. One method commonly used assumes that all dissolved species are at equilibrium, which allows the use of thermodynamic models to calculate the distribution of dissolved species. In this study, the computer program PHREEQC (Parkhurst and Appelo, 1999) is used to calculate the distribution and activities of dissolved species and the saturation state of ground water with respect to minerals (calcite, dolomite, and gypsum) and gases (such as carbon dioxide). The S.I. is a measure of the departure from equilibrium and is expressed as:

$$\text{S.I.} = \log\,(\text{IAP}/\text{KT}) \qquad (4)$$

where

S.I. is saturation index,
IAP is the ion activity product of the components of the solid or gaseous phase, and
KT is the solid or gaseous phase solubility equilibrium product at the specified temperature (at the time of sampling).

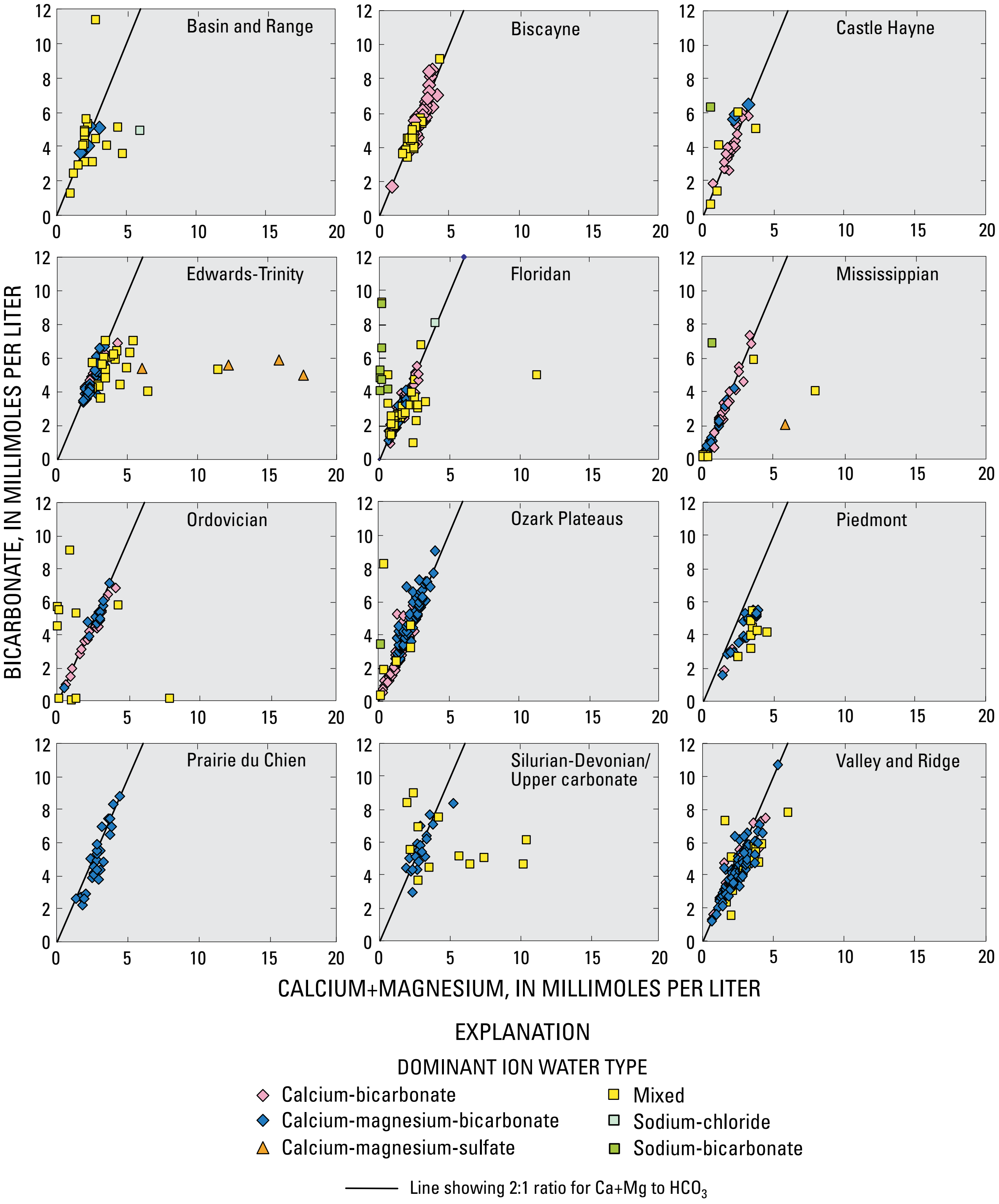


Figure 9. Ratio of calcium plus magnesium to bicarbonate for each aquifer in 12 carbonate aquifers or aquifer systems, 1993–2005.

When S.I. is equal to 0, the solid or gaseous phase is in equilibrium with the ground water. When S.I. is less than 0, the solid or gaseous phase is undersaturated, which means that the phase has thermodynamic potential to dissolve. When S.I. is greater than 0, the solid or gaseous phase is supersaturated, and the phase has the potential to precipitate or volatilize.

The S.I. values with respect to calcite, dolomite, and gypsum for water from the 12 carbonate aquifers were highly variable and reflect differences in their mineralogy. Most S.I. values with respect to calcite are within the -0.2 to 0.2 range considered to be at equilibrium with respect to calcite; however, most water samples from the Mississippian and Ordovician aquifers have calcite S.I. values lower than -0.2 (table 10; fig. 10). Median S.I. values with respect to calcite range from -1.19 in the Mississippian aquifer to 0.21 in the Prairie du Chien aquifer. The S.I. values with respect to dolomite showed that samples from most aquifers are undersaturated with respect to dolomite, except for the Basin and Range and Prairie du Chien aquifers. The Basin and Range carbonate aquifers are composed of limestone and dolomite (Plume, 1995) and the Prairie du Chien aquifer is composed of dolomite (Young and Siegel, 1992). Median S.I. values for dolomite ranged from -3.01 in the Mississippian aquifer to 0.23 in the Prairie du Chien aquifer. Water samples from all the carbonate aquifers are undersaturated with respect to gypsum (fig. 11). The median S.I. with respect to gypsum was -2.63 for all samples, and medians in individual aquifers ranged from -4.21 in the Castle Hayne aquifer to -2.00 in the Piedmont aquifer.

Geochemical indicators such as S.I. values and calcium-magnesium ratios are used in studies of karst aquifers to infer the residence time of the water, or whether flow in the aquifer is dominated by conduit flow or diffuse flow through fractures or pores. Previous studies have shown that waters with the longer transport times associated with diffuse flow and fracture permeability typically are more saturated with respect to calcite than waters moving rapidly through a conduit system with much less contact time with the bedrock. Data from White (1988) from karst waters in the North Central Appalachian Mountains show that diffuse-flow springs and wells have a higher S.I. with respect to calcite (-0.24 and -0.13, respectively) than conduit-flow springs (-0.89). The S.I. values, however, also vary relative to other issues such as the purity of the carbonate rock and pH, temperature, and source of the recharge water. A study in the Valley and Ridge aquifer by Langmuir (1971) indicated that the degree of saturation with respect to calcite and dolomite increased with residence time; however, this study also points out the control of lithology (limestone or dolomite) in these processes. A study in the Ordovician aquifer in Kentucky (Scanlon and Thrailkill, 1987) found that the calcite S.I. values did not differ significantly among major springs and high-level springs (analogous to conduit and diffuse springs in White's study).

Studies of the Ordovician aquifer in Kentucky determined that, in a limestone aquifer with a uniformly distributed minor amount of dolomite, higher calcium-magnesium ratios may indicate longer residence times (Scanlon, 1989). Another study in that area found that calcium-bicarbonate type water was frequently contaminated with nitrate, whereas calcium-magnesium-bicarbonate type water was not. This was attributed to the occurrence of calcium-bicarbonate water type in the shallow part of the aquifer, which is most susceptible to contamination, and the calcium-magnesium-bicarbonate water type occurring in the parts of the aquifer with longer residence time, allowing for denitrification (Scanlon, 1990). A study of cave drip waters in the Edwards aquifer indicated a similar relation between calcium-magnesium ratios and residence time (Musgrove and Banner, 2004).

The geochemical studies cited typically included detailed knowledge of the flowpath and specific lithology (limestone or dolomite), which are critical in interpreting mass transfer and reaction rates. In the present study, lithology at the location of the well is known, but the proximity of nearby lithologies and the position of the well on the flowpath is not known. Residence time is known for a subset of the wells and is limited to designations of recharge before 1953 or recharge in 1953 and later. The applicability of these indicators would be very different in a pure limestone aquifer than in a dolomite or limestone and dolomite aquifer. Thus, these geochemical indicators are important to analyze with respect to anthropogenic contaminants, but the techniques developed for a given region may not be transferrable and may be difficult to interpret on a national scale.

Data from the current study were analyzed for patterns indicating relations between geochemical indicators and conduit flow or residence time. Age-dating information was only available for a subset of 476 samples; however, a comparison on the basis of age of recharge water (from tritium concentrations, not including samples indicating mixed ground-water age) showed that samples representing water recharged before 1953 had higher concentrations of magnesium, more positive values of calcite S.I., more positive values of dolomite S.I., and lower calcium-magnesium ratios than samples representing water recharged in 1953 or later (Wilcoxon rank-sum test, p-value less than 0.05 for each comparison). These results support the relations posed by White (1988) and Scanlon (1989), and although a specific designation of conduit or diffuse flow may not be possible, a general relation between these measures and residence time is evident.

Oxidation-Reduction Status

Oxidation and reduction (redox) reactions play an important role in controlling many chemical processes in ground water, such as the speciation of naturally occurring elements (including sulfur, arsenic, and iron) and the transformation and biodegradation of anthropogenic compounds (including nitrate, pesticides, and VOCs). Redox reactions are typically microbially mediated in ground water and involve the transfer of electrons from one material to another. Inorganic compounds that can accept electrons and that allow oxidation of organic material are called electron acceptors (Chapelle,

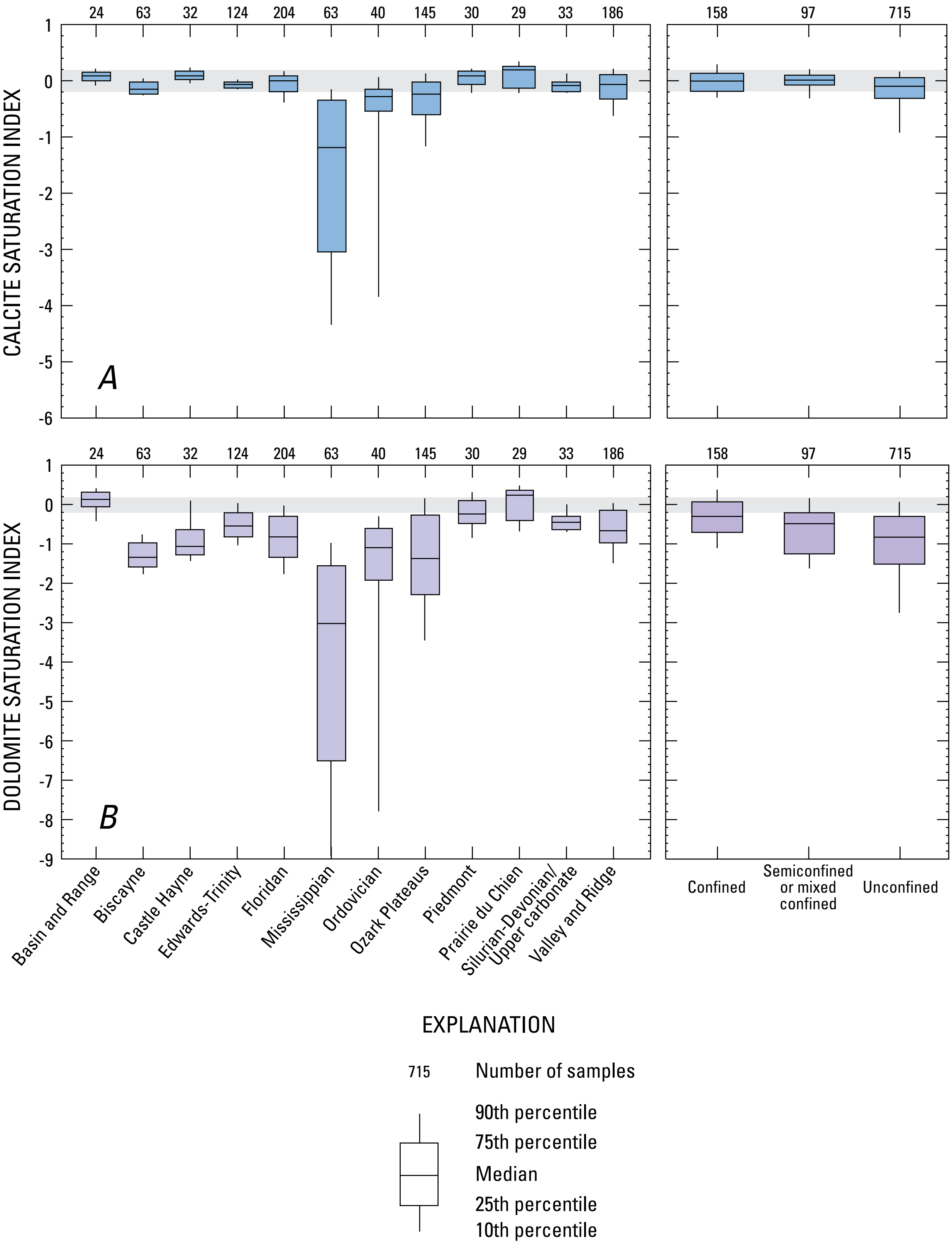


Figure 10. Distribution of saturation index values for A) calcite and B) dolomite by aquifer and confinement category in 12 carbonate aquifers or aquifer systems, 1993–2005.

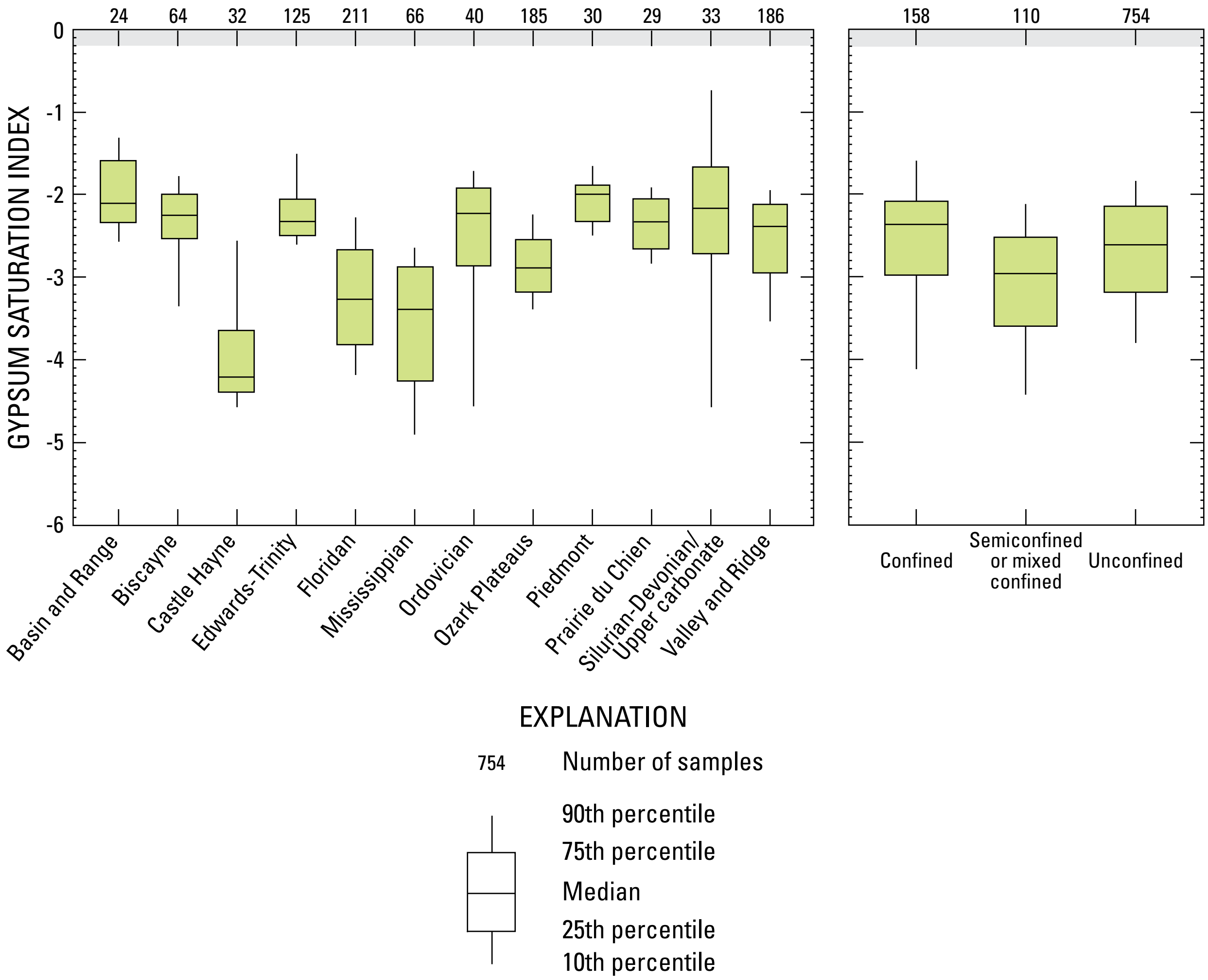


Figure 11. Distribution of saturation index values for gypsum by aquifer and confinement category in 12 carbonate aquifers or aquifer systems, 1993–2005.

1993). The most common electron acceptors in natural environments are oxygen, nitrate, iron, sulfate, and carbon dioxide. The electron donor is typically organic carbon, but sulfide minerals and anthropogenic organic compounds also can act as electron donors.

Dissolved oxygen in ground water originates from the atmosphere and is depleted in ground-water flow systems through reaction with organic carbon and other electron donors. Recently recharged, shallow ground water often contains more dissolved oxygen than older, deeper ground water. The median concentration of dissolved oxygen in all samples from the carbonate aquifers was 4.3 mg/L; however, median concentrations in individual aquifers and aquifer systems ranged from 0.1 mg/L in the Biscayne, Castle Hayne, Silurian-Devonian/Upper carbonate aquifers to 6.6 mg/L in the Ozark Plateaus aquifer system (fig. 12). Median concentrations of dissolved oxygen were also less than 1.0 mg/L in the Floridan aquifer system and the Prairie du Chien aquifer (fig. 12; table 10).

Concentration of dissolved oxygen varied by confinement categories in some aquifers or aquifer systems. In the Floridan aquifer system, the highest median concentration of dissolved oxygen was 4.3 mg/L in the 94 samples from areas where the aquifer is unconfined; median concentrations were 0.3 and 0.1 mg/L in semiconfined and confined areas, respectively (fig. 13). Similar results were seen in the Ozark Plateaus, Prairie du Chien, and Silurian-Devonian/Upper carbonate, where concentrations of dissolved oxygen were highest in the unconfined areas. In contrast, concentrations of dissolved oxygen were similar in water from wells in confined and unconfined areas in the Edwards-Trinity aquifer system (medians of 5.8 and 6.0, respectively) (fig. 13). Concentrations of dissolved oxygen were also elevated in the confined Basin and Range aquifer where the median was 2.6 mg/L. Differences in concentrations of dissolved oxygen are likely related to timing and amounts of recharge, presence of karst features such as sinkholes and large conduits, and presence of dissolved organic carbon.

Concentrations of dissolved organic carbon varied among the aquifers and aquifer systems. Dissolved organic carbon in ground water originates naturally from organic material but also may be contributed to ground water through waste disposal and animal production. The median concentration of dissolved organic carbon in all samples from the carbonate aquifers is low (0.4 mg/L), and median concentrations ranged from 0.3 mg/L in the Basin and Range, Piedmont, and Valley and Ridge aquifer systems to 11 mg/L in the Biscayne aquifer. The aquifers with the highest median concentrations of dissolved organic carbon—Biscayne (11 mg/L), Castle Hayne (2.51 mg/L), and Silurian-Devonian/Upper carbonate (1.2 mg/L) aquifers—were the three aquifers with the lowest median dissolved oxygen concentrations (table 10, fig. 12). Organic carbon is likely limiting the amount of oxygen in the ground water in these systems. The Biscayne and Castle Hayne aquifers are located in coastal areas and the wells are fairly shallow with shallow depths to water [10 ft or less (table 5)], but the median depth to water was much greater (about 59 ft) in the Silurian-Devonian/Upper carbonate aquifer (table 5). The Biscayne aquifer receives recharge directly from surface water, especially canals. Water samples from canals in southeastern Florida have a median concentration of total organic carbon of 21 mg/L; concentrations range from 5.0 to 46 mg/L (Radell and Katz, 1991).

Redox status in ground water varied among the carbonate aquifers (fig. 14). Redox status was determined on the basis of threshold concentrations of dissolved oxygen, manganese, and iron (McMahon and Chapelle, 2008) and were used to group the water-quality samples into three groups—oxic, mixed source, and anoxic (table 12). The percentage of samples designated as oxic was highest in the Valley and Ridge aquifer (91 percent), Edwards-Trinity aquifer system (85 percent), and Ozark Plateaus aquifer system (83 percent). Aquifers with the most samples designated as anoxic were the Biscayne (91 percent), Silurian-Devonian/Upper carbonate (91 percent), and Castle-Hayne (84 percent).

Comparison of samples according to redox status and confinement categories showed that most of the samples collected from unconfined areas were designated as oxic, and samples from confined areas contained similar numbers of samples designated as anoxic and oxic. Sixty-five percent (666 samples) of the 1,027 samples had a redox status designated as oxic, 29 percent were anoxic, and 6 percent were mixed. The majority of the samples were from sites classified as unconfined (75 percent of all sites), and within unconfined areas, 75 percent of these samples were designated as oxic (fig. 15). In confined areas, 52 percent of samples were designated as anoxic, and 43 percent were designated as oxic.

Classification of samples into groups on the basis of age of recharge water (from tritium concentrations) showed that most of the samples representing water recharged after 1953 were designated as oxic (fig. 16). About 85 percent of 476 samples represent recharge of water from 1953 or later and about 77 percent of these samples were classified as oxic. The high percentages of samples designated as anoxic in the older water samples (representing recharge prior to 1953) are consistent with the assumption that oxygen is consumed over time (McMahon and Chapelle, 2008).

Table 12. Threshold concentrations for identifying redox-status category.

[≥, greater than or equal to; >, greater than; <, less than; NA, no threshold applicable]

Redox-status category	Water-quality threshold (milligrams per liter)		
	Dissolved oxygen	Manganese	Iron
Oxic	≥ 0.5	< 0.05	< 0.1
Mixed source	≥ .5	> .05	> .1
Anoxic	< .5	NA	NA

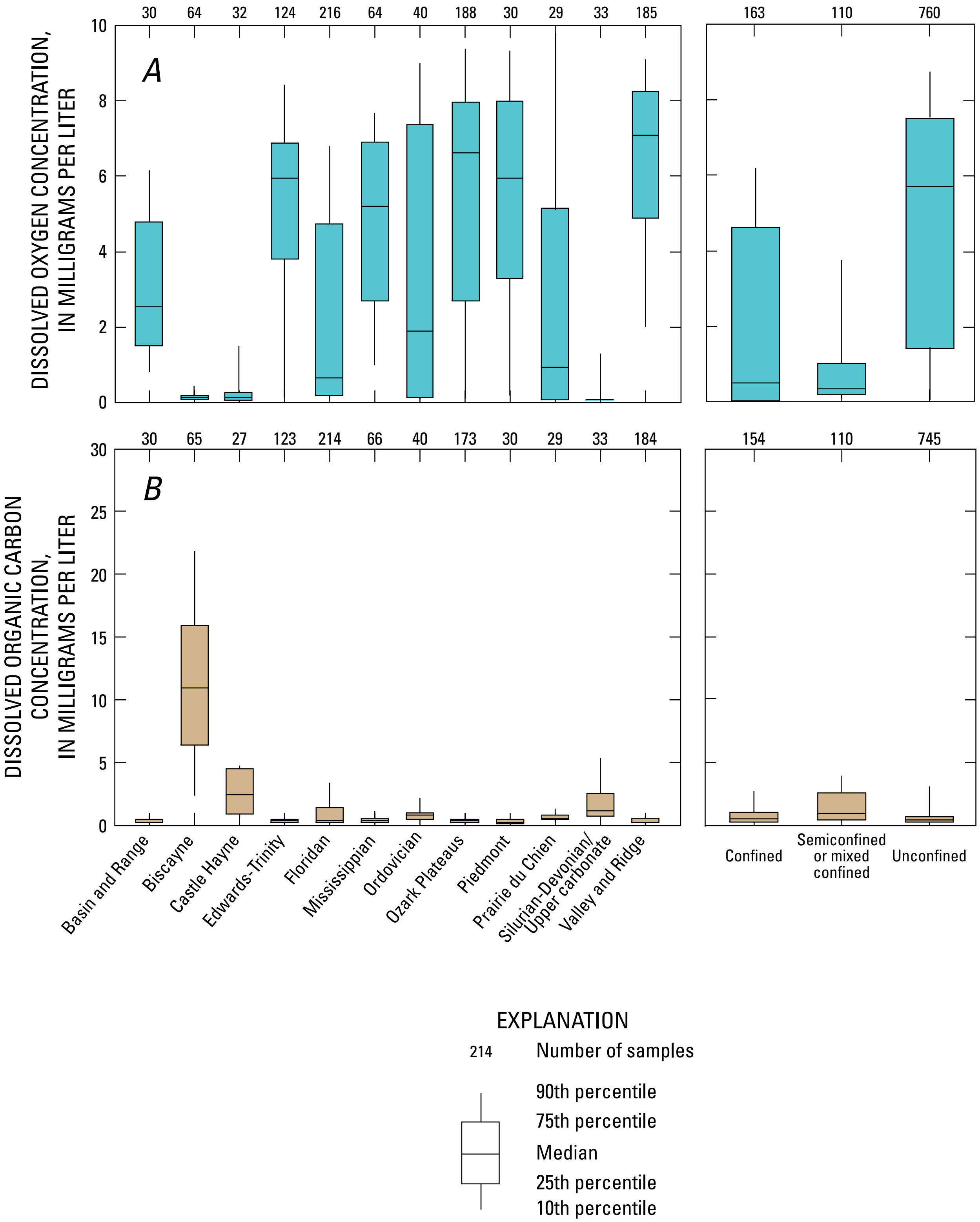


Figure 12. Distribution of A) dissolved oxygen and B) dissolved organic carbon by aquifer and confinement category in 12 carbonate aquifers or aquifer systems, 1993–2005.

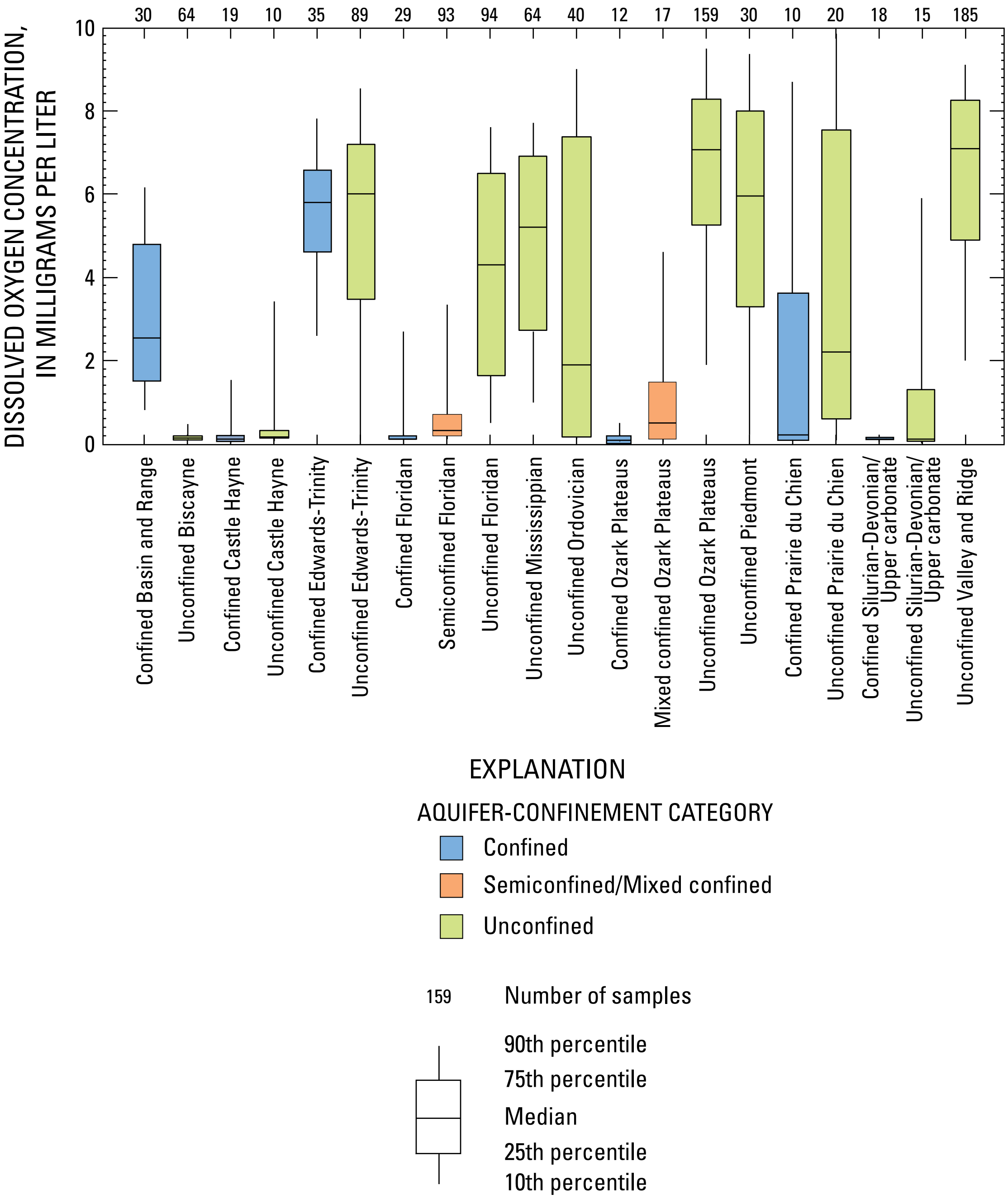


Figure 13. Distribution of dissolved oxygen by aquifer and confinement category in 12 carbonate aquifers or aquifer systems, 1993–2005.

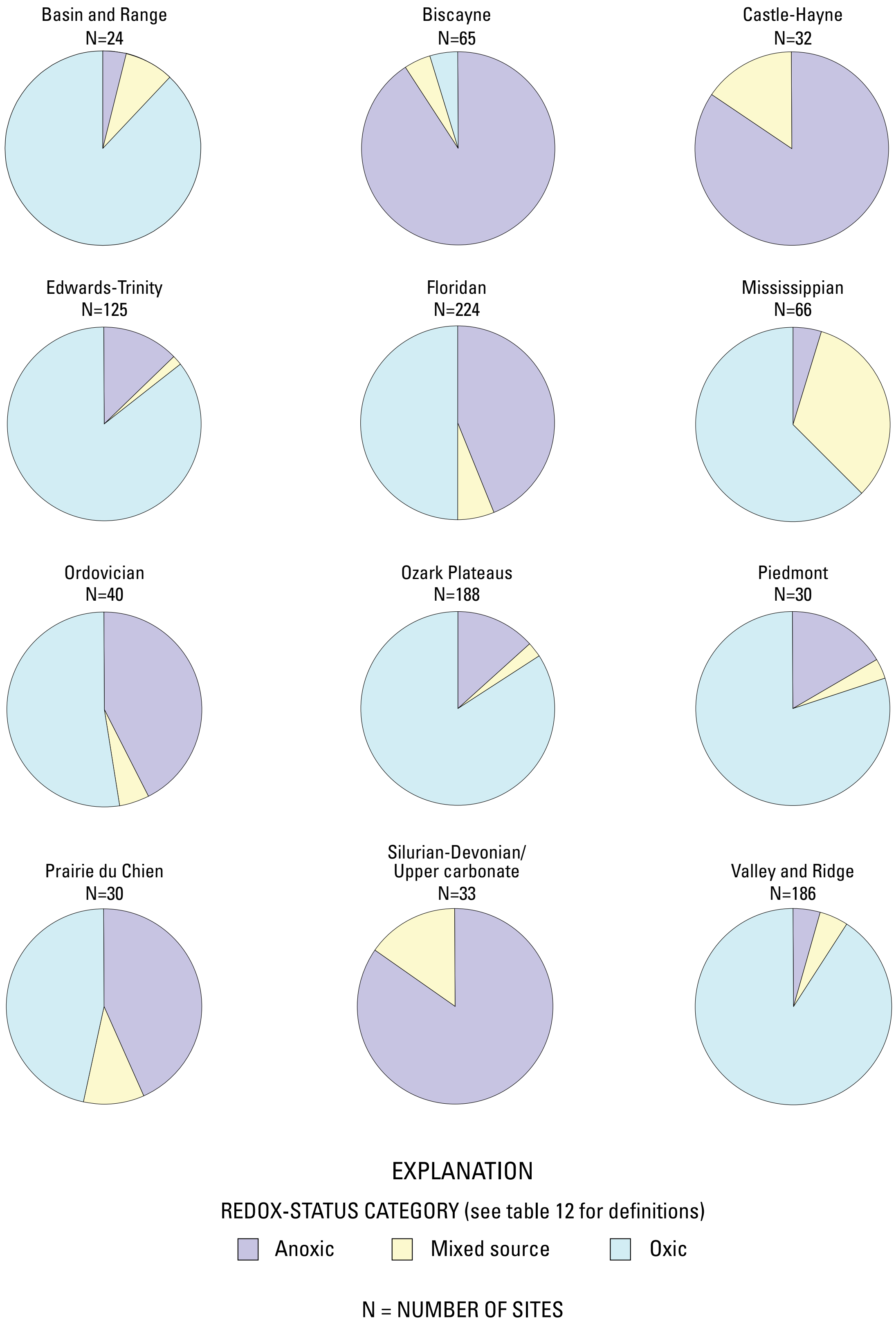


Figure 14. Oxidation-reduction (redox) status categories in 12 carbonate aquifers or aquifer systems, 1993–2005.

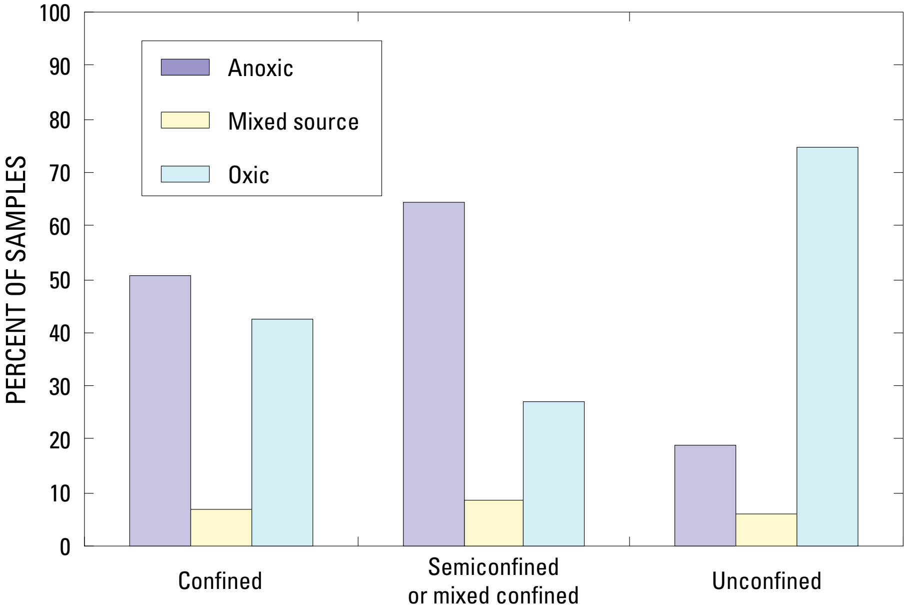


Figure 15. Redox status grouped by confinement category in 12 carbonate aquifers or aquifer systems, 1993–2005.

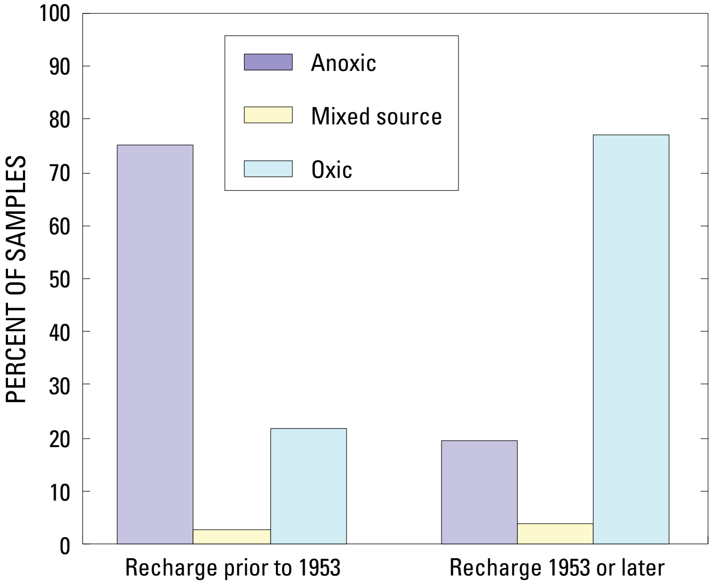


Figure 16. Redox status grouped by ground-water age in 12 carbonate aquifers or aquifer systems, 1993–2005.

Correlations with Well Depth

The relative concentrations of inorganic constituents (major ions, pH, and dissolved solids) are related to depth in the aquifer (well depth below land surface) and indicate the importance of ground-water residence time as a controlling factor on major-ion geochemistry. Wells in the Biscayne and Mississippian aquifers were the most shallow (median well depths of 45 and 53 ft, respectively) and water from these two aquifers had the lowest median pH values (6.80 and 6.54, respectively) (table 10). The water samples from the Mississippian aquifer also had the lowest median concentrations of dissolved solids, bicarbonate, calcium, sodium, potassium, and chloride, implying that samples from these wells have had shorter residence time than samples from other wells and (or) aquifers. The deepest wells were in the Basin and Range aquifer (median well depth 890 ft), and water from these wells had the highest median concentrations of sodium, potassium, chloride, silica, and fluoride, indicating that samples from these wells likely had longer residence times than samples from other wells and (or) aquifers.

Concentrations and values of many major ions and field characteristics were significantly correlated with well depth, which indicates that the position along a ground-water flowpath and ground-water residence time are important controlling variables. Results of the Spearman's rank correlation test (table 13) showed that values of specific conductance and pH, as well as concentrations of dissolved solids, magnesium, sodium, potassium, bicarbonate, silica, fluoride, barium, boron, bromide, calcite S.I., and dolomite S.I. were significantly correlated with well depth and had positive correlation coefficients, indicating values or concentrations increased as well depth increased. Concentrations of calcium, dissolved organic carbon, calcium-magnesium ratios, and radon also were inversely correlated with well depth, indicating concentrations or values decreased as well depth increased. Temperature and concentrations of dissolved oxygen, chloride, and strontium were not significantly correlated with well depth. The positive relation of magnesium, calcite S.I., and dolomite S.I. with well depth and the inverse relation between calcium-magnesium ratios and well depth are consistent with the concepts of White (1988) and Scanlon (1990), in that water from deeper wells would have longer residence times and be closer to saturation with respect to calcite and dolomite, and also have a lower calcium-magnesium ratio. The inverse correlation between calcium and well depth may indicate ion exchange with sodium, which has a positive correlation with well depth.

Table 13. Spearman's rank correlations between well depth and selected water characteristics in 12 carbonate aquifers or aquifer systems, 1993–2005.

[NS, correlation not significant–p-value greater than 0.05; <, less than]

Constituent	Number of samples	Correlation coefficient	p-value
Temperature	849	NS	0.24
Specific conductance	846	0.09	.01
Dissolved solids	846	.08	.02
Dissolved oxygen	845	NS	.73
pH	849	.27	< .0001
Bicarbonate	809	.09	.01
Calcium	847	-.07	.05
Magnesium	847	.34	< .0001
Sodium	847	.13	< .0001
Potassium	847	.16	< .0001
Sulfate	845	.18	< .0001
Chloride	845	NS	.64
Silica	847	.39	< .0001
Fluoride	842	.27	< .0001
Strontium	413	NS	.81
Barium	512	.25	< .0001
Boron	210	.22	< .0001
Bromide	778	.27	< .0001
Dissolved organic carbon	828	-.27	< .0001
Calcite saturation index	797	.15	< .0001
Dolomite saturation index	797	.42	< .0001
Calcium-magnesium molar ratio	797	-.34	< .0001
Radon	651	-.29	< .0001

Radon

Radon concentrations were highly variable in the individual carbonate aquifers, and median concentrations ranged from 104 pCi/L in the Castle Hayne aquifer to 710 pCi/L in the Piedmont aquifer (table 10). The median concentration of radon for all samples in carbonate aquifers was 360 pCi/L (table 9). The maximum value was 5,994 pCi/L in the Floridan aquifer system. Most radon concentrations in water from the Basin and Range, Biscayne, Mississippian, Piedmont, Prairie du Chien, and Valley and Ridge aquifers were greater than the USEPA proposed MCL of 300 pCi/L (fig. 17) (U.S. Environmental Protection Agency, 2006). Median radon concentrations were highest in the water in unconfined areas—the median concentration was 401 pCi/L in unconfined areas (548 samples) compared to 267 pCi/L in semiconfined/mixed confined areas (66 samples) and 230 pCi/L in confined areas (124 samples). Radon exceeded the proposed MCL in 423 of 735 wells sampled, of which 309 were drinking-water supplies.

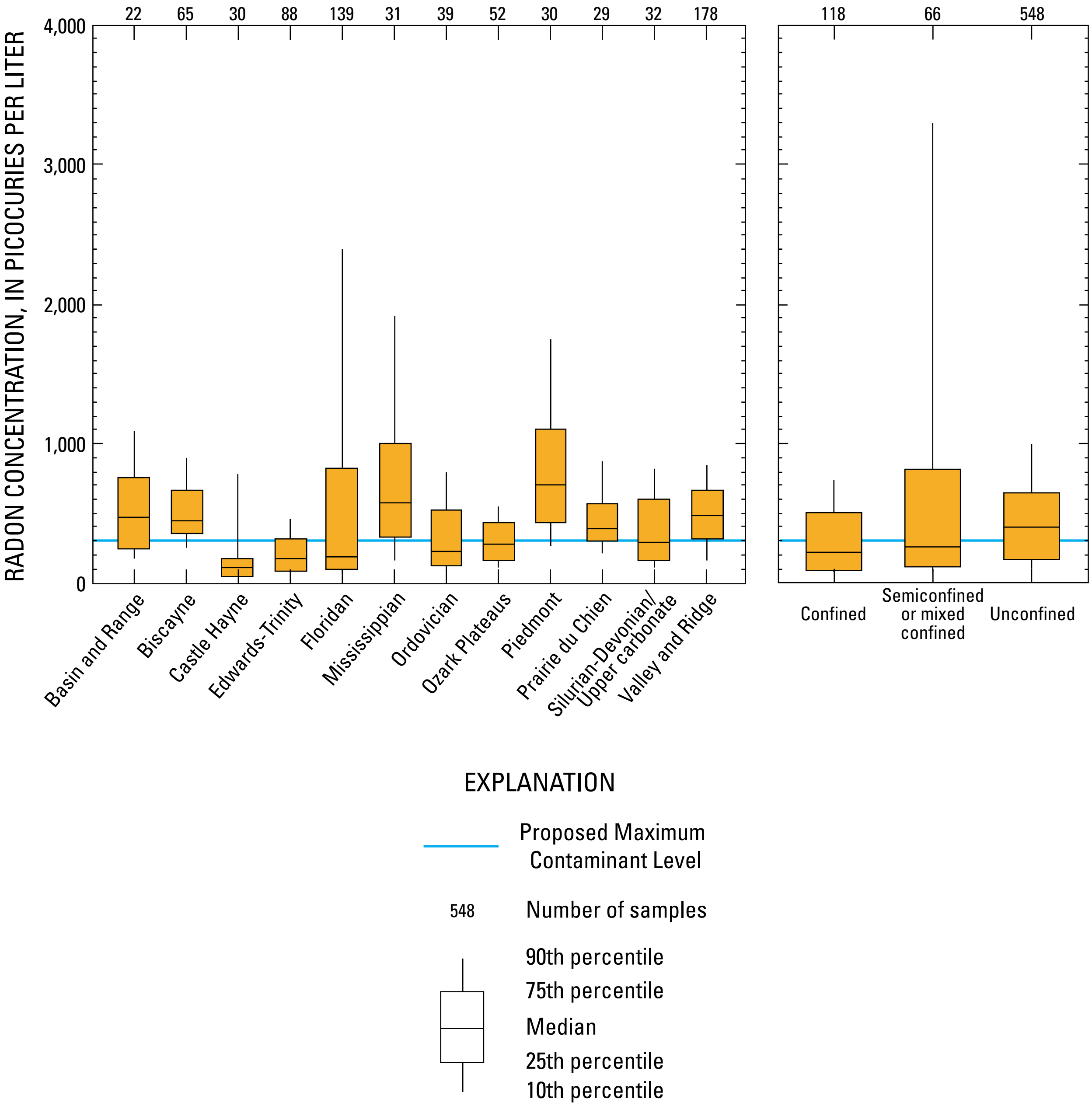


Figure 17. Distribution of radon values in aquifers and by confinement category in 12 carbonate aquifers or aquifer systems, 1993–2005.

Factors Affecting Anthropogenic Contaminants

The NAWQA Program sampled a number of constituents that are considered anthropogenic contaminants. The primary anthropogenic contaminants that were widely sampled for and analyzed were nitrate, pesticides, and VOCs. The following sections detail the concentrations, occurrence, and factors affecting nitrate, pesticides, and VOCs in the 12 carbonate aquifers.

Nitrate

Nitrate is potentially the most widespread contaminant in ground water (Hallberg and Keeney, 1993). Nitrogen is widely used as a fertilizer for agricultural activities and is also present in human waste, animal waste, and combustion by-products; therefore, the land surface is exposed to a large amount of nitrogen from various sources. Nitrogen in soils can be in the form of organic nitrogen, ammonia (NH_4), nitrite (NO_2), or nitrate (NO_3). Nitrate is a highly soluble form of nitrogen that can readily leach into the ground water and can also be denitrified to the form of N_2 gas. The concentrations of nitrate in ground water are a concern because of the potential human-health effects, specifically methemoglobinemia in infants, which has led the USEPA to set the drinking-water standard for nitrate at 10 mg/L as nitrogen or “as N” (U.S. Environmental Protection Agency, 2006). The widespread occurrence of nitrate, in combination with its potential for human health effects, makes nitrate in ground water an important issue to understand.

Distribution of Nitrate Concentrations

Samples from 1,037 wells and springs were analyzed for nitrate by the NAWQA Program in the 12 carbonate aquifers. The laboratory results for nitrate are reported as NO_3 plus NO_2, in milligrams per liter as N; however, because NO_2 concentrations are very low (877 of the 1,037 samples were less than the LRL of 0.01 mg/L and the 95th percentile was 0.02 mg/L), the value of NO_3 plus NO_2 is assumed to be equivalent to NO_3 as N and is referred to hereafter as nitrate. Nitrate was detected at concentrations greater than 0.06 mg/L in 793 of 1,037 samples. Concentrations ranged from below the detection limit of 0.06 mg/L to 25 mg/L. Although not all the sample locations represent drinking-water supplies, the majority are used for public or domestic supply. Many of those samples from sites that are not used for drinking water are representative of a part of a flow system that is a drinking-water-supply aquifer. When comparing the results to the USEPA drinking-water standard for nitrate, samples from 54 sites exceed the MCL of 10 mg/L, of which 52 sites were sources used for domestic supply. The exceedances were mostly from the Valley and Ridge aquifer, with 26 samples exceeding the MCL (14 percent), and the Piedmont aquifer, with 19 samples exceeding the MCL (63 percent). In the rest of the aquifers, only nine samples (about 1 percent) exceeded the MCL for nitrate. Median nitrate concentrations were highest in the Piedmont and Valley and Ridge carbonate aquifers, and lowest in the Biscayne, Castle Hayne, and Silurian-Devonian/Upper carbonate aquifers (fig. 18).

The results in figure 18 should be interpreted in the context of the design of the studies that were used in each aquifer. Sampling is not equally distributed among each aquifer or land-use type. Wells in some of the aquifers are predominantly of a single land use, and in some cases, shallow wells in that land use were targeted for study (table 3). The characteristics of the wells sampled also vary among the aquifer types (table 5). The land-use distribution near the wells is illustrated in figure 3. Thus the potential factors affecting nitrate concentration differ among the various aquifers. This range of network and well characteristics, however, provides an opportunity to analyze the potential effect of these characteristics in carbonate aquifers.

Factors Affecting Nitrate Concentrations

Concentrations of nitrate in the 12 carbonate aquifers are related to the inherent susceptibility of the aquifer to contamination, the intensity of the source of nitrogen, and the interaction between the two. Water from wells in agricultural land-use studies had higher median concentrations than water from wells in other study types. Nitrate concentrations were rarely elevated in confined aquifers and in wells where age-dating indicated that the water was predominantly recharged prior to 1953. The concentrations of nitrate were closely related to the redox status of the water. The susceptibility of the aquifer to contaminants is based on transport factors and includes physical factors that allow nitrate to move into the aquifer, as well as biological and chemical factors that may facilitate or attenuate the movement of nitrate. The intensity of the source of nitrogen is determined by surrogates such as land use and, where possible, estimates of the actual amount of nitrogen at the land surface.

Source Factors

Nitrogen in ground water typically is from nonpoint sources. Some of the major nonpoint sources are fertilizers, animal manure, atmospheric deposition, and septic systems. The intensity of most of these nitrogen sources has been compiled for a 1,640-ft radius around each well from records of fertilizer sales, animal density, and measurements of nitrogen in precipitation (fig. 5). A general indicator of the intensity of nitrogen sources is land use; agricultural land use typically is the largest contributor of nitrogen. Both land use and nitrogen sources are continuous variables in this data set; therefore, the Spearman’s rank correlation was used to determine the relations between these variables and nitrate concentration in ground water from carbonate aquifers. The strongest

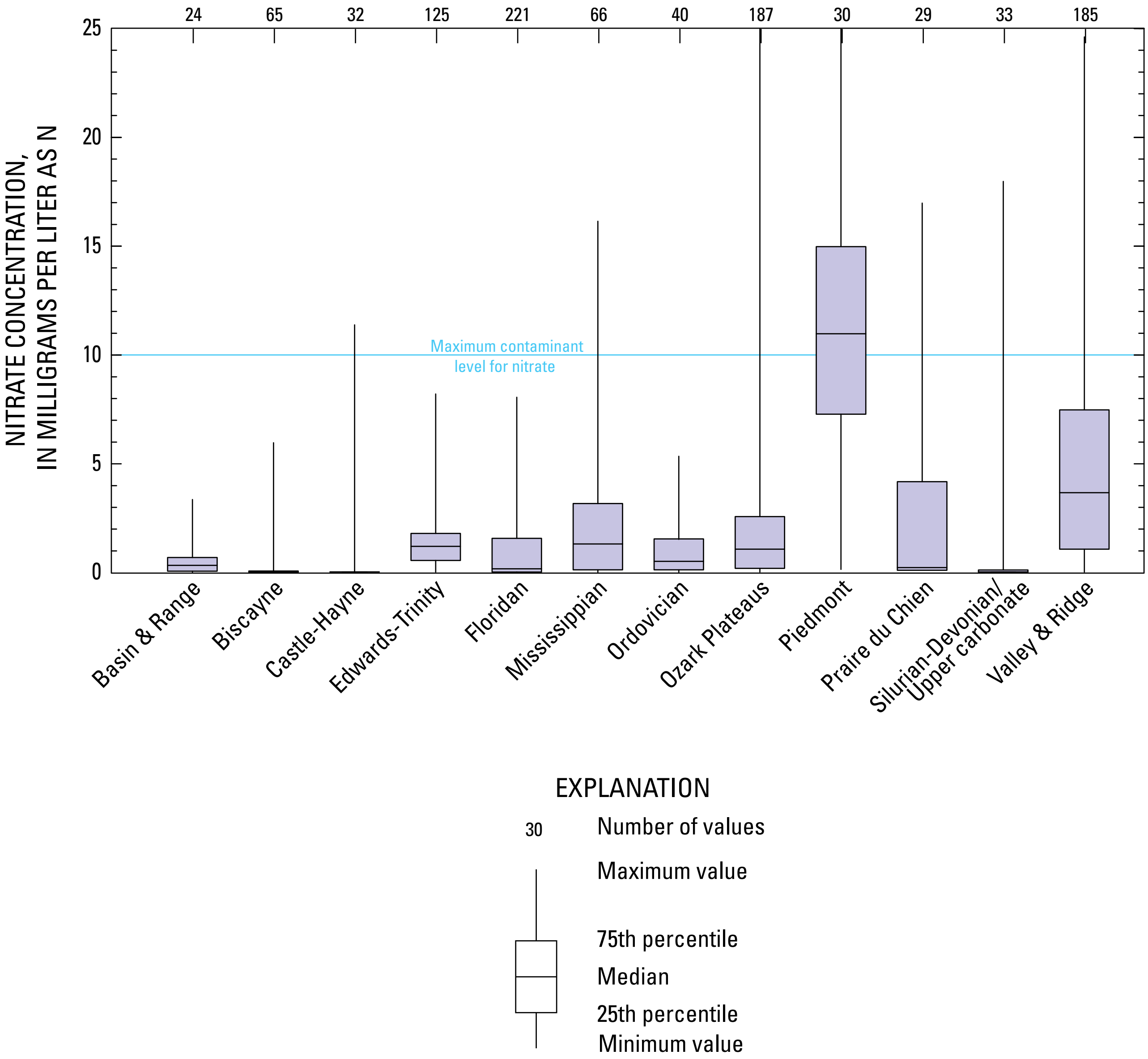


Figure 18. Distribution of concentrations of nitrate in 12 carbonate aquifers or aquifer systems, 1993–2005.

correlation was between agricultural land use and nitrate concentration. Strong positive correlations were also noted between potential nitrogen sources (manure, fertilizer, septic systems, and atmospheric deposition) and nitrate concentration (table 14). A weak positive correlation was found between the population on private septic systems and nitrate concentration. Correlations within individual aquifers are highly dependent on the number of samples, which accounts for the small number of significant correlations for the aquifers with 30 or fewer samples.

When analyzing these data by study types, water from wells in the agricultural land-use studies and the agricultural flowpath study had the highest median concentrations of nitrate, and water from wells in the other study types, with less agricultural land use, had lower nitrate concentrations. The distribution of nitrogen by atmospheric deposition is relatively even, and the population on private septic systems is apparently a minor contributing factor in nitrate concentration; therefore, the factors that have the most variation are those related to agricultural land use. Although much of the nitrogen applied to the agricultural land is taken up by plants, the difference between application from all sources and crop uptake is apparently large enough to make agricultural land use a major factor affecting elevated concentrations of nitrate.

Fate and Transport Factors

The movement of nitrate in ground water from a source to the sampling point depends on numerous factors that are collectively termed fate and transport factors. Transport factors include the speed at which the water travels, the distance from the recharge area to the well, and whether or not there is a confining layer. Fate factors are microbial and geochemical processes that affect transformations to the constituent of concern during the movement of the water. Most of these factors cannot be measured directly; however, data collected at a sampling point can be used to infer some of these processes. Dissolved oxygen concentration, dissolved organic carbon concentration, soils characteristics, and well characteristics are indirect measures of these processes. Some wells had data from age-dating tracers that could be used to determine traveltime in the aquifer. Some of the variables that can be used as indicators of fate and transport factors include water-quality measurements, calculated mineral saturation indexes, hydrologic variables, well-construction data, and soils information. These variables have been compiled for the 1,640-ft radius around the well, and correlations between these variables and nitrate concentration are used to infer possible fate and transport mechanisms that facilitate or impede movement of nitrate.

Ground-Water Age

Nitrate concentrations and age-dating tracers were available for a subset of 486 of the wells sampled (not including samples with a mixed ground-water age). Although a small number of samples could be assigned a specific recharge date from CFCs or other techniques, most samples were categorized as having recharge dates that were prior to 1953 or 1953 and later. Therefore, all samples were assigned a recharge date of pre-1953 or 1953 and after, in order to be comparable. The samples with age dates represent a subset of the entire data set. No age-dating data were available in the Basin and Range, Castle Hayne, Ordovician, or Piedmont aquifers. All samples with recharge dates prior to 1953 were from wells (no springs). Of these 74 wells, 34 were from areas designated as confined, 6 were from semiconfined or mixed confinement, and 34 were unconfined. Aquifers or aquifer systems in the subset of wells that had recharge dates prior to 1953 include the Edwards-Trinity, Floridan, Ozark Plateaus, Prairie du Chien, and Silurian-Devonian/Upper carbonate. Samples with recharge dates of 1953 and after included 317 wells and 95 springs. Of these, 40 were from confined aquifers, 9 were from semiconfined or mixed confinement, and 363 were from unconfined aquifers. Aquifers or aquifer systems in the subset of wells that had recharge dates after 1953 include the Biscayne, Edwards-Trinity, Floridan, Mississippian, Ozark Plateaus, Prairie du Chien, Silurian-Devonian/Upper carbonate, and Valley and Ridge. A Wilcoxon rank-sum analysis showed that the median concentration of nitrate in the older water (less than 0.06 mg/L) was significantly lower than the median concentration of nitrate in water that was recharged more recently (1.4 mg/L) (p-value less than 0.0001) (fig. 19). This result is possibly a combination of source factors—older water was recharged when application rates of fertilizer and manure were much lower—and fate and transport factors—the longer traveltimes allowed for processes such as denitrification to occur. No sample from a well with a recharge date prior to 1953 had a concentration of nitrate that exceeded the USEPA MCL of 10 mg/L.

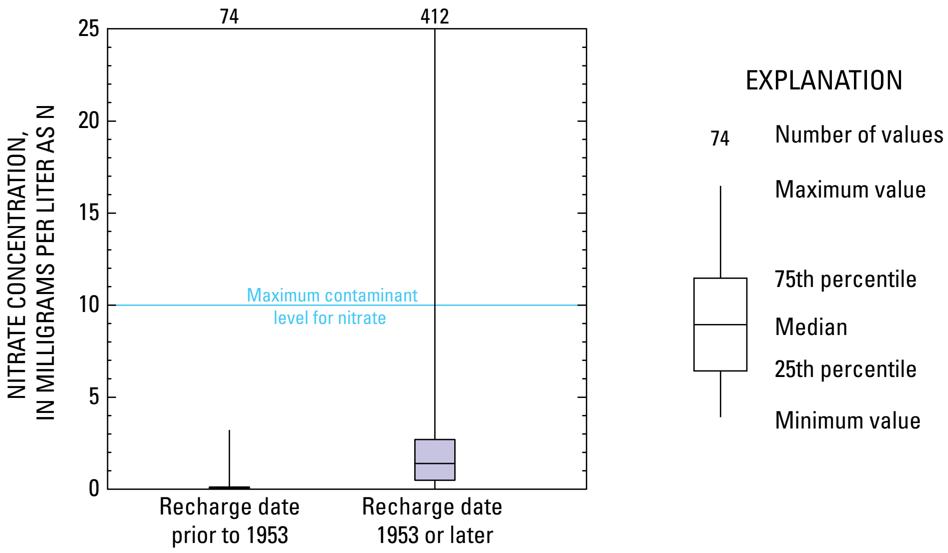
Degree of Confinement

The presence of a confining layer is a key factor affecting nitrate transport to ground water. A determination of the degree of aquifer confinement—unconfined, semiconfined, mixed confinement (wells penetrating more than one aquifer type), or confined—was made for all but three of the wells and springs. A nonparametric Tukey's test indicated that the median concentration of nitrate from wells in unconfined aquifers (1.4 mg/L) was higher than those in semiconfined/mixed confined or confined aquifers (fig. 20) (p-value less than 0.0001). Both the confined and semiconfined/mixed confined categories had median concentrations below the detection limit of 0.06 mg/L. All samples that had concentrations of nitrate that exceeded the USEPA MCL of 10 mg/L were from wells in an unconfined aquifer, with the exception of one sample from a well in a confined aquifer. That sample was identified by the age-dating tracers as having a mixture of old and young water, which typically indicates a 'short-circuit' in the system allowing old water to be mixed with younger water. The comparison of confinement categories by aquifer also illustrates the importance of confinement. In most of the confined aquifers, nitrate concentrations are low. In cases

Table 14. Spearman's rank correlations between nitrate concentration in ground water and variables representing nitrogen sources, in 12 carbonate aquifers or aquifer systems, 1993–2005.

[Land use from U.S. Geological Survey (1999); Price and others (2007); Census data from U.S. Bureau of Census (1990, 1991, 1992); Nitrogen source data from Ruddy and others (2006); NS, correlation not significant–p-value greater than 0.05]

Category	Variable	All data	Basin and Range	Biscayne	Castle Hayne	Edwards-Trinity	Floridan	Mississippian	Ordovician	Ozark Plateaus	Piedmont	Prairie du Chien	Silurian-Devonian/ Upper carbonate	Valley and Ridge
Number of samples		137	30	65	32	125	236	66	40	187	30	30	33	197
Land use	Percent agricultural land use	0.43	NS	0.29	NS	NS	0.21	0.43	NS	0.43	NS	NS	NS	0.68
	Percent forest land use	-.13	NS	NS	NS	-.39	NS	-.46	NS	-.25	NS	NS	NS	-.67
	Percent wetlands	-.35	NS	NS	NS	NS	-.31	NS	NS	NS	NS	NS	NS	NS
Census data	Population density, 1990	.06	NS	NS	NS	.33	NS	NS	NS	NS	NS	NS	NS	NS
	Population on private septic systems	.19	NS	.43	NS	NS	NS	NS	NS	.24	NS	NS	NS	NS
Potential nitrogen sources and land use	Nitrogen from atmospheric deposition, septic systems, fertilizer, and manure	.30	NS	NS	NS	.29	.20	NS	NS	.49	NS	NS	NS	.52



GROUND-WATER-AGE CATEGORY

Recharge date prior to 1953: (74 wells)

34 Confined
6 Semiconfined or mixed confined
34 Unconfined
Edwards-Trinity, Floridan, Ozark Plateaus, Prairie du Chien, and Silurian-Devonian/Upper carbonate aquifers

Recharge date 1953 or later: (317 wells and 95 springs)

40 Confined
9 Semiconfined or mixed confined
363 Unconfined
Biscayne, Edwards-Trinity, Floridan, Mississippian, Ozark Plateaus, Prairie du Chien, Silurian-Devonian/Upper carbonate, and Valley and Ridge aquifers

Figure 19. Distribution of concentrations of nitrate by ground water-age category in eight carbonate aquifers or aquifer systems, 1993–2005.

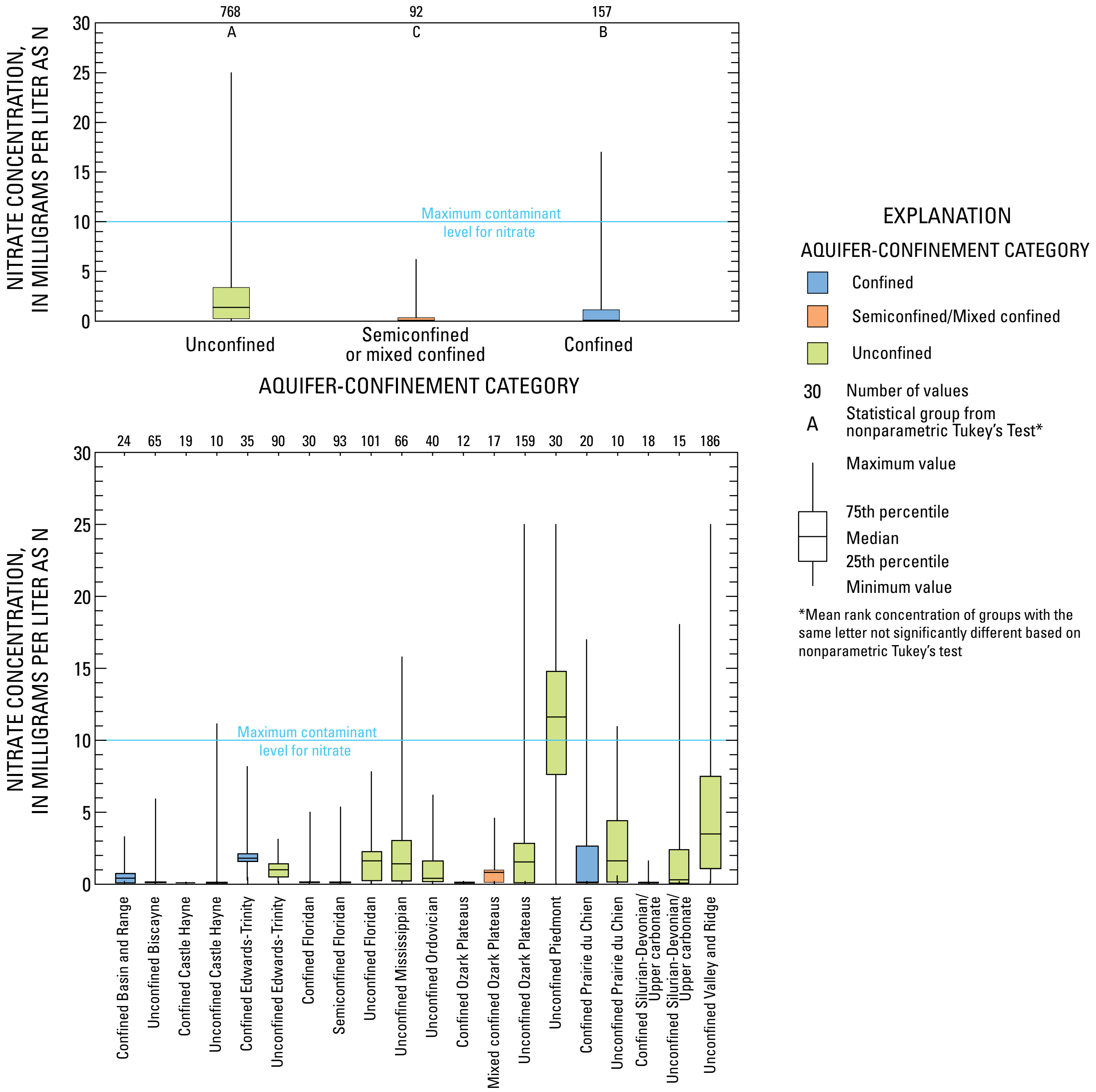


Figure 20. Distribution of concentrations of nitrate by confinement category and aquifer in 12 carbonate aquifers or aquifer systems, 1993–2005.

where an aquifer has both confined and unconfined areas, the unconfined area has higher nitrate concentrations in all except one of the comparisons (fig. 20).

Karst Features

Presence of karst features is a potential indicator of transport of contaminants to ground water. The categories from the karst map of Davies (1970) are generally divided by karst-feature size into 'long' (fissures, tubes, and caves over 1,000 ft long; 50 ft to over 250 ft vertical extent), 'short' (fissures, tubes, and caves generally less than 1,000 ft long; 50 ft or less vertical extent), and 'absent.' Categories are then subdivided on the basis of bedrock type, dip angle, and presence of noncarbonate rock overlying carbonate rock. A Kruskal-Wallis test was used to make comparisons of nitrate concentrations among main karst-feature categories (long, short, and caves absent) and showed no significant difference among these categories at a 95-percent confidence interval. Comparisons of karst-feature categories grouped by predominant land-use type also showed no significant differences with the exception of a subset in which the 'urban karst features absent' category had a statistically significant higher nitrate concentration than the urban areas with karst features. In some cases, wells from the current study plotted outside of the area mapped as carbonate on the Davies map. These wells were alternately treated as 'karst features absent' and included in the analysis, and as 'no data' and thus excluded from the analysis. Neither method of analysis of those wells changed the findings.

This general lack of correlation between nitrate concentrations and the categories from the national karst map is most likely related to the scale of the national karst data set. Several hundred wells are in aquifers identified as carbonate but are not located within the area designated by the national karst map as carbonate, so some of the areas designated as 'karst features absent' may be incorrectly identified from the karst map. Also, the categories of 'short' and 'long' both could have karst features measuring in the hundreds of feet in length, so both could potentially have similar effects on water quality at a specific well.

Because of the potential importance of karst features, and the lack of explanatory power of the categories from the national karst map, an attempt was made to gather data on individual sinkholes and make comparisons between sinkhole density and water quality. Although these data are available for some states, the data are unavailable for much of the study area, thus negating the possibility of a comprehensive analysis of this issue for the entire data set.

Redox Status

A key factor in determining the fate of nitrate is the redox status of the water sampled. This is important because it affects the possibility or degree of denitrification. As previously described, redox status was determined as oxic, anoxic, or mixtures of two or more types of waters if water-quality measurements indicated a mix over a range of redox states. A nonparametric Tukey's test indicated a significant relation between redox conditions and nitrate concentrations (fig. 21); oxic waters had the highest nitrate concentrations, followed by mixed-source waters, and anoxic waters had the lowest nitrate concentrations.

As noted in the section on geochemistry, redox status is closely related to ground-water age and degree of confinement (figs. 14 and 15). A confining layer or a long transport distance can affect ground-water age. Water that is in the aquifer for a long period of time has an increased likelihood of having the oxygen that was dissolved in the water depleted by microbial or chemical activity. Organic carbon is essential for the microbial processes that utilize the oxygen.

Dissolved oxygen concentration can be an indicator of microbial processes, flowpath length, or soil characteristics. Denitrifying bacteria are facultative and will only use nitrate as an oxygen source in the absence of free dissolved oxygen (Chapelle, 1993). Therefore, aquifers with concentrations of dissolved oxygen greater than 1.0 mg/L typically have sufficient oxygen available so that microbial denitrification does not remove large quantities of nitrate. A Spearman's rank correlation indicated a strong positive statistical relation between nitrate concentration and dissolved oxygen concentration (table 15). This correlation was strong for the entire data set, but also within individual aquifers; 7 of the 12 aquifer groups had significant correlations and positive correlation coefficients that were 0.50 or greater. Dissolved oxygen, therefore, is an important factor determining the presence and concentration of nitrogen. The presence of dissolved oxygen can be an indicator of short flowpath length, but microbial consumption rates of oxygen are dependent on numerous factors and cannot be directly converted to ground-water traveltime. Karst conduits can also have turbulent flow that mixes atmospheric air with ground water after recharge, which can also be a cause of higher concentrations of dissolved oxygen. Both short flowpaths and conduit flow increase the likelihood of nitrate being present. Organic carbon is also necessary for the microbial processes that result in denitrification. Dissolved organic carbon concentration was inversely correlated with dissolved oxygen concentration and nitrate concentration for the entire data set, although this inverse correlation was not consistent within most of the aquifers (table 15). Aquifers that lack dissolved organic carbon and are well oxygenated are, therefore, more likely to transport nitrate longer distances from the source than aquifers with higher dissolved organic carbon and anaerobic conditions.

Saturation Indexes and Geochemistry

Saturation indexes for calcite and dolomite were compared to nitrate concentration in order to evaluate their utility as indicators of residence time or conduit flow systems. Calcite and dolomite S.I. can be related to several factors, including residence time in the aquifer and the purity of the mineral in the aquifer material. Results of the Spearman's rank correlation showed significant inverse correlations between

Table 15. Spearman's Rank correlations between nitrate concentration and fate and transport variables in 12 carbonate aquifers or aquifer systems, 1993–2005.

[NS, correlation not significant–p-value greater than 0.05]

Category	Variable	All data	Basin and Range	Biscayne	Castle Hayne	Edwards-Trinity	Floridan	Mississippian	Ordovician	Ozark Plateaus	Piedmont	Prairie du Chien	Silurian-Devonian/ Upper carbonate	Valley and Ridge
Number of samples			30	65	32	125	236	66	40	187	30	30	33	197
Water-quality characteristics	Dissolved oxygen	0.68	0.67	0.25	NS	0.50	0.71	0.55	0.56	0.46	0.43	0.65	0.52	0.40
	pH	NS	.43	NS	NS	-.18	NS	NS	-.44	-.36	NS	NS	NS	.18
	Specific conductance	NS	NS	NS	NS	-.34	-.34	NS	NS	NS	.45	NS	NS	.56
	Dissolved organic carbon	-.33	NS	-.28	NS	NS	-.63	NS	NS	.26	.45	NS	NS	.22
Geochemical indicators	Calcite saturation index	NS	NS	NS	NS	-.19	NS	NS	-.36	-.26	NS	-.45	-.44	.49
	Dolomite saturation index	-.06	NS	NS	NS	-.55	-.22	NS	-.52	-.42	NS	-.44	-.57	.43
	Calcium-magnesium molar ratio	NS	NS	NS	NS	.53	.27	NS	.50	.41	NS	NS	.40	.15
Well-specific data	Water level	.22	NS	NS	NS	-.36	.28	.25	NS	NS	NS	NS	-.53	NS
	Well depth	NS	-.64	NS	-.35	NS	NS	NS	NS	NS	NS	NS	-.43	-.20
	Depth to top of open interval	NS	-.59	NS	NS	NS	NS	NS	NS	-.40	NS	NS	NS	NS

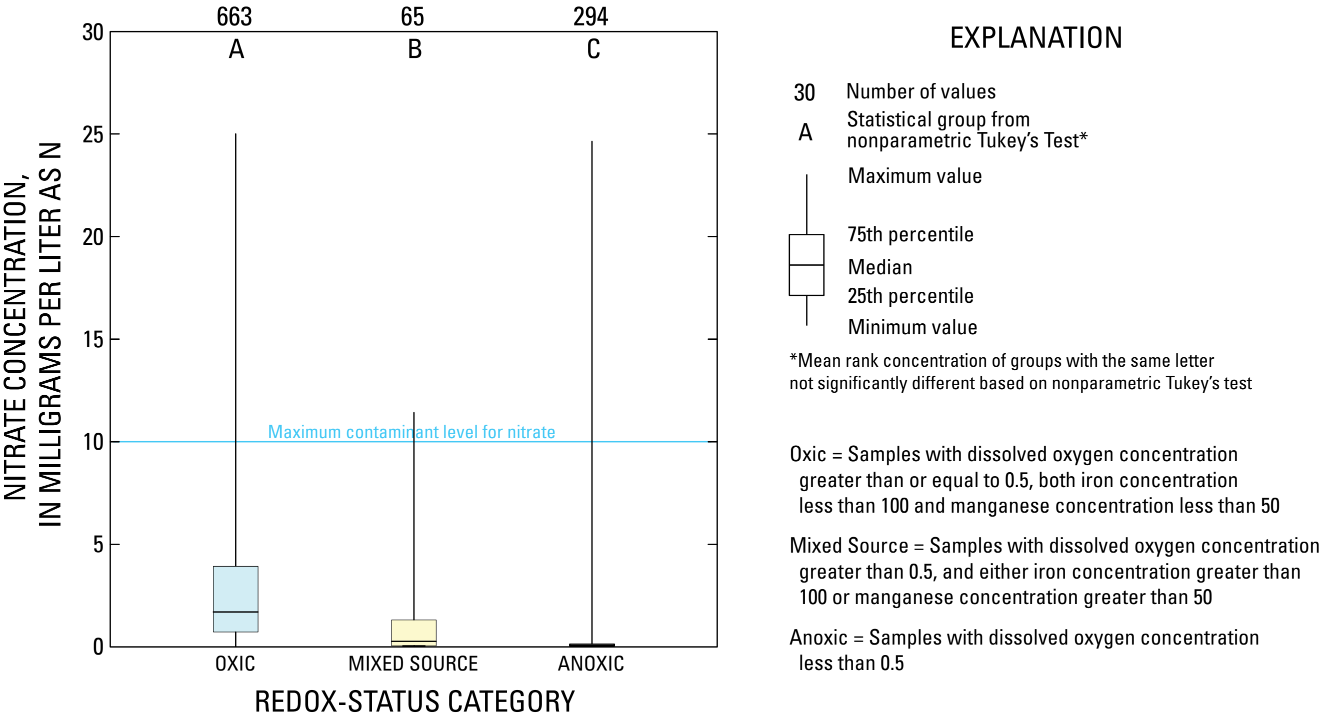


Figure 21. Distribution of concentrations of nitrate related to the redox status in 12 carbonate aquifers or aquifer systems, 1993–2005.

dolomite S.I. and nitrate concentration in the Edwards-Trinity, Floridan, Ordovician, Ozark Plateaus, Prairie du Chien, and Silurian Devonian/Upper carbonate aquifers/aquifer systems. Significant inverse correlations were also noted between calcite S.I. and nitrate concentration for the Edwards-Trinity, Ordovician, Ozark Plateaus, Prairie du Chien, and Silurian Devonian/Upper carbonate aquifers/aquifer systems (table 15). The inverse correlations between calcite and dolomite S.I. and nitrate concentration may be because a higher S.I. is associated with water that has a longer residence time in the aquifers, which has already been shown to be related to lower nitrate concentrations. In the case of the Valley and Ridge aquifer, the correlation between both calcite and dolomite S.I. and nitrate concentration is positive. This is most likely because water from wells and springs in the Upper Tennessee River Basin study unit had low concentrations of nitrate and was undersaturated with respect to calcite and dolomite. In contrast, wells in the Lower Susquehanna and Potomac River Basin study units had some of the highest concentrations of nitrate and were closer to saturation with respect to calcite and dolomite, thus making this correlation positive in the Valley and Ridge. These differences in nitrate concentration are mainly attributable to the greater percentage of agricultural land use in the Lower Susquehanna and Potomac River Basin study units. In the overall data set, the lack of correlation between calcite S.I. and nitrate concentration, and the weak correlation between dolomite S.I. and nitrate concentration may be because land use has more of an effect on nitrate concentrations than the geochemical indicators of residence time, similar to the situation within the Valley and Ridge aquifer.

Calcium-magnesium ratios were positively correlated with nitrate concentration in the Edwards-Trinity, Floridan, Ordovician, Ozark Plateaus, Silurian Devonian/Upper carbonate, and Valley and Ridge aquifers/aquifer systems. This finding is in concordance with the findings of Scanlon (1990), who found higher nitrate concentrations in calcium type water than in calcium-magnesium type water. The strongest geochemical correlations with nitrate concentration were dolomite S.I. and calcium-magnesium ratios, which support the concept that residence time, and thus concentrations of nitrate, are related to the evolution of water from a calcium water type to a calcium-magnesium water type.

Well-Specific Information

Well-construction data such as water level, well depth, and depth to top of open interval also are used as indicators of transport distance. A shallow depth to water can mean a short transport distance, which could lead to higher concentrations of nitrate, but very shallow water depths can lead to waterlogged soils that have also been shown to inhibit movement of nitrate (Nolan and others, 2002); water level can have either a positive or inverse relation with nitrate concentration depending on which factor is dominant. Deep wells imply a greater depth to the water-bearing zone, which typically is used as an indicator that water has a longer traveltime between recharge and entering the well. Depth to top of open interval similarly indicates a depth to the shallowest water-bearing zone but is also an indicator of the thickness of the unconsolidated material above bedrock. In the entire data set, water level and nitrate concentration had a weak positive correlation. Water level was inversely correlated with nitrate concentration in the Edwards-Trinity aquifer system and Silurian-Devonian/Upper carbonate aquifer and positively correlated with nitrate concentration in the Floridan aquifer system and the Mississippian aquifer. Well depth was inversely correlated with nitrate concentration in the Basin and Range, Castle Hayne, Silurian-Devonian/Upper carbonate, and Valley and Ridge aquifers individually (table 15). Depth to top of open interval was inversely correlated with nitrate concentration for the Basin and Range aquifer and the Ozark Plateaus aquifer system.

Interaction of Source, Fate, and Transport Factors

The analysis of transport factors has illustrated how ground-water age, degree of confinement, dissolved oxygen concentration, and well depth all affect nitrate concentrations. The analysis of source factors indicates a strong relation between nitrate concentration and agricultural land. It is not possible to tell from these analyses, however, whether these variables are actually independent. For example, all the wells in unconfined aquifers may be in areas that have a higher percentage of agricultural land than wells in confined aquifers, making the analysis of confinement a surrogate for land use. In order to assess the combined effect of transport and source factors, the data were analyzed by combinations of source and transport characteristics.

One combination of source and transport factors is an analysis of the combined effect of degree of confinement and land use. From the previous analysis, aquifers with confining layers and semiconfined aquifers or aquifers with mixed confinement would be less susceptible to elevated nitrate concentrations than unconfined aquifers. Agricultural land use, having been identified as a significant factor in determining nitrate concentration, is a source factor. Analysis of the combination of degree of confinement and land-use groups indicates that, for unconfined aquifers, nitrate concentrations vary by land-use category, with the highest concentrations in the agricultural areas and the lowest concentrations in the undeveloped areas (table 16). This pattern is not evident in confined aquifers. In fact, the wells in confined aquifers with agricultural land use around the well had lower nitrate concentrations than wells in confined aquifers with undeveloped land use around the well. This result is not unexpected in confined aquifers, because the recharge area for these wells may be far removed from the locations of the wells sampled. The semiconfined/mixed confined group had the lowest concentrations of nitrate overall. A nonparametric Tukey's test showed that the category with the combination of agricultural land use and unconfined aquifer type has significantly higher concentrations of nitrate than all the other categories (p-value less than 0.0001).

An analysis of nitrate concentrations in relation to the combination of redox status and land-use groupings shows a similar pattern with respect to the land-use groups. Within each of the redox-status categories of oxic, mixed-source waters, and anoxic waters, a pattern related to sources is evident; the highest nitrate concentrations are in agricultural areas and the lowest in undeveloped areas (table 17). The primary factor, however, appears to be the redox status; most of the oxic waters have the highest nitrate concentrations, and most

Table 16. Comparison of nitrate mean rank concentrations by type of confinement and land-use grouping in 12 carbonate aquifers or aquifer systems, 1993–2005.

[Shading indicates aquifer-confinement category]

Aquifer-confinement category	Predominant land-use grouping	Number of samples	Mean rank	Statistical Group from nonparametric Tukey's test (groups with the same letter are not significantly different)					
Unconfined	Agricultural	329	724	A					
Unconfined	Mixed land use	185	538		B				
Confined	Urban	31	471		B	C			
Unconfined	Urban	131	436		B	C	D		
Unconfined	Undeveloped	123	430		B	C	D		
Confined	Mixed land use	35	383		B	C	D	E	
Confined	Undeveloped	32	357			C	D	E	F
Confined	Agricultural	59	341			C	D	E	F
Semiconfined or mixed confined	Agricultural	22	324			C	D	E	F
Semiconfined or mixed confined	Mixed land use	32	293				D	E	F
Semiconfined or mixed confined	Urban	27	230					E	F
Semiconfined or mixed confined	Undeveloped	28	180						F

Table 17. Comparison of nitrate mean rank concentrations by redox-status category and land-use grouping in 12 carbonate aquifers or aquifer systems, 1993–2005.

[Shading indicates redox-status category]

Redox-status category	Predominant land-use grouping	Number of samples	Mean rank	Statistical Group from nonparametric Tukey's test (groups with the same letter are not significantly different)						
Oxic	Agricultural	298	763	A						
Oxic	Urban	86	630	A	B					
Oxic	Mixed land use	159	598		B	C				
Mixed Source	Agricultural	25	527		B	C	D			
Oxic	Undeveloped	120	461			C	D	E		
Mixed Source	Mixed land use	19	393				D	E	F	
Mixed Source	Urban	10	316					E	F	G
Anoxic	Agricultural	85	248						F	G
Anoxic	Mixed land use	70	232						F	G
Anoxic	Urban	91	205							G
Anoxic	Undeveloped	48	191							G
Mixed Source	Undeveloped	11	184							G

of the anoxic waters have the lowest nitrate concentrations. The land-use/source factor appears to be a secondary grouping variable. To further evaluate this issue, the data also were analyzed using only those samples designated as having water recharged after 1953. Samples of old water could alter the analysis because they are designated with a land-use category that may not have been present at the time of recharge. In this analysis of younger water only, the effect of redox status is even more evident. All the highest ranks for nitrate concentrations are oxic waters, and all the lowest ranks for nitrate concentrations are anoxic waters (table 18). Even the samples from undeveloped areas in oxic waters had higher nitrate concentrations than water from agricultural areas in anoxic waters. This analysis only includes samples from 8 of the 12 aquifers but illustrates that redox status can be a more important factor than land use in determining nitrate concentrations.

Another way to analyze the interaction between variables is to build regression models to determine which factors are the most important in determining nitrate concentration. A logistic regression model was built to determine the probability that nitrate would exceed a concentration of 4 mg/L. Explanatory factors that were included in the model were factors that had a statistically significant correlation with nitrate concentration (tables 14 and 15) and included soils characteristics and hydrologic variables (described and summarized on tables 7 and 8). Some of these variables are highly correlated with each other, and although they provide unique information in a correlation context, they do not provide useful information in a regression. Therefore, not every variable that had a significant correlation with nitrate concentration was included in the model. Variables that were significant in the model but had a sign that was the opposite of the result of the Spearman's rank correlation result were removed from the model. Models that had a Hosmer-Lemeshow test p-value of less than 0.05 were rejected, and the variable with the highest p-value in that model was removed to create subsequent models. Degree of confinement is a categorical variable but has an important effect on nitrate concentration; therefore, a numeric variable was created to represent the aquifer confinement. Confined aquifers were assigned a value of 1, semiconfined/mixed confined aquifers were assigned a value of 2, and unconfined aquifers were assigned a value of 3. This is not exactly in order of the nitrate concentrations in these areas but made the most hydrologic sense. Reversing the values assigned to confined aquifers with the semiconfined/mixed confined aquifers had little effect on the statistical results.

The results of the logistic regression model showed that the probability of nitrate concentration exceeding 4 mg/L was positively related to an increase in dissolved oxygen concentration and potential nitrogen input from all sources, and inversely related to percent soils in hydrologic group D (which indicates poorly drained soils), calcium-magnesium ratio (which indicates longer residence time), and percent forested land (table 19). These are variables that represent a combination of source factors and transport factors. The logistic regression model is sensitive to the selected threshold (4 mg/L) and to the input variables, but the significant variables were fairly consistent in the alternate models attempted. The regression model had a concordance of 89.7 percent. This indicates that when comparing the predicted probability values for sites that exceeded 4 mg/L to predicted probability for sites with concentrations less than 4 mg/L, the sites that exceeded 4 mg/L

Table 18. Comparison of nitrate mean rank concentrations by redox-status category and land-use grouping for water recharged in 1953 or later, in 8 of the 12 carbonate aquifers or aquifer systems, 1993–2005.

[Shading indicates redox-status category]

Redox-status category	Predominant land-use grouping	Number of samples	Mean rank	Statistical Group from nonparametric Tukey's test (groups with the same letter are not significantly different)			
Oxic	Agricultural	131	262	A			
Oxic	Urban	42	217	A			
Oxic	Mixed land use	77	207	A	B		
Oxic	Undeveloped	58	146		B	C	
Anoxic	Agricultural	10	121			C	D
Anoxic	Mixed land use	12	108			C	D
Anoxic	Urban	53	60				D

Table 19. Results of logistic regression model predicting probability of nitrate being detected at a threshold of greater than 4 milligrams per liter in 12 carbonate aquifers or aquifer systems, 1993–2005.

Parameter	Parameter estimate	Chi-square	p-value	Standardized estimate
Intercept	-2.79	72.0	< 0.0001	
Hydrologic group D soils	-.08	20.1	< .0001	-1.04
Dissolved oxygen	.35	98.1	< .0001	.66
Percent forested land	-.04	33.4	< .0001	-.59
Nitrogen from atmospheric deposition, septic systems, fertilizer, and manure	.0002	25.8	< .0001	.30
Calcium-magnesium molar ratio	-.024	4.7	.031	-.15

had a higher predicted probability 89.7 percent of the time. The r-square value (not the same as the r-square value for linear regression) was 0.30, and the maximum rescaled r-square value was 0.51. These values indicate the model is moderately good for explaining the factors affecting the probability of nitrate exceeding the threshold concentration of 4 mg/L. Model validation was not attempted, because this model was created for explanatory purposes and not predictive purposes.

Previous studies within each of the 12 aquifers provide additional insight on factors affecting nitrate concentrations in ground water. The factors described in these studies were generally categorized into issues related to sources (agricultural land use), susceptibility to contaminant infiltration (karst features), and fate and transport through the aquifer (denitrification, degree of confinement, and ground-water age). All these factors interact with each other in determining the vulnerability of the aquifer. For example, confined aquifers may have older water, which is more likely to undergo denitrification, and areas with karst features and agricultural land are more vulnerable to nitrate contamination than an area with only one of those characteristics.

Agricultural land use was mentioned as a key factor in several studies. In the Mississippian aquifer, higher concentrations of nitrate were associated with agricultural land use (Woodside and others, 2004). Intensity of agricultural land use was a factor affecting nitrate concentration in ground water in the Piedmont aquifer and the northern part of the Valley and Ridge aquifer (Lindsey and others, 1997). Ferrari and Ator (1995) found that the percentage of row-crop land use near a well was more likely to cause elevated concentrations of nitrate than pasture land in the Valley and Ridge. In the southern part of the Valley and Ridge aquifer, where nitrate concentrations were lower, the percentage of row-crop land use was only 4 percent (Johnson, 2002). The lower percentage of row-crop land use in the southern part of the Valley and Ridge aquifer compared to the northern part of that aquifer is a likely reason for the relatively lower concentrations of nitrate (Hampson and others, 2000).

For the Floridan aquifer system, areas with numerous karst features were at the greatest risk for elevated nitrate concentrations (Berndt and others, 1998). Karst features were noted as a potential route of contamination in the Mississippian aquifer (Woodside and others, 2004). For the

Ozark Plateaus aquifer system, karst features were found to be an important factor affecting ground-water quality (Petersen and others, 1998). Karst features were noted as potential causes of the high concentration of nitrate in ground water in the Piedmont aquifer and the northern part of the Valley and Ridge aquifer (Lindsey and others, 1997).

The characteristics of aquifers that would either enhance or prevent denitrification were noted in several studies. The low concentrations of nitrate in the Biscayne aquifer and the Castle Hayne aquifer are consistent with the fact that these aquifers are overlain by organic-rich soils, which can increase microbiological activity and enhance denitrification (Spruill and others, 1998). In the Mississippian aquifer, denitrification was associated with samples with low dissolved oxygen concentrations, which was attributed to the attenuated movement of water through the overlying fine-grained soils (Woodside and others, 2004). In the Ordovician aquifer, denitrification was also noted as a factor affecting nitrate concentrations (Woodside and others, 2004). The exchange of air in the unsaturated zone, leading to high dissolved oxygen concentrations and thus little opportunity for denitrification, was also noted as a factor related to elevated nitrate concentrations in the Piedmont aquifer and the northern part of the Valley and Ridge aquifer (Lindsey and others, 1997).

Presence of a confining layer and the location of a confined aquifer with respect to the recharge area were found to be important in several aquifers. The Edwards-Trinity aquifer system is highly transmissive, but it is confined where the urban and agricultural land uses overlie the aquifer, with more undeveloped land uses located in the recharge area (Bush and others, 2000). For the Ozark Plateaus aquifer system, the presence of a confining layer was related to lower nitrate concentrations (Petersen and others, 1998). In the Silurian-Devonian/Upper carbonate aquifers, nitrate concentrations were much lower in areas protected by a bedrock confining unit or more than 100 ft of Quaternary-age deposits (Savoca and others, 1999). Water in the Basin and Range aquifer sampled in discharge areas tends to be very old (thousands of years) and located a long distance away from the recharge areas, making the presence of anthropogenic contaminants unlikely. Water sampled near an outcrop was more likely to have contaminants detected (Schaefer and others, 2005).

The comparison of the factors affecting nitrate concentrations, as determined by studies within individual aquifers, to the factors affecting nitrate concentrations in the 12 aquifers illustrates a similar pattern of factors. In some cases, the degree of confinement is a major factor within an aquifer; in others, karst features, organic carbon concentrations, dissolved oxygen concentrations, flowpath length, or land use may be the factor that is the most important for that area. Most of the aquifers probably are affected by the same factors to a certain degree; however, the factors that are the most important vary among the 12 aquifers.

The concentrations of nitrate in the 12 carbonate aquifers were related to several factors. Karst features may be a primary factor, but data were not available to allow quantitative analysis of the presence of karst features for this study. Redox status appears to be a very important factor in determining nitrate concentration. Other physical characteristics controlling nitrate concentration that could be quantified are land use, composition of soils, and degree of confinement. Ground-water age is important because of the link to sources and denitrification, but age is closely related to other factors such as confinement. Geochemical indicators such as calcium S.I., dolomite S.I., and calcium-magnesium ratio are important in some aquifers and are surrogates for residence time.

Pesticides

Samples were collected from wells or springs for pesticide analysis at 1,027 sites for 47 pesticides or pesticide degradates (table 20). Each site is represented by data from one sampling event. For sites with multiple samples, the most recent sample was used for this study. The primary method of pesticide analysis for these samples was gas chromatography/mass spectrometry with selected-ion monitoring (Zaugg and others, 1995), which provides low-level analyses. The results of pesticide sampling for the 12 carbonate aquifers are analyzed with respect to the distribution of pesticides, a screening-level assessment of potential human-health concerns, and factors affecting concentrations and detections of pesticides.

Detection Levels and Data-Analysis Methods

The pesticide data include a high proportion of nondetects, frequently resulting in data sets that are highly censored from a data-analysis standpoint. In addition, analytical sensitivity and LRLs vary within and among pesticides, resulting in multiple censoring levels, and the data include estimated values that are reliable detections but less certain quantitative determinations. In order to understand techniques used to analyze the pesticide data, it is necessary to understand how nondetects and estimated values were treated for various statistical methods.

The frequency of detecting a pesticide above a given concentration is directly affected by the threshold concentration level used to determine whether or not a concentration is considered a detection, with fewer detections for higher concentration thresholds. Three types of concentration thresholds are referred to and used in this report:

1. Laboratory Reporting Levels (LRLs): A LRL is the “less than” concentration reported when a pesticide is determined to not be present (for example: < 0.005 μg/L).

2. Common Assessment Levels: Common assessment levels are used to allow a common comparison among samples for the same pesticide if the LRL changed over time or to allow comparisons among several pesticides that had different LRLs.

Table 20. Detection frequency for 47 pesticides in 12 carbonate aquifers or aquifer systems, 1993–2005.

[Pesticide types: D, degradate; H, herbicide; I, insecticide; N/A, Not applicable, MCL, Maximum Contaminant Level (U.S. Environmental Protection Agency, 2006); HBSL, Health-Based Screening Level (Toccalino and others, 2007)]

Pesticide name	Pesticide type	Number of analyses	Number of detections[1]	Percent detections	Benchmark level (µg/L) [upper HBSL][2]	Benchmark type	Benchmark exceedance
Deethylatrazine	D	1,021	383	37.5	NONE	N/A	N/A
Atrazine	H	1,020	379	37.2	3	MCL	0
Prometon	H	1,027	187	18.2	400	HBSL	0
Simazine	H	1,027	178	17.3	4	MCL	0
Metolachlor	H	1,027	153	14.9	700	HBSL	0
Tebuthiuron	H	1,017	99	9.7	1000	HBSL	0
p,p´-DDE	D, I	992	30	3.0	.1 [10]	HBSL	0
Alachlor	H	1,018	28	2.8	2	MCL	0
Dieldrin	I	1,019	21	2.1	.002 [.2]	HBSL	20
Diazinon	I	1,024	12	1.2	1	HBSL	1
Cyanazine	H	990	11	1.1	1	HBSL	0
2,6-Diethylaniline	D	1,024	7	.7	NONE	N/A	N/A
EPTC	H	989	6	.6	200	HBSL	0
Carbaryl	I	1,025	6	.6	40 [4,000]	HBSL	0
Metribuzin	H	1,024	6	.6	90	HBSL	0
Chlorpyrifos	I	1,019	5	.5	2	HBSL	0
Trifluralin	H	1,023	5	.5	20	HBSL	0
Carbofuran	I	989	4	.4	40	MCL	0
Napropamide	H	988	4	.4	800	HBSL	0
Acetochlor	H	853	3	.3	1 [100]	HBSL	0
Butylate	H	989	3	.3	400	HBSL	0
Lindane	I	990	3	.3	.2	MCL	0
Pebulate	H	990	3	.3	50	HBSL	0
Benfluralin	H	1,027	3	.3	4	HBSL	0
Propanil	H	988	2	.2	6	HBSL	0
Terbacil	H	989	2	.2	90	HBSL	0
Dacthal (DCPA)	H	1,027	2	.2	70	HBSL	0
Pendimethalin	H	1,025	2	.2	70	HBSL	0
Pronamide	H	1,025	2	.2	1 [100]	HBSL	0
Linuron	H	991	1	.1	5	HBSL	0
Propargite	I	991	1	.1	1 [100]	HBSL	0
alpha-HCH	I	992	0	.0	.006 [.6]	HBSL	0
Azinphos-methyl	I	1,026	0	.0	10	HBSL	0
cis-Permethrin	I	1,027	0	.0	4 [400][3]	HBSL	0
Disulfoton	I	992	0	.0	.9	HBSL	0

Table 20. Detection frequency for 47 pesticides in 12 carbonate aquifers or aquifer systems, 1993–2005.—Continued

[Pesticide types: D, degradate; H, herbicide; I, insecticide; N/A, Not applicable, MCL, Maximum Contaminant Level (U.S. Environmental Protection Agency, 2006); HBSL, Health-Based Screening Level (Toccalino and others, 2007)]

Pesticide name	Pesticide type	Number of analyses	Number of detections[1]	Percent detections	Benchmark level (µg/L) [upper HBSL][2]	Benchmark type	Benchmark exceedance
Ethalfluralin	H	992	0	0.0	30	HBSL	0
Ethoprop	I	992	0	.0	1 [100]	HBSL	0
Fonofos	I	1,027	0	.0	10	HBSL	0
Malathion	I	1,027	0	.0	50	HBSL	0
Molinate	H	992	0	.0	.7	HBSL	0
Parathion	I	992	0	.0	.02	HBSL	0
Parathion-methyl	I	1,027	0	.0	1	HBSL	0
Phorate	I	1,027	0	.0	4	HBSL	0
Propachlor	H	992	0	.0	1 [100]	HBSL	0
Terbufos	I	1,027	0	.0	.4	HBSL	0
Thiobencarb	H	992	0	.0	70	HBSL	0
Triallate	H	992	0	.0	20	HBSL	0

[1] Assessment level of 'all detections' used for this analysis.

[2] Some compounds have a high and a low value for HBSLs. For those compounds that have both a high and a low value, the high value is given in brackets.

[3] HBSLs were not developed for cis-Permethrin; concentrations of cis-Permethrin can be compared to the HBSL range of 4-400 µg/L for Permethrin (Toccalino and others, 2007)

3. Human-Health Benchmarks: USEPA MCLs (U.S. Environmental Protection Agency, 2006) and HBSLs. HBSLs are benchmark concentrations of contaminants in water that may be of potential concern for human health, if exceeded. HBSLs are non-enforceable benchmarks that were developed by the USGS in collaboration with USEPA and others using USEPA methodologies for establishing drinking-water guidelines and the most current, USEPA peer-reviewed, publicly available human-health toxicity information (Toccalino and others, 2004, 2007).

For some data analyses, all detections, including estimated or 'E' values (reliable detections with less certain quantitative determinations), are used even if they are below LRLs for unqualified quantitation. When comparing pesticides to each other, a common assessment level of 0.01 µg/L is used so that the detection rates are comparable. A very small number of samples had LRLs that were higher than the maximum common LRL (table 21). Nondetections with LRLs greater than the maximum common LRL are likely indications of analytical problems such as matrix interference (Gilliom and others, 2006), and therefore were not included in the statistical analysis.

The variation in frequency of pesticide detections in relation to the reporting level or assessment level used for the analysis is shown in figure 22. Some comparisons can be misleading if care is not taken; for example, the relative change from the 'all detections' assessment level to the 0.01 µg/L assessment level is greatest for prometon and least for atrazine and deethylatrazine. Thus, statistical analyses using the 'all detections' assessment level could have a different outcome than if the 0.01 µg/L assessment level were used.

Statistical methods used to evaluate pesticide concentration as a continuous variable used the rank of concentration rather than the reported value, because the data are not normally distributed and generally do not conform to a single distribution (Helsel and Hirsch, 2002). When ranking pesticides for a statistical test, all nondetects were assigned a rank lower than the lowest 'E-coded' value. All quantified detections, including those coded as estimated, were assigned ranks on the basis of the reported values. This method has been used in other national assessments of pesticides and has a detailed explanation in Gilliom and others (2006).

Occurrence and Distribution

Initial analysis of pesticide occurrence focused on the presence of the 47 pesticides analyzed. Analysis of 'all detections,' regardless of data LRLs, indicates that 1 or more pesticides were detected in 509 of the 1,027 samples (50 percent). Detections of multiple pesticides in the same sample were common; 401 samples had 2 or more pesticides detected

Table 21. Method detection limits and common reporting levels for frequently detected pesticides in 12 carbonate aquifers or aquifer systems, 1993–2005.

Pesticide	Maximum long-term method detection limit[1]	Maximum common laboratory reporting limit (CRLMAX)[1]	Number of nondetects with reporting limit exceeding CRLMAX
Atrazine	0.004	0.007	7
Deethylatrazine	.003	.006	6
Metolachlor	.006	.013	0
Prometon	.007	.018	0
Simazine	.006	.011	0

[1] Gilliom and others, 2006.

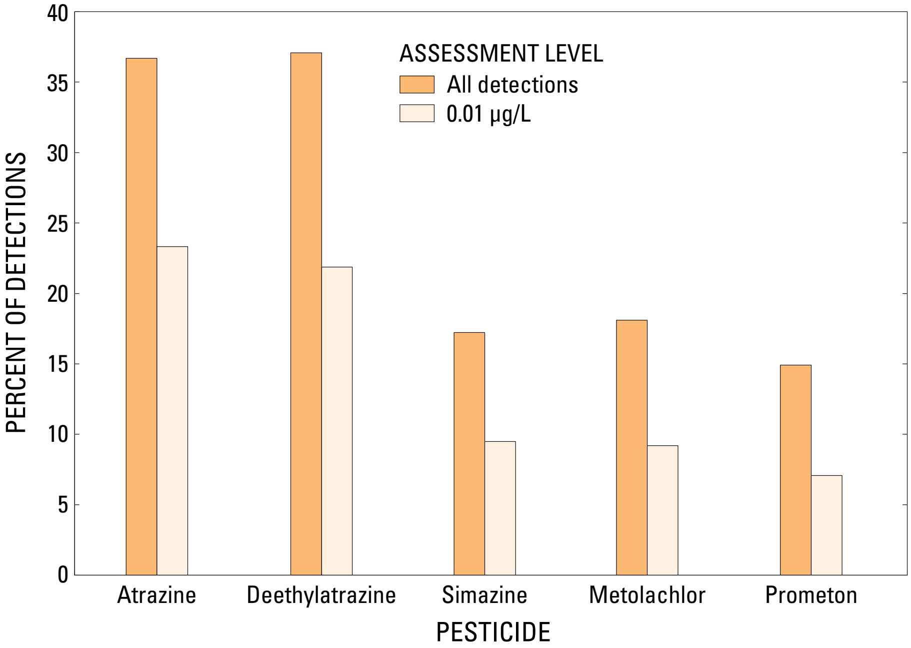


Figure 22. Percent of detections for the herbicides atrazine, deethylatrazine (a degradate of atrazine), simazine, metolachlor, and prometon by assessment level in 12 carbonate aquifers or aquifer systems sampled during 1993–2005.

(39 percent), and 45 samples had 6 or more pesticides detected (4 percent).

The data collected for pesticide analysis cover a time period in which there were a number of major changes in pesticide use, including the introduction and increased use of acetochlor and declining use of cyanazine and alachlor (Gilliom and others, 2006). The samples for this study, however, were not collected in a manner that allows interpretation of relations between temporal usage trends and pesticide occurrence. Therefore, interpretation of the pesticide data does not take into account the potential effect of changes in pesticide use during the sampling period.

The frequency of pesticide detections varied widely among the 12 aquifers (figs. 23 and 24). The three aquifers with the most frequent detections were the Biscayne, Piedmont, and Valley and Ridge aquifers, which had at least 1 of the 47 pesticides detected in more than 80 percent of the samples, and multiple detections per sample were common. In the Piedmont and Valley and Ridge aquifers, in particular, more than 10 percent of the samples had more than six pesticides detected. The three aquifers with the least frequent detections were the Basin and Range, Castle Hayne, and Silurian-Devonian/Upper carbonate aquifers, with one or more pesticides detected in less than 20 percent of samples. The other six aquifers sampled were intermediate between these high and low frequencies. As mentioned previously, the sampling within each aquifer was not balanced with respect to land use and type of well sampled, so the results within aquifers may not reflect the actual distribution of pesticide occurrence in each aquifer. This range of characteristics can, however, be used to interpret the factors affecting pesticides occurrence in carbonate aquifers.

Assessment of Potential Human-Health Significance

Potential human-health significance of pesticides in drinking water was evaluated by comparing measured concentrations to human-health benchmarks. MCLs were used as benchmarks for compounds regulated under the Safe Drinking Water Act, and HBSLs were used as benchmarks for unregulated compounds. As previously stated, not all the sample locations represent drinking-water supplies, but the majority of the sites are used for public or domestic supply; therefore, comparisons to human-health benchmarks determined for drinking water are presented as a way to put the sampling results in context. Of the 47 pesticides analyzed, 5 have MCLs, 40 have HBSLs, and 2 have no human-health benchmarks available (table 20). For carcinogens, HBSLs are presented as an HBSL range (table 20), representing the contaminant concentration in drinking water that corresponds to an excess lifetime cancer risk of 1 chance in 1 million to 1 chance in 10 thousand (Toccalino and others, 2007). For this analysis, in addition to comparing concentrations to human-health benchmarks (MCLs or HBSLs), benchmark quotients (BQ) were calculated to determine how close a concentration is to the benchmark. A BQ is calculated by dividing a concentration by its human-health benchmark, so a sample with a BQ of 1 has a concentration equal to its benchmark level. For unregulated carcinogens, BQ values were calculated using the low end of the HBSL range, which corresponds to a 1 in 1 million cancer risk. When a BQ is greater than or equal to 0.1, it is at a concentration that is at or above 10 percent of the human-health benchmark, and on this basis may warrant continued monitoring and evaluation. Regular monitoring of contaminants with a BQ greater than 0.1 would enable analysis of trends in their occurrence and provide an early indication of concentrations that approach MCLs or HBSLs (Toccalino and others, 2007). Thus, BQ values can be used as a planning tool so that potential issues can be identified as early as possible.

No sample had a pesticide concentration that was greater than a USEPA MCL; however, two pesticides had concentrations that were greater than HBSLs in one or more samples. Dieldrin concentrations were greater than the HBSL of 0.002 µg/L in 20 samples, 9 of which were from either domestic or public supply wells. Dieldrin is an insecticide that has been banned in the United States since 1987 but had a detection frequency of 2 percent (table 20). Dieldrin concentrations were greater than the HBSL in one or more wells in the Biscayne, Floridan, Mississippian, Ozark Plateaus, Piedmont, and Valley and Ridge aquifer/aquifer system (fig. 25). Most of these samples were from wells in urban or mixed land-use areas. The highest concentration of dieldrin was 0.81 µg/L in a sample from a site in an agricultural area in the Mississippian aquifer. That site was not used as a source of drinking water. The frequent exceedances of the HBSLs for dieldrin is because of its environmental persistence and the relatively low HBSL (0.002 µg/L), reflecting its relatively high toxicity. A diazinon concentration of 19 µg/L was greater than the HBSL (1 µg/L) in a single sample from a domestic supply well in the Prairie du Chien aquifer (fig. 26). Two other samples, both from domestic supply wells, had BQ values between 0.1 and 1, one in the Floridan aquifer system and the other in the Prairie du Chien aquifer (fig. 26). Diazinon, also an insecticide, was detected in about 1 percent of the samples. None of the other pesticides were detected at concentrations greater than either a MCL or HBSL.

The most frequently detected pesticides were the herbicides atrazine, prometon, simazine, metolachlor, and the atrazine degradate deethylatrazine (table 20). Although human-health benchmarks for these pesticides were not exceeded in any samples, BQs for atrazine were greater than 0.1 for 35 samples in agricultural areas (Mississippian, Ordovician, Ozark Plateaus, Piedmont, Prairie du Chien, and Valley and Ridge aquifer/aquifer system), 4 samples in mixed land-use areas (Ozark Plateaus, Piedmont, Prairie du Chien, and Valley and Ridge aquifer/aquifer system), and 2 samples in urban areas (Biscayne and Valley and Ridge aquifers) (fig. 27). Of the 41 samples with BQ greater than 0.1 for atrazine, 31 were from domestic supply wells. Only one sample, from a domestic well in an agricultural area of the Valley and Ridge

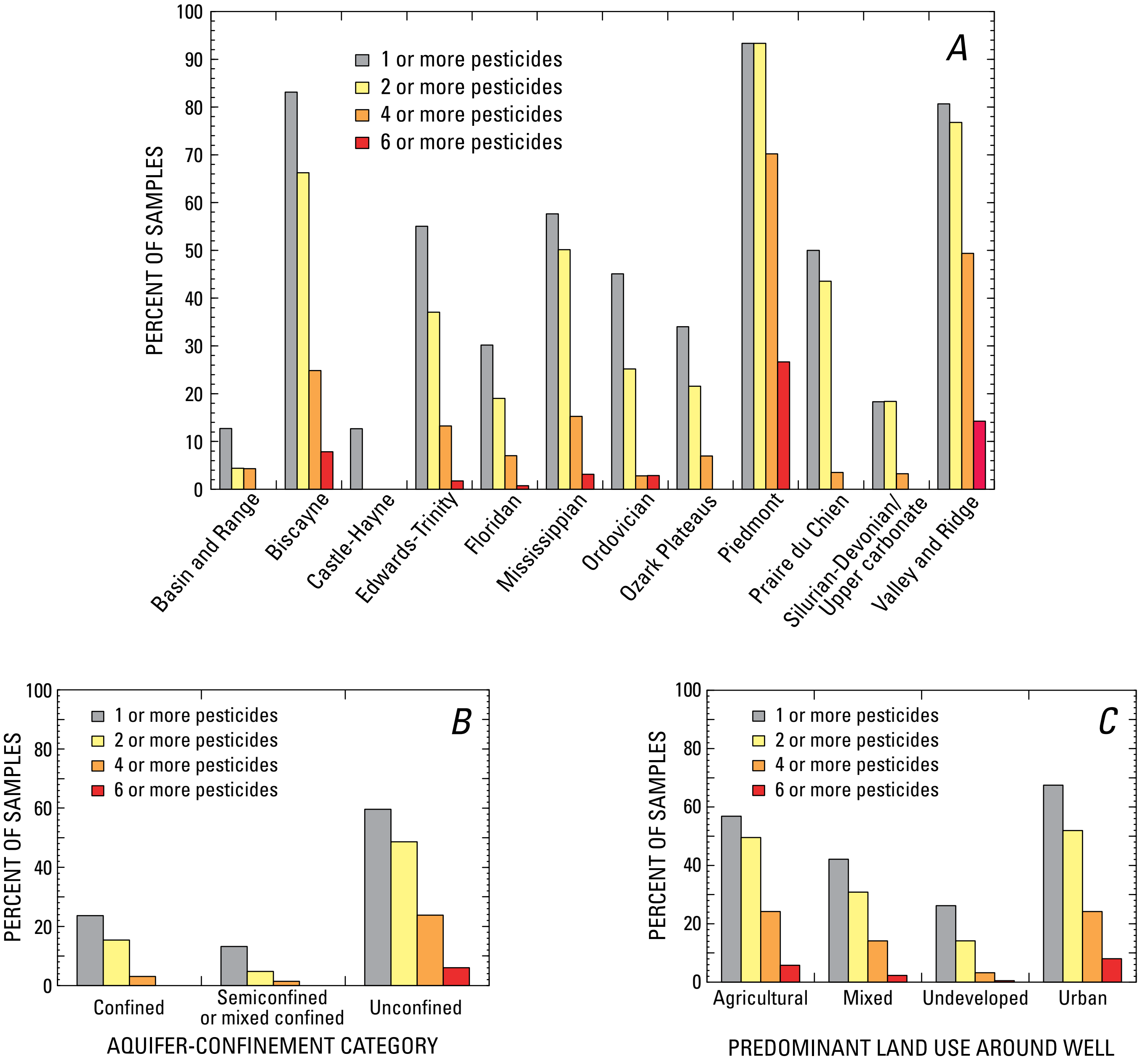


Figure 23. Frequencies of individual and multi-compound detections in relation to A) aquifer or aquifer system, B) degree of confinement, and C) predominant land use around well. Results are based on analysis of 47 pesticide compounds in 12 carbonate aquifers or aquifer systems during 1993–2005 (assessment level, all detections).

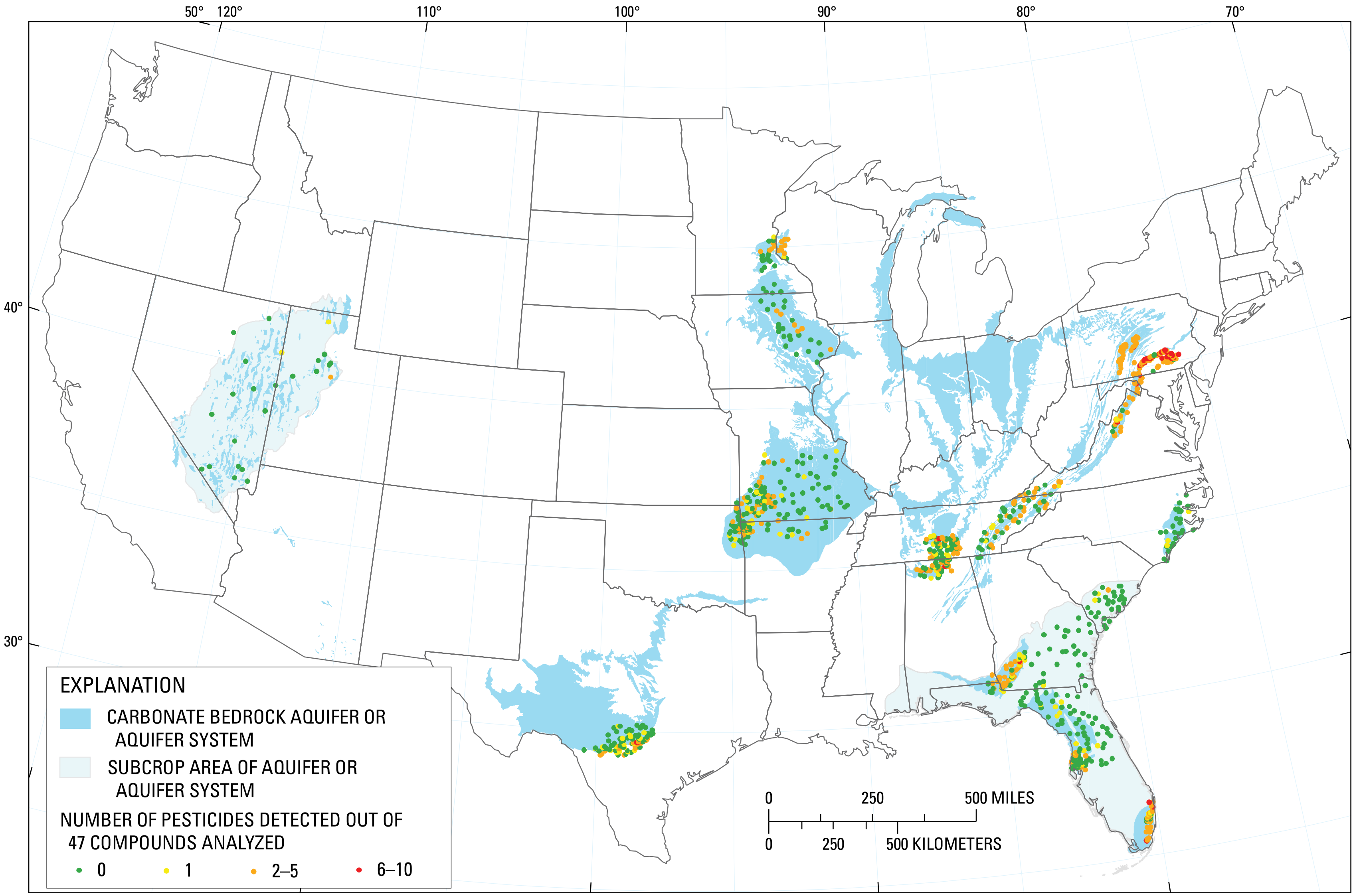


Figure 24. Sample locations and number of pesticides detected out of 47 pesticides analyzed in 12 carbonate aquifers or aquifer systems (assessment level, all detections).

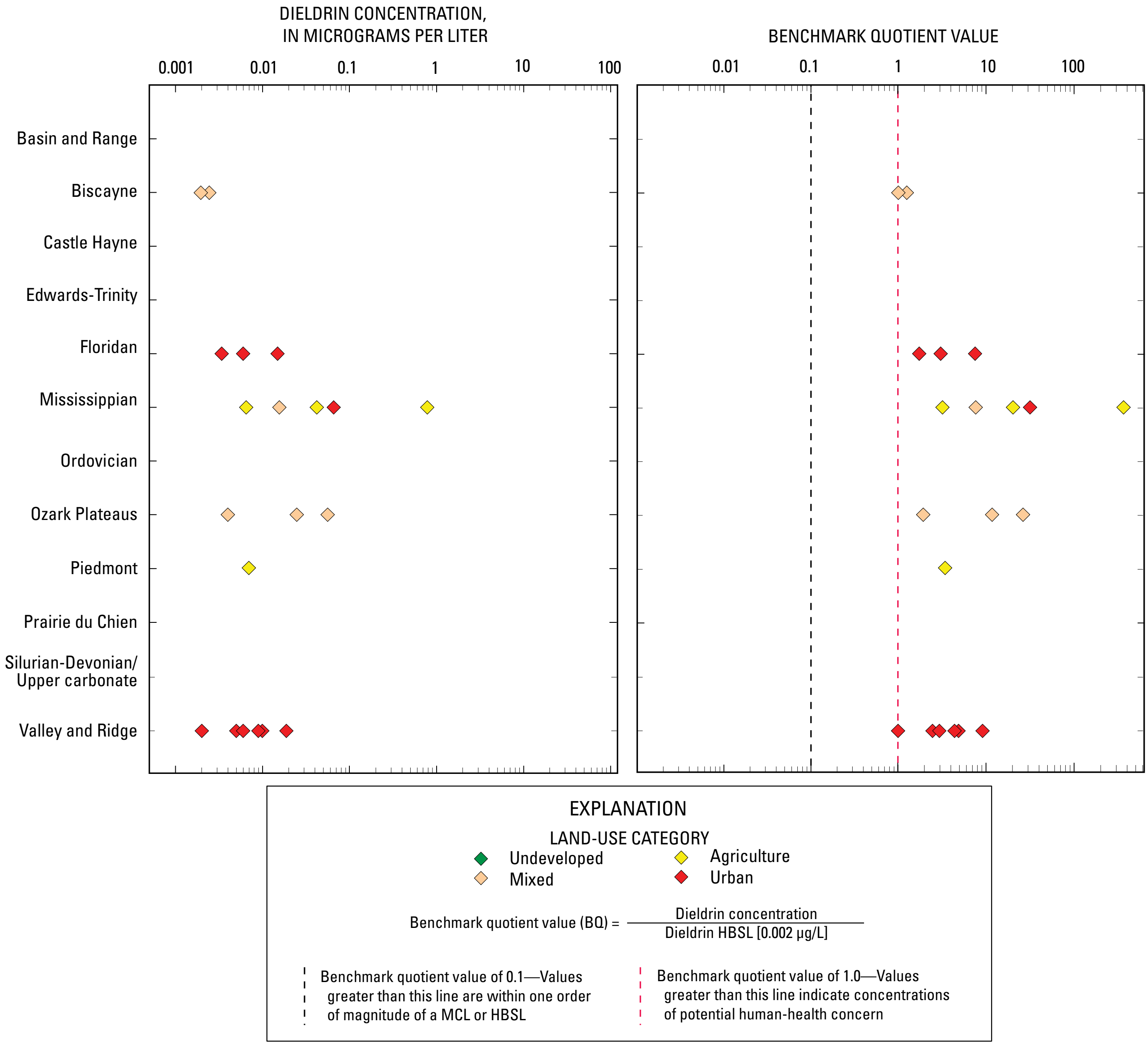


Figure 25. Concentrations of dieldrin and human-health benchmarks in various land-use categories in 12 carbonate aquifers or aquifer systems (assessment level, all detections). MCL is Maximum Contaminant Levels for regulated compounds (U.S. Environmental Protection Agency, 2006); HBSL is Health-Based Screening Level concentrations for unregulated compounds (Toccalino and others, 2004).

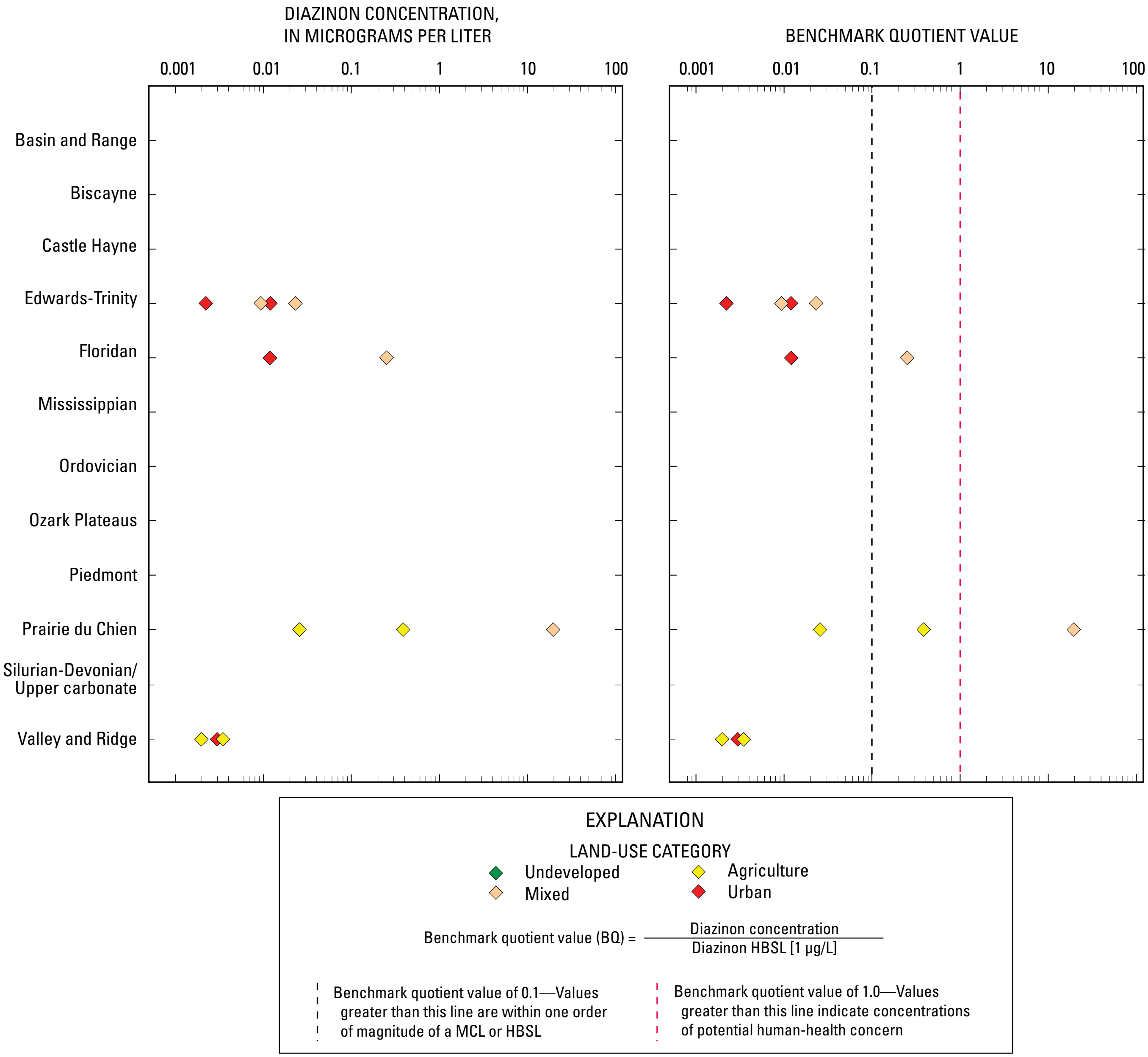


Figure 26. Concentrations of diazinon and human-health benchmarks in various land-use categories in 12 carbonate aquifers or aquifer systems (assessment level, all detections). MCL is Maximum Contaminant Levels for regulated compounds (U.S. Environmental Protection Agency, 2006); HBSL is Health-Based Screening Level concentrations for unregulated compounds (Toccalino and others, 2004).

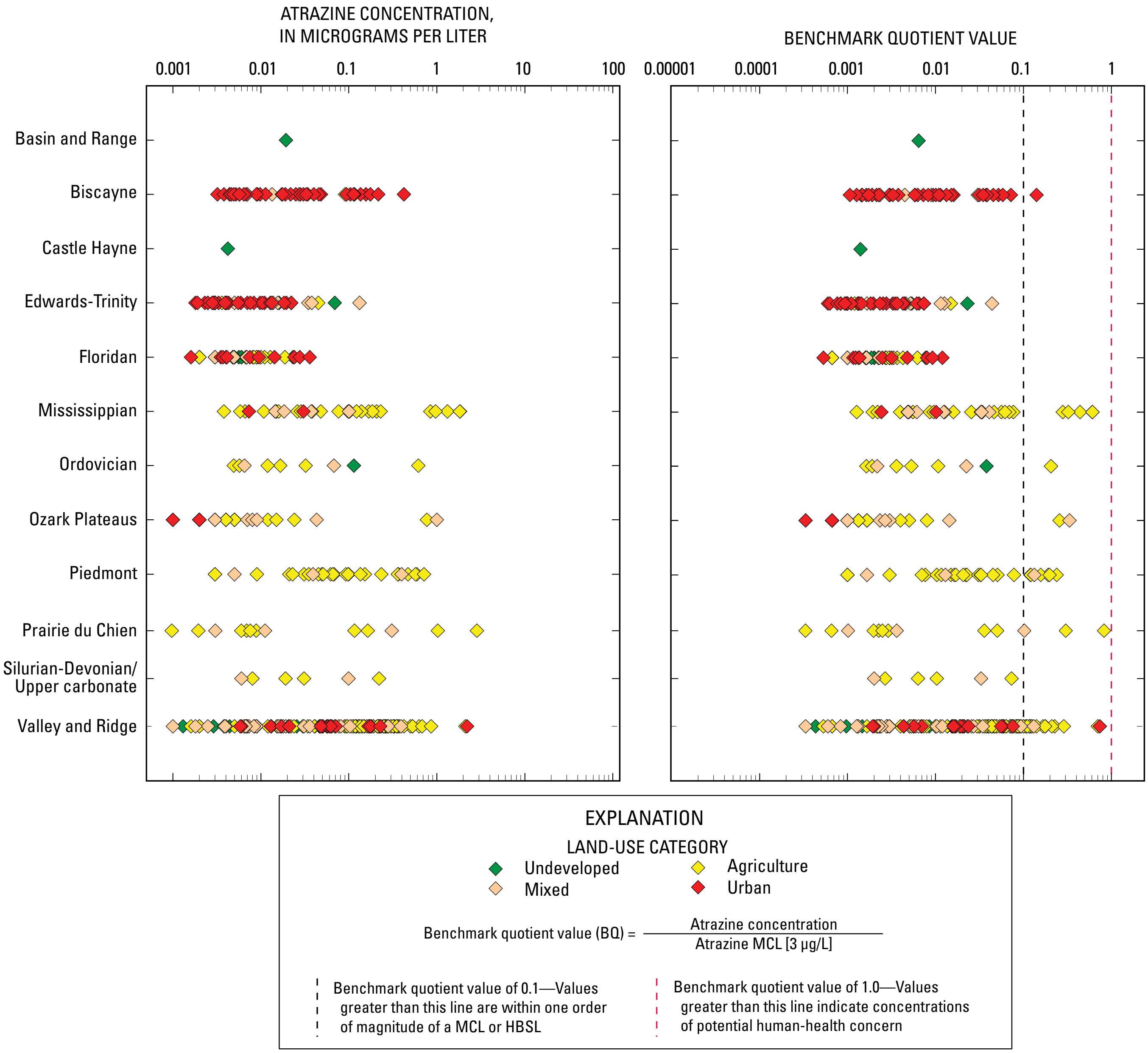


Figure 27. Concentrations of atrazine and human-health benchmarks in various land-use categories in 12 carbonate aquifers or aquifer systems (assessment level, all detections). MCL is Maximum Contaminant Levels for regulated compounds (U.S. Environmental Protection Agency, 2006); HBSL is Health-Based Screening Level concentrations for unregulated compounds (Toccalino and others, 2004).

aquifer, had a BQ greater than 0.1 for simazine (fig. 28), and no samples for prometon or metolachlor had BQs greater than 0.1 (figs. 29 and 30). It is important to note that deethylatrazine, the pesticide compound with the largest number of detections, is one of the three compounds that does not have a MCL or an HBSL and therefore is not analyzed in this context. The geographic distribution of detections and BQs for the herbicides atrazine, simazine, metolachlor, and prometon are illustrated in figure 31. The remaining 40 pesticides had detection frequencies of less than 10 percent (table 20). Of those 40 pesticides, concentrations were typically low relative to benchmarks. Only two samples each of lindane and cyanazine and one sample each for alachlor, acetochlor, and propargite had a BQ greater than 0.1.

Overall, results indicate that concentrations of the pesticides studied rarely exceeded available water-quality benchmarks for human health. Of the 44 compounds for which benchmarks are presently available, only 2 insecticides had concentrations greater than their benchmarks; the majority of the exceedances were for dieldrin (2 percent of samples). In addition, only atrazine had BQ values that were frequently greater than 0.1, indicating a potential priority for monitoring in agricultural areas in the Valley and Ridge aquifer. These findings closely match the findings of the national study of pesticides by Gilliom and others (2006) that indicated dieldrin accounted for the vast majority of cases where ground-water samples exceeded human-health benchmarks, and atrazine was the most frequently detected pesticide.

Factors Affecting Occurrence of Frequently Detected Pesticides

The most frequently detected pesticides were the herbicides atrazine, simazine, prometon, metolachlor, and the atrazine degradate deethylatrazine (table 20). The statistical analysis of the pesticide data focuses primarily on these five frequently detected compounds, because statistical techniques used in this analysis are not effective if detection frequency is less than 10 percent. Occurrence of the five frequently detected pesticides in carbonate aquifers was evaluated with respect to a number of different factors, including aquifer, type of study, fate and transport factors, and source factors. A combination of issues such as pesticide use, amount and type of agricultural land use, degree of confinement, ground-water age, and other issues causes the patterns of pesticide occurrence. Some of these factors are related to the sources of the contaminants, and others are indicators of transport of the pesticide from the land surface to the sampling point. The following is an analysis of the factors related to the occurrence of pesticides in carbonate aquifers.

Aquifers and Study Types

Detections of these five frequently occurring pesticide compounds varied widely among the carbonate aquifers. Frequencies of detection at a common assessment level of 0.01 µg/L were greatest in the Biscayne, Mississippian, Piedmont, and Valley and Ridge aquifers, which had one or more of the five compounds detected in greater than 30 percent of the wells sampled, and least in the Basin and Range, Castle Hayne, Floridan, and Ozark Plateaus aquifer/aquifer systems, in which no pesticide had a detection frequency of greater than 10 percent (fig. 32).

Detection frequencies also varied with the type of study. In particular, agricultural and urban land-use studies had a higher rate of detection of the five frequently occurring pesticides than the other types of studies (fig. 33), which is generally expected because most of the sampled wells in these studies were relatively shallow and surrounded by agricultural or urban land uses [results of a nonparametric Tukey's test confirmed that the agricultural and urban land-use study wells were shallower than wells in the major-aquifer studies or the source-water-quality assessments (p-value less than 0.0001)]. Consistent with their shallower depth, available age-dating data show that the wells in agricultural and urban land-use studies almost all had water recharged in 1953 or later, whereas the major-aquifer studies tended to have more water classified as recharged before 1953. The percentage of samples with one or more pesticides detected and the percentage of samples with multiple detections per sample were greater in the unconfined aquifers than in the semiconfined/mixed confined or confined aquifers. The only samples with more than six pesticides detected were from sites in unconfined aquifers. The percentage of samples with one or more pesticides detected and the percentage of samples with multiple detections were greater in the agricultural and urban areas than in areas with mixed land use or undeveloped land use (fig. 23.)

Source Factors

Analysis of detections of the five frequently occurring pesticides indicates a pattern in which pesticides are more frequently detected in agricultural and urban areas, where pesticides are most heavily used (figs. 23 and 33). Most of the studies with atrazine detected in greater than 50 percent of the samples were agricultural land-use studies. Some studies did not follow this pattern. Studies in urban areas in the Edwards-Trinity aquifer system and the Biscayne aquifer also had high detection frequencies that may be related to source areas not matching the land use near the sampling site (the study in the Edwards-Trinity aquifer system was a spring study) or the urban use of atrazine. A few studies had high percentages of agricultural land use but low detection frequencies of atrazine. The studies in the Silurian-Devonian/Upper carbonate aquifer and the Ozark Plateaus aquifer system had relatively low frequencies of pesticide detections; however, the exceptions to the pattern in those areas are likely because of transport factors such as the presence of a confining unit.

The Spearman's rank correlation test was used to evaluate relations between concentrations of the five frequently detected pesticides and various potential source factors

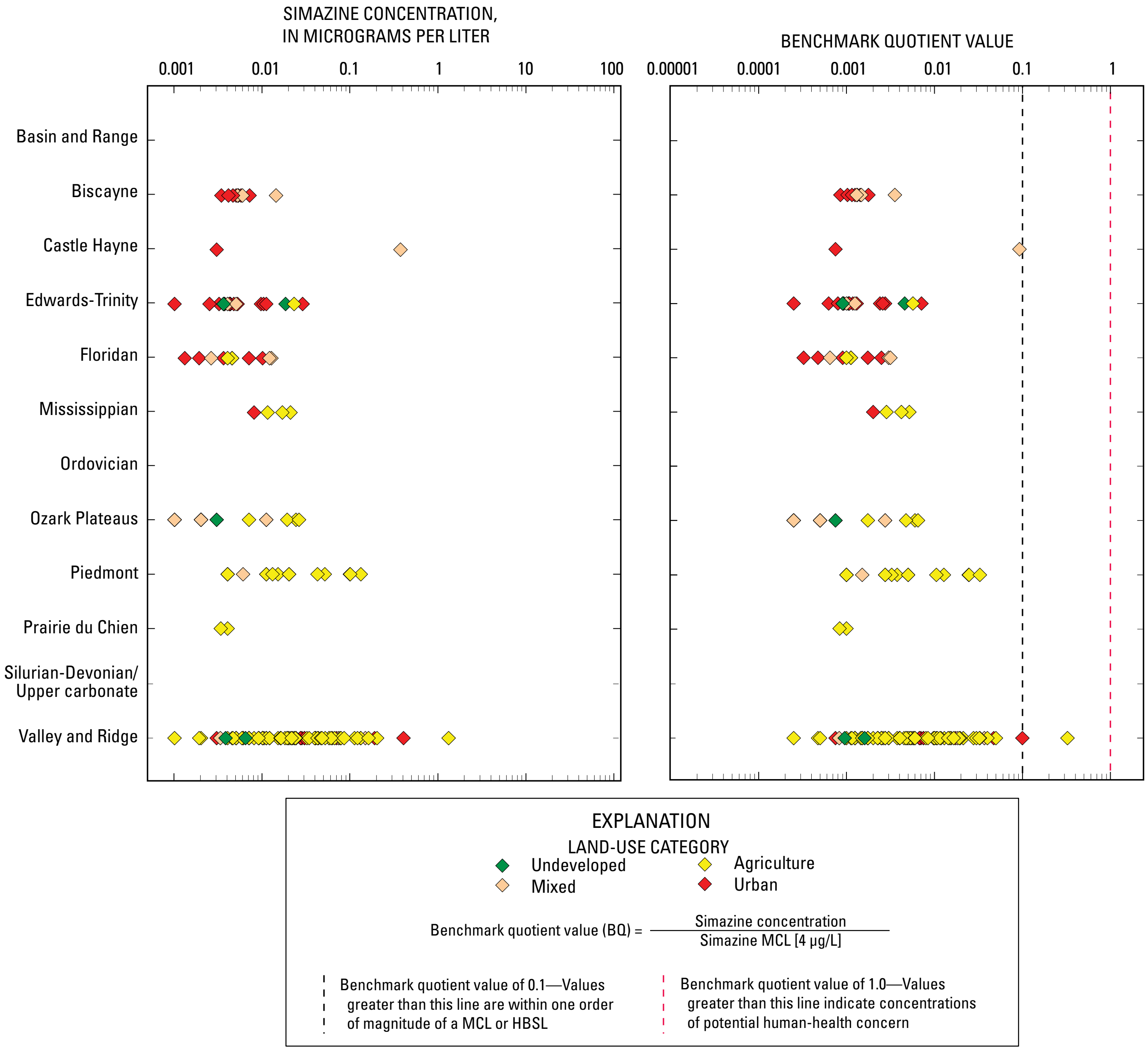


Figure 28. Concentrations of simazine and human-health benchmarks in various land-use categories in 12 carbonate aquifers or aquifer systems (assessment level, all detections). MCL is Maximum Contaminant Levels for regulated compounds (U.S. Environmental Protection Agency, 2006); HBSL is Health-Based Screening Level concentrations for unregulated compounds (Toccalino and others, 2004).

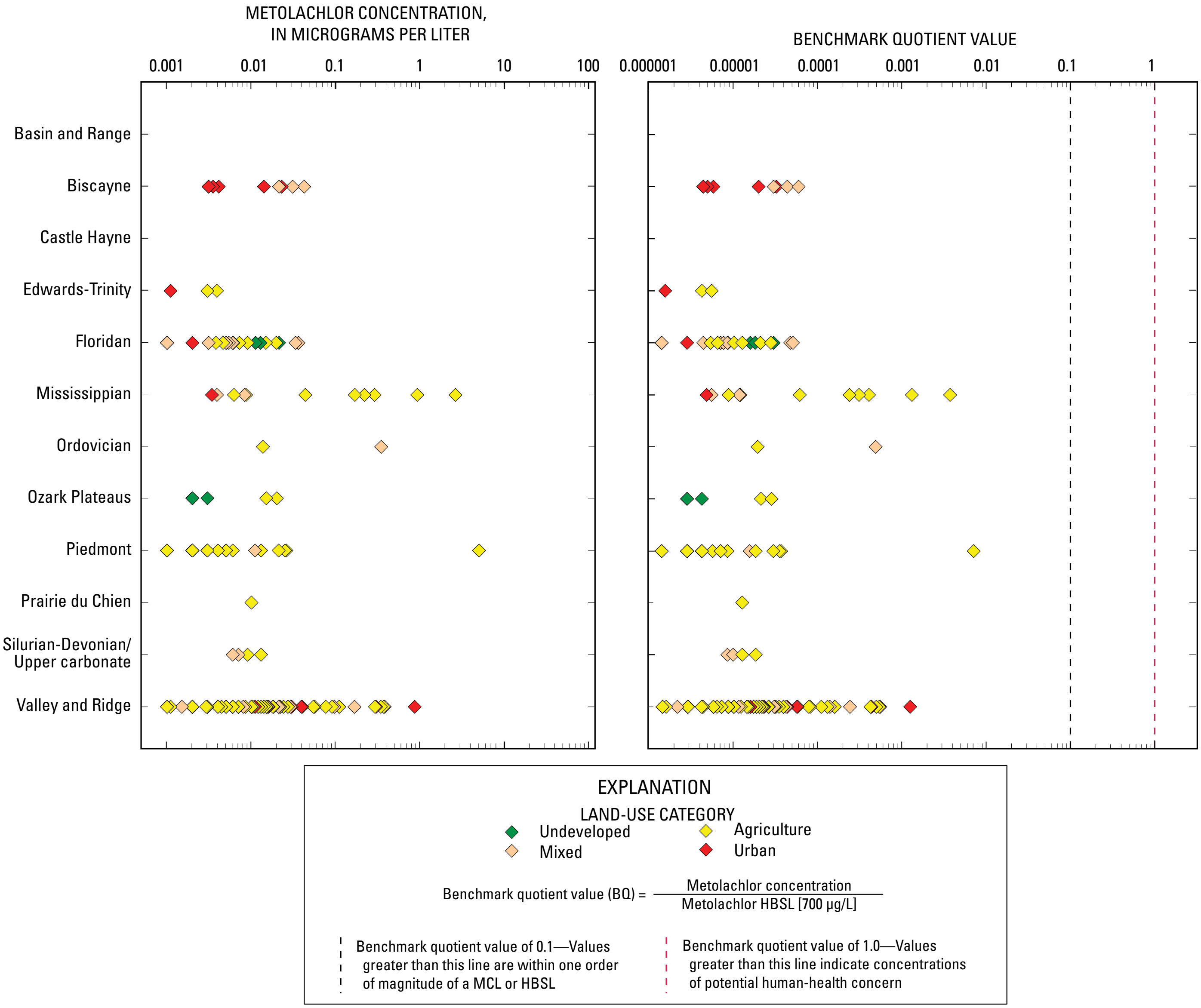


Figure 29. Concentrations of metolachlor and human-health benchmarks in various land use categories in 12 carbonate aquifers or aquifer systems (assessment level, all detections). MCL is Maximum Contaminant Levels for regulated compounds (U.S. Environmental Protection Agency, 2006); HBSL is Health-Based Screening Level concentrations for unregulated compounds (Toccalino and others, 2004).

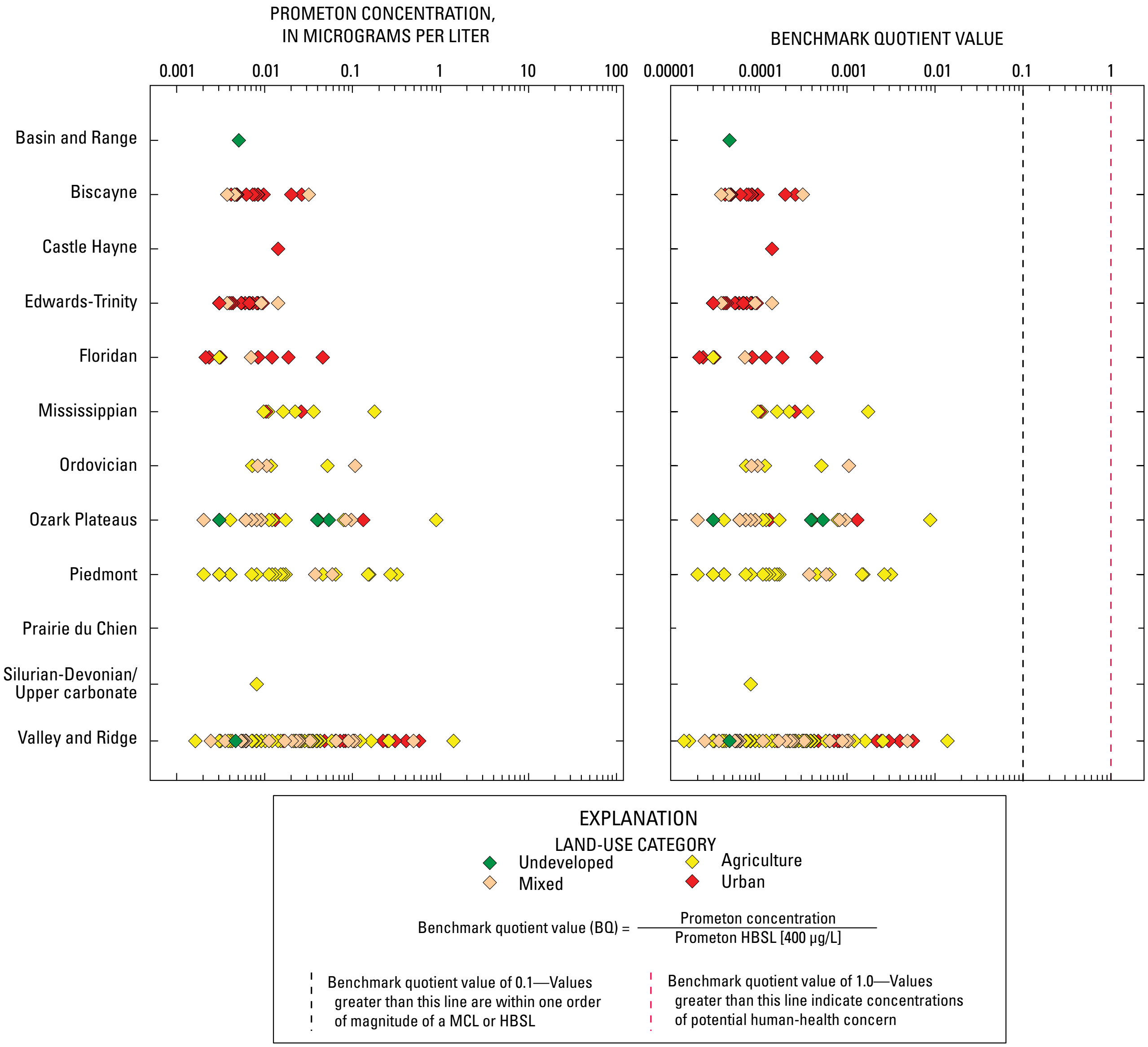
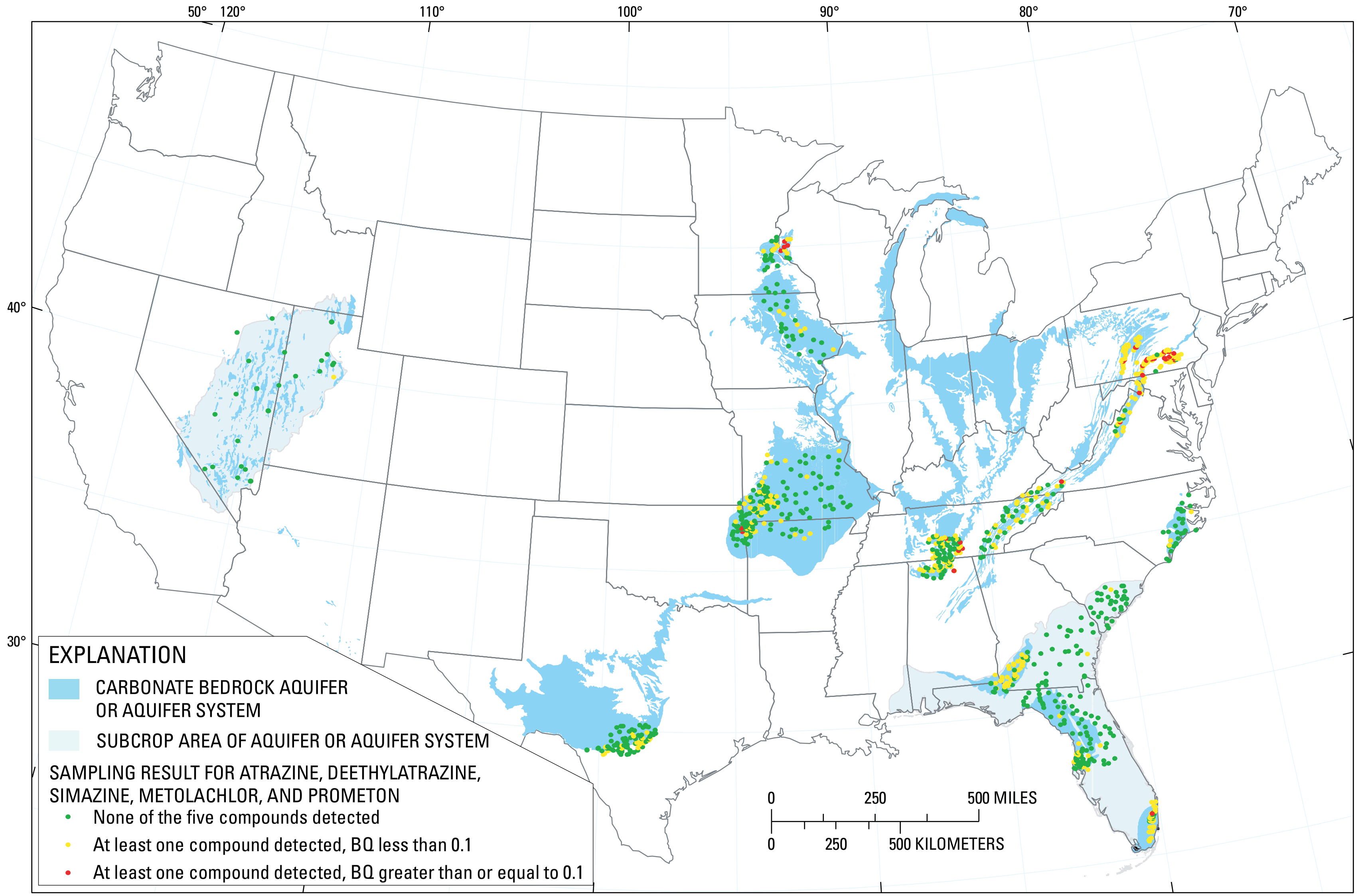


Figure 30. Concentrations of prometon and human-health benchmarks in various land use categories in 12 carbonate aquifers or aquifer systems (assessment level, all detections). MCL is Maximum Contaminant Levels for regulated compounds (U.S. Environmental Protection Agency, 2006); HBSL is Health-Based Screening Level concentrations for unregulated compounds (Toccalino and others, 2004).



Benchmark Quotient (BQ) = Measured concentration/Maxium contaminant level OR Health-based screening level. BQ does not apply to deethylatrazine.

Figure 31. Sample locations and comparison to human-health benchmarks for atrazine, deethylatrazine, simazine, metolachlor, and prometon, in 12 carbonate aquifers or aquifer systems (assessment level, all detections).

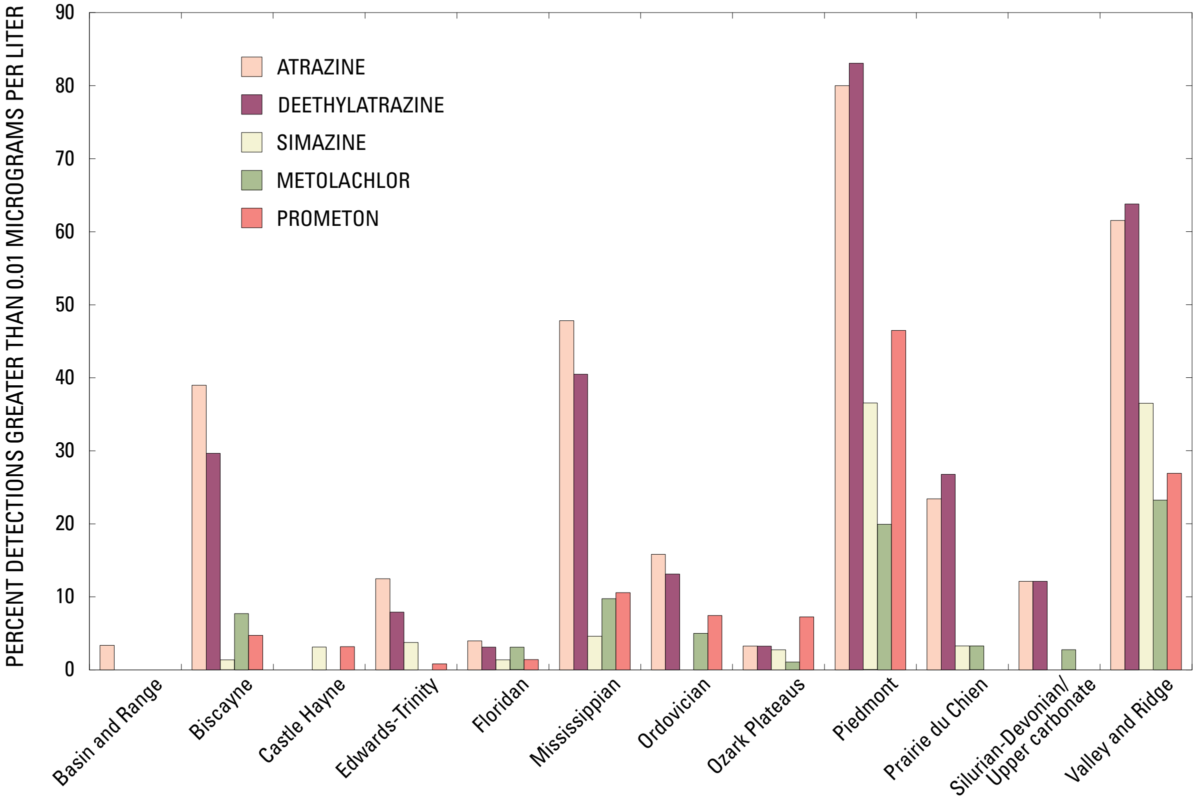


Figure 32. Frequency of detections of the five frequently occurring pesticides by aquifer, in 12 carbonate aquifers or aquifer systems, 1993–2005 (common assessment level, 0.01 µg/L).

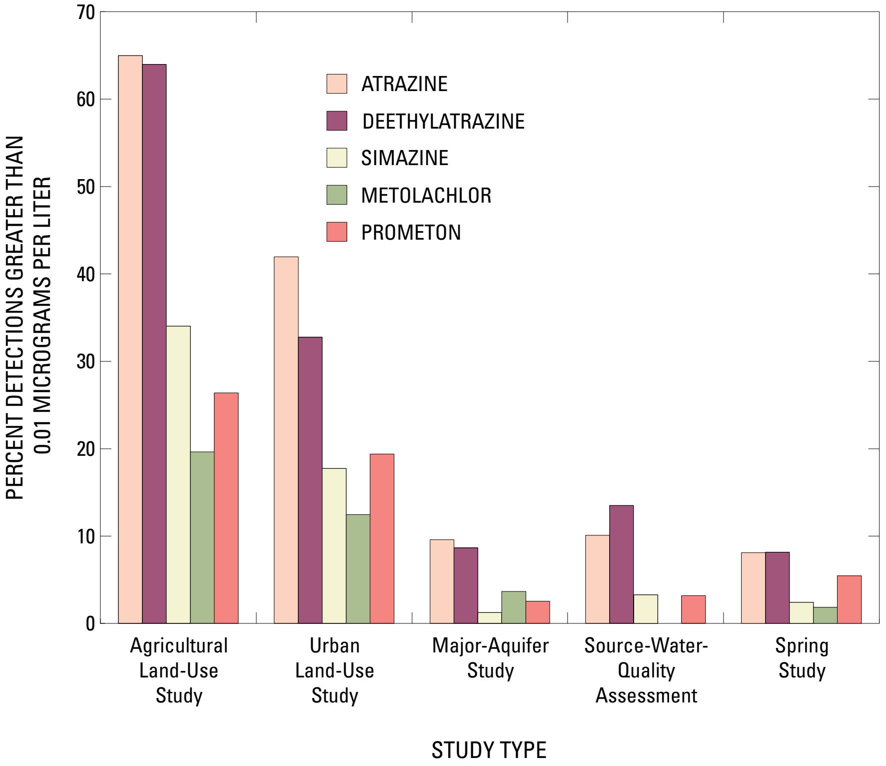


Figure 33. Frequency of detections of the five frequently occurring pesticides by type of National Water-Quality Assessment study in 12 carbonate aquifers or aquifer systems, 1993–2005 (common assessment level, 0.01 µg/L).

(table 22). This test analyzes for a monotonic relation between the pesticide concentration and the explanatory variable. These results can be difficult to interpret because of the large amount of interaction among the explanatory variables, but this step is conducted to help determine potential variables to use in the later multivariate analysis.

Pesticide occurrence was compared to land use and the application rate of pesticides. Data on the percentage of land covers during the mid-1990s from the National Land Cover Data (NLCD) have been compiled for a 1,640-ft (500 m) radius around each well in the NAWQA data set (U.S. Geological Survey, 1999; Price and others, 2007). Data on the use of pesticides in 1997 in this radius around each well in the NAWQA data set were estimated by Nakagaki and Wolock (2005), by extrapolating county-level pesticide-use data to agricultural land in each county. Population data from the 1990 U.S. Census (U.S. Bureau of Census, 1990, 1991) and 2000 U.S. Census (GeoLytics, 2001; U.S. Bureau of Census, 2001) were used to estimate the population density. The use of these data for the 1,640-ft radius does not imply that the defined circle is the recharge area of a well, but it serves as an indication of activities at the land surface in the immediate vicinity of the well.

The largest rank correlation coefficients were between individual pesticides and the agricultural application rate of that pesticide. The pesticide-use estimates were available for both 1992 and 1997. Pesticide-use estimates were tested during statistical analysis, including using 1992-use estimates for all samples, 1997-use estimates for all samples, and a combination of 1992-use estimates for samples collected in the early part of the study and 1997-use estimates for those samples collected later in the study. The differences in the results of these tests were minor, but the 1997-use estimates provided the best correlations with pesticide occurrence and were used for the statistical analysis. Atrazine, deethylatrazine, simazine, and metolachlor were significantly correlated with the estimated agricultural application rate of the active ingredient within a 1,640-ft radius of the well (table 22). Estimates of prometon use were not available.

All five of the pesticide compounds had statistically significant positive correlations with agricultural land use (table 22). Prometon, a general-use herbicide not registered for agricultural uses, had the weakest correlation with agricultural land use (table 22). The five compounds also were inversely correlated to the percentage of forested land use. In addition, all five pesticides, particularly atrazine, deethylatrazine, and prometon were positively correlated to population density (table 22). Prometon is an herbicide used for highway and utility right-of-ways and around structures and, as noted above, is not labeled for use on crop land. The positive correlation between prometon and both urban and agricultural land use is likely to be a reflection of the use of prometon in both urban and rural settings as a general-use herbicide. The relation between atrazine and population density is likely because of its use for right-of-ways, landscaping, and turf-grass management.

When correlations between source factors and pesticides were determined within each aquifer, the pattern of correlations for most source factors was similar to the pattern seen in the overall data set. For atrazine and deethylatrazine, the Edwards-Trinity, Ozark Plateaus, and Valley and Ridge aquifers/aquifer systems had significant correlations between sources and pesticides (table 22). For metolachlor, the correlations between sources and pesticides were the strongest for samples from the Valley and Ridge aquifer. The Edwards-Trinity, Ozark Plateaus, and the Valley and Ridge had significant correlations between pesticide source factors and prometon concentration. For simazine, the correlations were most significant for the Valley and Ridge aquifer. One of the few cases where the correlations indicated different results was for the Valley and Ridge aquifer, in which urban land use had an inverse correlation with atrazine and deethylatrazine concentration. This was the opposite of the correlations found for the rest of the data set. In the Valley and Ridge aquifer, atrazine was detected in nearly every sample; however, concentrations were lower in the urban areas than in the agricultural areas, which is why this correlation is reversed from the findings in the other areas. In general, though, the pattern of correlations between pesticides and sources was similar in individual aquifers to the pattern determined for the entire data set.

The correlations (or lack thereof) for the source factors are affected by several issues. Because of lower numbers of samples and detections when analyzing for correlations by individual aquifer, fewer correlations were statistically significant. The correlations are constrained by the type of study; significant correlations were found between pesticide use and pesticide concentration in land-use studies (shallow wells) but not in major-aquifer studies or source-water-quality assessments (deeper wells). Also, the significant correlations were in aquifers with high percentages of agricultural land use. For aquifers where a pesticide was detected in less than 10 percent of the samples, the Spearman's rank correlation was not calculated because the results could be misleading when based on such a small number of observations. The Basin and Range and Castle Hayne aquifers did not have sufficient numbers of detections of any pesticides for the Spearman's rank correlation test to be run. In general, the Biscayne and Piedmont aquifers had few significant correlations between source factors and pesticides. Lindsey and others (2006) reported similar results in the Piedmont aquifer. The degree of confinement has an effect on whether or not potential source data are correlated to pesticide occurrence. For wells in unconfined aquifers, which comprise most of the data, the correlations were similar in significance and magnitude to the correlations from the entire data set. Correlations between source factors and pesticide occurrence were weak or non-existent for wells in confined aquifers, reflecting their greater isolation from surface sources. The number of samples, type of sampling network, amount of agricultural land use, and degree of confinement all affect the outcome of the Spearman's rank correlation tests. For the most part, there is much less variation within an aquifer for an explanatory variable than the amount of variation among aquifers.

Table 22. Spearman's rank correlations between potential source factors and pesticides in 12 carbonate aquifers or aquifer systems, 1993–2005.

[Pesticide-use data from Nakagaki and Wolock (2005); land use from U.S. Geological Survey (1999) and Price and others (2007); census data from U.S. Bureau of Census (1990, 1991, 1992); Spearman's rho only shown for correlations with p-values less than 0.05; NA, not applicable because of a detection rate less than 10 percent; NS, correlation not significant–p-value greater than 0.05]

Category	Variable	All data	Basin and Range	Biscayne	Castle Hayne	Edwards-Trinity	Floridan	Mississippian	Ordovician	Ozark Plateaus	Piedmont	Prairie du Chien	Silurian-Devonian/ Upper carbonate	Valley and Ridge
Number of samples		1,027	24	65	32	122	223	66	40	177	30	30	33	185
Atrazine														
Pesticide Use	Atrazine application rate	0.36	NA	NS	NA	NS	NS	0.30	NS	NS	0.44	NS	NS	0.68
Land Cover	Row crop, Hay and Pasture	.28	NA	NS	NA	NS	NS	NS	NS	NS	NS	.47	NS	.58
	Forest	-.31	NA	NS	NA	NS	NS	-.30	NS	-.18	-.40	NS	NS	-.60
	Urban	NS	NA	NS	NA	.37	NS	NS	NS	.25	NS	NS	NS	-.27
Census	1990 population density	.33	NA	NS	NA	.59	NS	-.25	NS	.25	NS	NS	NS	NS
Deethylatrazine														
Pesticide Use	Atrazine application rate	.38	NA	NS	NA	NS	NS	.28	NS	NS	.48	NS	NS	.71
Land Cover	Row crop, Hay and Pasture	.29	NA	NS	NA	NS	NS	NS	NS	NS	NS	.43	NS	.61
	Forest	-.31	NA	-.31	NA	NS	NS	NS	NS	-.18	NS	NS	NS	-.63
	Urban	NS	NA	NS	NA	.40	NS	NS	NS	.23	NS	NS	NS	-.30
Census	1990 population density	.32	NA	NS	NA	.58	NS	-.32	NS	.24	NS	NS	NS	NS
Simazine														
Pesticide Use	Simazine application rate	.28	NA	NS	NA	NS	NA	NA	NA	NA	NS	NA	NA	.43
Land Cover	Row crop, Hay and Pasture	.23	NA	NS	NA	NS	NA	NA	NA	NA	NS	NA	NA	.37
	Forest	-.25	NA	-.33	NA	NS	NA	NA	NA	NA	NS	NA	NA	-.55
	Urban	NS	NA	NS	NA	.25	NA	NA	NA	NA	NS	NA	NA	NS
Census	1990 population density	.24	NA	NS	NA	.42	NA	NA	NA	NA	NS	NA	NA	.21
Metolachlor														
Pesticide Use	Metolachlor application rate	.35	NA	.48	NA	NA	NA	NS	NA	NA	NS	NA	NS	.30
Land Cover	Row crop, Hay and Pasture	.24	NA	NS	NA	NA	NA	NS	NA	NA	NS	NA	NS	.19
	Forest	-.21	NA	NS	NA	NA	NA	NS	NA	NA	NS	NA	NS	-.47
	Urban	NS	NA	NS	NA	NA	NA	NS	NA	NA	NS	NA	NS	NS
Census	1990 population density	.16	NA	NS	NA	NA	NA	NS	NA	NA	NS	NA	NS	.31
Prometon														
Land Cover	Row crop, Hay and Pasture	.12	NA	NS	NA	NS	NA	NS	NS	NS	NS	NA	NA	NS
	Forest	-.23	NA	NS	NA	-.18	NA	-.27	NS	NS	NS	NA	NA	-.40
	Urban	.15	NA	NS	NA	.35	NA	.33	NS	.18	NS	NA	NA	.22
Census	1990 population density	.32	NA	.26	NA	.34	NA	NS	NS	.27	NS	NA	NA	.48

Fate and Transport Factors

Transport factors can facilitate or prevent the movement of the pesticide from the source to the sampling point. These factors are not always directly measurable but include degree of confinement, characteristics of soils, hydrology, and well construction. Geochemistry and ground-water age are results of transport factors that can be measured, and ground-water age is also a fate factor. Fate factors represent conditions that enhance or impede degradation of a pesticide in the aquifer.

Ground-water age, which is the length of time between ground-water recharge and the time of sampling, can be thought of as both a transport factor (pesticide travels slowly through the aquifer and thus had not arrived at the sampling point) or a fate factor (pesticide moves so slowly through the aquifer that degradation occurred prior to sampling). Age-dating tracers and pesticide analyses were available for a subset of 483 of the wells sampled, including wells in 8 of the 12 carbonate aquifers. As previously discussed, many of the samples with age-dating tracers were categorized as recharged prior to 1953 (old, 65 samples) or 1953 and later (young, 410 samples). Eight samples were designated as mixtures of young and old water. The mixed-age waters are not included in the statistical analysis because of the small number of samples in that category. Pesticides were more frequently detected in waters designated as young than in waters designated as old. Using a contingency table analysis, the difference between the rate of detection between old and young water was statistically significant for all of the five compounds evaluated—atrazine, deethylatrazine, simazine, metolachlor and prometon (table 23). The statistics indicate that ground-water age is an important factor indicating the likelihood that pesticides are present. This finding is not surprising, because these compounds were not in use when the old water was recharged. The age data were not adequate to allow comparisons among more discrete intervals of ground-water age.

Another factor related to transport is the presence or absence of a confining layer. A confining layer can be a physical barrier to movement of water and pesticides, at least greatly slowing movement. The water in confined aquifers is usually older than in unconfined aquifers. As previously discussed, the correlations between pesticide concentrations and sources were weak or non-existent for wells in confined aquifers, possibly because the recharge area is not close to the well itself or the confined water is too old to contain pesticides. Comparisons of detections of pesticides in confined, semi-confined/mixed confined, and unconfined aquifers indicated a statistically significant higher frequency of pesticide detection for unconfined aquifers (table 24).

Soil properties also can influence the transport and fate of pesticides because water and pesticides move from land surface to ground water during recharge. The soils characteristics summarized for the 1,640-ft radius around the well were compared to pesticide occurrence, but correlations commonly were contradictory. One of these contradictions is that all the pesticides had a statistically significant inverse correlation to the percentage of sand, and a positive correlation to percentage of silt and percentage of clay. In the case of carbonate aquifers, it may be an indication that infiltration through the soils is not necessarily the route for pesticide transport. Issues such as macropore flow and, more importantly, karst features that allow water to bypass the clay soils are likely to be the reason for the unexpected correlation between clay and pesticides. Bouwer (1990) and Graham and others (1992) have both noted the importance of preferential flowpaths through fractures, wormholes, and root holes in clay soils. Soil organic matter can affect fate and transport of pesticides because pesticides tend to bind to the organic matter, which reduces pesticide transport to ground water, and organic matter can also affect the degradation of pesticides; however, the correlations between pesticide occurrence and soil organic matter for the overall data set were weak or not existent. It is also important to note that soils are highly correlated with other factors such as land use, thus making conclusions on the basis of a Spearman's rank correlation between soils and pesticides, although statistically sound, a less than definitive answer. Thus, the analysis of soils will be further explored in the multivariate analysis.

Table 23. Comparison of detection frequency of pesticides for water recharged before 1953 and in 1953 or later for 8 of the 12 carbonate aquifers or aquifer systems, 1993–2005.

Pesticide	Recharge date group and numbers of detections[1]		Statistics from contingency tables	
	Water recharged before 1953 detections (65 samples)	Water recharged in 1953 or later detections (410 samples)	Chi-square value from contingency table	p-value from Chi-square test
Atrazine	4	172	30.8	0.0001
Deethylatrazine	2	176	38.0	.0001
Simazine	2	69	8.3	.0039
Metolachlor	2	50	4.8	.029
Prometon	2	73	9.1	.003

[1] Assessment level for this analysis is 'all detections.'

Table 24. Comparison of detection frequency of pesticides for ground-water sites by aquifer-confinement category in 12 carbonate aquifers or aquifer systems, 1993–2005.

Pesticide	Aquifer-confinement category and numbers of detections[1]			Statistics from contingency tables	
	Confined (146 samples)	Semiconfined or mixed confined (110 samples)	Unconfined (768 samples)[2]	Chi-square value	p-value from Chi-square test
Atrazine	21	5	353	110.	0.0001
Deethylatrazine	30	5	348	90.4	.0001
Simazine	4	6	167	43.1	.0001
Metolachlor	5	1	148	43.4	.0001
Prometon	8	8	171	30.5	.0001

[1] Assessment level for this analysis is ‘all detections.’

[2] Only 761 samples for unconfined category for atrazine and 762 samples for unconfined category for deethylatrazine.

Dissolved oxygen concentrations in ground water can be an indicator of processes that influence either the fate or the transport of pesticides. One of the most important processes associated with pesticide fate is microbial metabolism, which can lead to the oxidation of organic matter and some pesticides along with the simultaneous consumption of dissolved oxygen, when the latter is present at detectable concentrations (aerobic conditions). Because several of the chemical pathways by which atrazine is transformed by microorganisms involve oxidation (dealkylation to form deethylatrazine, deisopropyl atrazine and, through the further dealkylation of either of these products, deethyl deisopropyl atrazine), high concentrations of dissolved oxygen might be expected to be correlated with lower concentrations of atrazine.

Concentrations of dissolved oxygen are also related, however, to flowpath length, connectivity to the atmosphere, and subsurface residence time and thus to the transport of atrazine and other surface-derived contaminants. In solution-weathered carbonate aquifers that are dominated by short flowpaths through subsurface conduits, the water in the aquifer tends to have high concentrations of dissolved oxygen, presumably because of rapid transport rates. Additionally, some of these subsurface flow channels can be partially filled with air, leading to the physical mixing of the air and water in the conduits, and thus a further elevation of concentrations of dissolved oxygen above those contributed by the atmosphere prior to recharge. Thus, for a given depth below the water table, high concentrations of dissolved oxygen imply more rapid transport through the aquifer than do lower concentrations.

In aquifers with pesticide sources at the land surface, the concentrations of atrazine (or any other pesticide that is oxidized by microorganisms in situ) might therefore be either directly or inversely correlated with concentrations of dissolved oxygen, depending on whether transport or transformation (respectively) exerts the greater control. Indeed, both patterns of correlation between atrazine and oxygen concentrations have been observed during previous studies (Barbash and Resek, 1996). In the present investigation, the concentrations of each of the most frequently detected pesticides were positively correlated with dissolved oxygen concentrations (table 25). For atrazine and deethylatrazine, this pattern was also observed within some of the individual aquifers. These results suggest that in the highly oxygenated aquifers examined for this study, transport may exert a greater control over the concentrations of these pesticides than microbial transformation, even for those compounds such as atrazine, deethylatrazine, simazine (Kaufman and Kearney, 1970) and metolachlor (Seybold and Mersie, 1999) that undergo microbial oxidation.

Dissolved organic carbon has a strong inverse correlation with pesticide concentration in the Biscayne, Floridan, and Prairie du Chien aquifers. In the Edwards-Trinity, Ordovician, Piedmont, and Valley and Ridge aquifers/aquifer systems, the correlation between dissolved organic carbon and pesticides was typically positive, which is counter to what would be expected. In the Ordovician, Piedmont, and Valley and Ridge aquifers, agricultural land use is positively correlated with soil organic carbon, so this may be the cause of this finding. In general, the aquifers with the positive correlation between pesticides and dissolved organic carbon had very low concentrations of dissolved organic carbon and very small variability in the concentrations of dissolved organic carbon.

Comparisons of geochemical indicators to pesticides showed correlations between calcium-magnesium ratios, calcite S.I., and dolomite S.I. with pesticides were weak or non-existent when using all data (table 25). For calcite S.I. and dolomite S.I., the result is affected by the correlations within the Valley and Ridge, which were opposite from the correlations in the other aquifers. Correlations with pesticides within individual aquifers are affected by the numbers of pesticide detections. The calcium-magnesium ratio was correlated with atrazine and deethylatrazine in the Edwards-Trinity, Floridan, Silurian-Devonian/Upper carbonate, and Valley and Ridge aquifers/aquifer systems. Inverse correlations between dolomite S.I. and atrazine and deethylatrazine were detected in the Edwards-Trinity, Floridan, Ozark Plateaus, Prairie du Chien, and Silurian-Devonian/Upper carbonate aquifers/aquifer systems. These correlations are concordant with the

Table 25. Spearman's rank correlations between site-specific factors and pesticides in 12 carbonate aquifers or aquifer systems, 1993-2005.

[Spearman's rho only shown for correlations with p-values less than 0.05; NA, not applicable ; NS, correlation not significant–p-value greater than 0.05]

Constituent	All data	Basin and Range	Biscayne	Castle Hayne	Edwards-Trinity	Floridan	Mississippian	Ordovician	Ozark Plateaus	Piedmont	Prairie du Chien	Silurian-Devonian/ Upper carbonate	Valley and Ridge
Number of samples	1,027	24	65	32	122	223	66	40	177	30	30	33	185
							Atrazine						
Dissolved oxygen	0.31	NA	NS	NA	0.31	0.42	NS	NS	NS	NS	0.84	0.43	0.31
Dissolved organic carbon	NS	NA	-.37	NA	.29	-.37	NS	0.33	NS	0.41	NS	NS	.26
Calcium-magnesium molar ratio	NS	NA	NS	NA	.63	.40	NS	.56	NS	NS	NS	.51	.21
Calcite saturation index	NS	NA	NS	NA	NS	NS	NS	NS	-0.21	NS	-.69	NS	.55
Dolomite saturation index	NS	NA	NS	NA	-.58	-.23	NS	NS	-.25	NS	-.62	-.56	.45
Casing length	-.10	NA	NS	NA	-.27	NS	NS	NS	NS	NS	NS	NS	NS
Well depth	-.19	NA	NS	NA	-.35	NS	-0.27	NS	NS	NS	NS	NS	-.21
Water level	NS	NA	NS	NA	NS	NS	NS	NS	NS	NS	NS	NS	NS
							Deethylatrazine						
Dissolved oxygen	.34	NA	NS	NA	.43	.38	NS	NS	.21	NS	.84	.43	.34
Dissolved organic carbon	NS	NA	-.55	NA	.28	-.39	NS	NS	.24	NS	-.41	NS	.25
Calcium-magnesium molar ratio	NS	NA	NS	NA	.68	.37	NS	.63	NS	NS	NS	.52	.19
Calcite saturation index	.07	NA	NS	NA	-.17	NS	NS	NS	-.25	NS	-.70	NS	.55
Dolomite saturation index	NS	NA	NS	NA	-.66	-.19	NS	NS	-.27	NS	-.62	-.56	.47
Casing length	NS	NA	NS	NA	NS	-.19	NS	NS	NS	NS	NS	NS	.18
Well depth	-.14	NA	NS	NA	-.24	NS	NS	NS	NS	NS	NS	NS	-.17
Water level	.08	NA	NS	NA	NS	NS	NS	NS	NS	.45	NS	NS	NS

Table 25. Spearman's rank correlations between site-specific factors and pesticides in 12 carbonate aquifers or aquifer systems, 1993-2005.—Continued

[Spearman's rho only shown for correlations with p-values less than 0.05; NA, not applicable ; NS, correlation not significant–p-value greater than 0.05]

Constituent	All data	Basin and Range	Biscayne	Castle Hayne	Edwards-Trinity	Floridan	Mississippian	Ordovician	Ozark Plateaus	Piedmont	Prairie du Chien	Silurian-Devonian/ Upper carbonate	Valley and Ridge
							Simazine						
Dissolved oxygen	0.27	NA	NS	NA	0.24	NA	NA	NA	NA	NS	NA	NA	0.17
Dissolved organic carbon	NS	NA	-0.40	NA	.28	NA	NA	NA	NA	NS	NA	NA	.34
Calcium-magnesium molar ratio	NS	NA	NS	NA	.52	NA	NA	NA	NA	NS	NA	NA	.28
Calcite saturation index	.16	NA	NS	NA	NS	NA	NA	NA	NA	NS	NA	NA	.46
Dolomite saturation index	.12	NA	NS	NA	-.50	NA	NA	NA	NA	NS	NA	NA	.34
Casing length	NS	NA	NS	NA	-.22	NA	NA	NA	NA	NS	NA	NA	NS
Well depth	-.07	NA	NS	NA	-.33	NA	NA	NA	NA	NS	NA	NA	-.30
Water level	.10	NA	NS	NA	NS	NA	NA	NA	NA	NS	NA	NA	-.20
							Metolachlor						
Dissolved oxygen	.2	NA	NS	NA	NA	NA	0.22	NA	NA	NS	NA	NS	.15
Dissolved organic carbon	-.07	NA	-.41	NA	NA	NA	NS	NA	NA	0.39	NA	NS	.3
Calcium-magnesium molar ratio	NS	NA	NS	NA	NA	NA	NS	NA	NA	NS	NA	0.32	.30
Calcite saturation index	.15	NA	NS	NA	NA	NA	NS	NA	NA	NS	NA	-.44	.43
Dolomite saturation index	.09	NA	NS	NA	NA	NA	NS	NA	NA	NS	NA	-.49	.30
Casing length	NS	NA	NS	NA	NA	NA	NS	NA	NA	NS	NA	NS	NS
Well depth	-.11	NA	NS	NA	NA	NA	NS	NA	NA	NS	NA	NS	-.27
Water level	NS	NA	NS	NA	NA	NA	NS	NA	NA	NS	NA	NS	-.17

Table 25. Spearman's rank correlations between site-specific factors and pesticides in 12 carbonate aquifers or aquifer systems, 1993-2005.—Continued

[Spearman's rho only shown for correlations with p-values less than 0.05; NA, not applicable ; NS, correlation not significant–p-value greater than 0.05]

Constituent	All data	Basin and Range	Biscayne	Castle Hayne	Edwards-Trinity	Floridan	Mississippian	Ordovician	Ozark Plateaus	Piedmont	Prairie du Chien	Silurian-Devonian/ Upper carbonate	Valley and Ridge
							Prometon						
Dissolved oxygen	0.18	NA	NS	NA	NS	NA	NS	NS	NS	NS	NA	NA	NS
Dissolved organic carbon	NS	NA	-0.26	NA	0.22	NA	NS	0.34	NS	0.37	NA	NA	0.34
Calcium-magnesium molar ratio	NS	NA	NS	NA	.24	NA	0.25	NS	NS	NS	NA	NA	.31
Calcite saturation index	.09	NA	NS	NA	NS	NA	NS	NS	NS	NS	NA	NA	.36
Dolomite saturation index	NS	NA	NS	NA	-.23	NA	NS	NS	NS	NS	NA	NA	.20
Casing length	NS	NA	.41	NA	NS	NA	NS	NS	NS	NS	NA	NA	NS
Well depth	NS	NA	.43	NA	NS	NA	NS	NS	NS	NS	NA	NA	-.21
Water level	NS	NA	NS	NA	-.27	NA	NS	NS	NS	NS	NA	NA	-.17

concepts that calcium-magnesium ratios and dolomite S.I. are indicators of residence time, as previously discussed. In the Valley and Ridge aquifer the correlation between both calcite S.I. and dolomite S.I. with atrazine, deethylatrazine, simazine, metolachlor, and prometon were all positive. This opposite correlation in the Valley and Ridge aquifer was evident when analyzing nitrate also, and is likely due to the greater amount of agricultural land use in the part of the Valley and Ridge where the water is closer to saturation with respect to calcite and dolomite.

Water levels and well-construction data such as well depth and depth to the top of the open interval are also used as indicators of vertical transport distance. A shallow water level would indicate a short distance between the land surface and the water table in an unconfined aquifer. Well depth and depth to top of open interval both determine the depth at which water can enter the well. Larger depth to top of open interval indicates that the water has to travel deeper into the aquifer in order to be drawn into the well. The total depth of the well may indicate that the water-bearing zones are deep, but that may not be true if the open interval between the bottom of the casing and the bottom of the well is large.

The depth to the top of the open interval was inversely correlated with atrazine for the entire data set and within the Edwards-Trinity aquifer system (table 25). This indicates a tendency for wells with shallow casings to have higher concentrations of atrazine. That correlation was not present for deethylatrazine, simazine, metolachlor, or prometon.

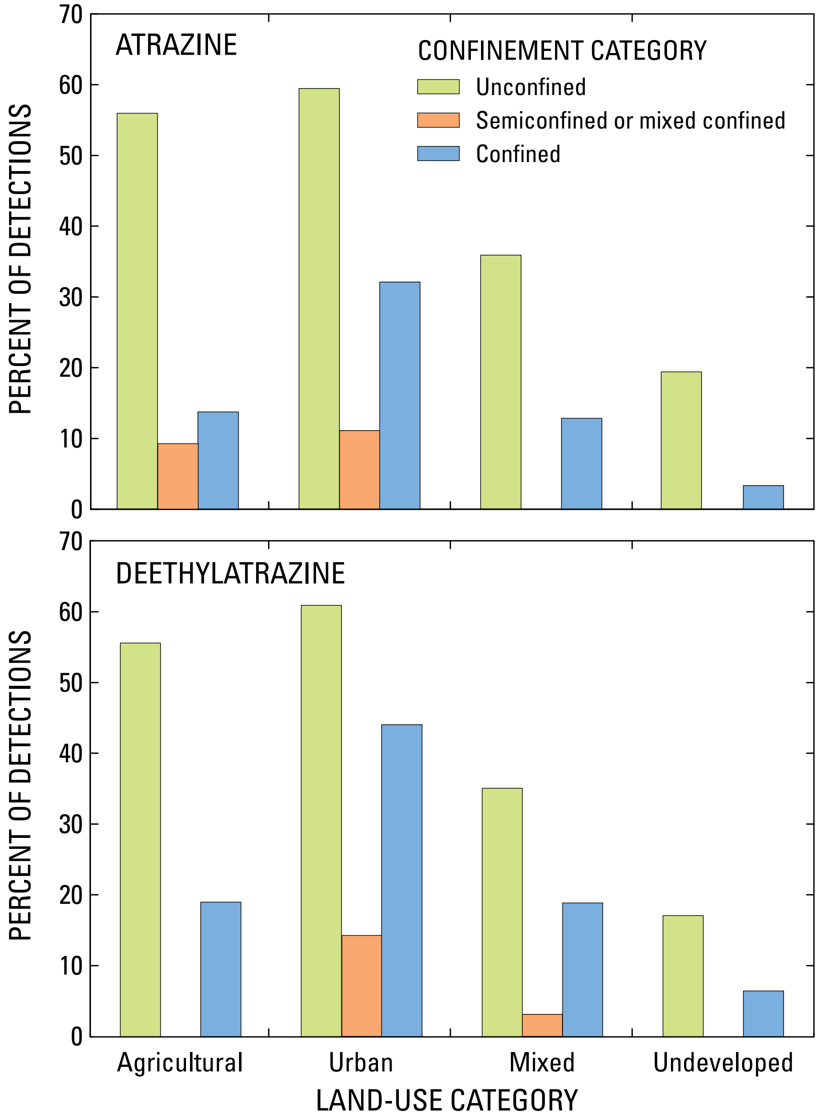
Well depth was inversely correlated with atrazine, deethylatrazine, simazine, and metolachlor for the overall data set as well as several individual aquifers, indicating lower concentrations of pesticides in deeper wells. Well depth had a positive correlation with prometon in the Biscayne aquifer, but this aquifer has very shallow well depths. Correlations between water levels and pesticide concentrations were weak or nonexistent. The exception was in the Valley and Ridge aquifers, where inverse correlations were found between water level and metolachlor and prometon.

Interaction of Source, Fate, and Transport Factors

The occurrence of pesticides in ground water is ultimately determined by a combination of source, fate, and transport factors. The analysis of all three factors is an important step in identifying variables affecting pesticide occurrence, but analyzing the interaction among them is needed to provide the best understanding of pesticides in ground water. Multivariate analysis is essential because of the multiple factors involved simultaneously and because many of the factors are correlated among themselves.

One way to analyze the combination of source and transport factors is to group the categories that were previously identified as important factors on an individual basis. Two variables strongly associated with pesticide detections were land use and degree of confinement, representing one important source variable and one important transport variable. Analysis of the detection frequency of pesticides using degree of confinement and land-use categories indicates a consistent pattern (figs. 34-36). The detection frequency for all five pesticides was greater in unconfined aquifers than in confined aquifers for all land-use groupings. Using the 'all detections' assessment level, the frequency of detection for agricultural and urban land-use groupings is greater than the mixed land use and undeveloped settings for all unconfined aquifers and most confined aquifers. The only categories in which there were no detections were in confined or semiconfined/mixed confined aquifers. This example indicates that, although both land use and degree of confinement are important factors affecting the occurrence of pesticides independently, the combined effect of both of these factors provides an even more powerful explanation of pesticide occurrence in carbonate aquifers. The samples from wells in the unconfined aquifers with agricultural, urban, or mixed land use make up 71 percent of the samples, yet they account for 87 percent of the detections for atrazine, 85 percent for deethylatrazine, 92 percent for simazine, 90 percent for metolachlor, and 90 percent for prometon.

Effects of the combinations of factors affecting pesticide occurrence are further illustrated by comparing the Piedmont and Silurian Devonian/Upper carbonate aquifers, two of the aquifers with high percentages of agricultural land use and the highest use of atrazine and metolachlor (fig. 6). Although the study in the Silurian-Devonian/Upper carbonate aquifer was not designed as a land-use study, the percentage of land use around the sampling sites (fig. 3) was similar to that of the agricultural land-use study in the Piedmont aquifer. The depths to water, well depths, and depth to top of open interval for wells in the Silurian-Devonian/Upper carbonate aquifer were slightly larger than for wells in the study in the Piedmont aquifer (table 5). These aquifers both had pesticide application rates that were appreciably higher than in any of the other aquifers (fig. 6), yet the occurrence of these pesticides was quite different from each other. Atrazine and deethylatrazine were detected at a concentration greater than 0.01 µg/L in about 80 percent of the samples in the Piedmont aquifer, but only 12 percent in the Silurian Devonian/Upper carbonate aquifer (fig. 32). Metolachlor was detected in about 20 percent of the samples in the Piedmont aquifer and about 3 percent of the samples in the Silurian Devonian/Upper carbonate aquifer. The differences in detection frequency, despite similar high application rates, indicate the influence of factors that affect transport. Many of the samples in the Silurian Devonian/Upper carbonate aquifer were classified as having a recharge date prior to 1953. Using the 10 samples in this area that were considered young ground water, the detection frequency was 50 percent for atrazine and deethylatrazine and 30 percent for metolachlor, much closer to the frequency in the Piedmont. The degree of aquifer confinement had a similar influence. All the wells in the Piedmont sampled unconfined ground water, and all the detections of atrazine, deethylatrazine, and metolachlor were in the unconfined part of the Silurian Devonian/Upper carbonate aquifer. Concentrations of dissolved organic



LAND USE IN 1,640-FOOT RADIUS AROUND WELL

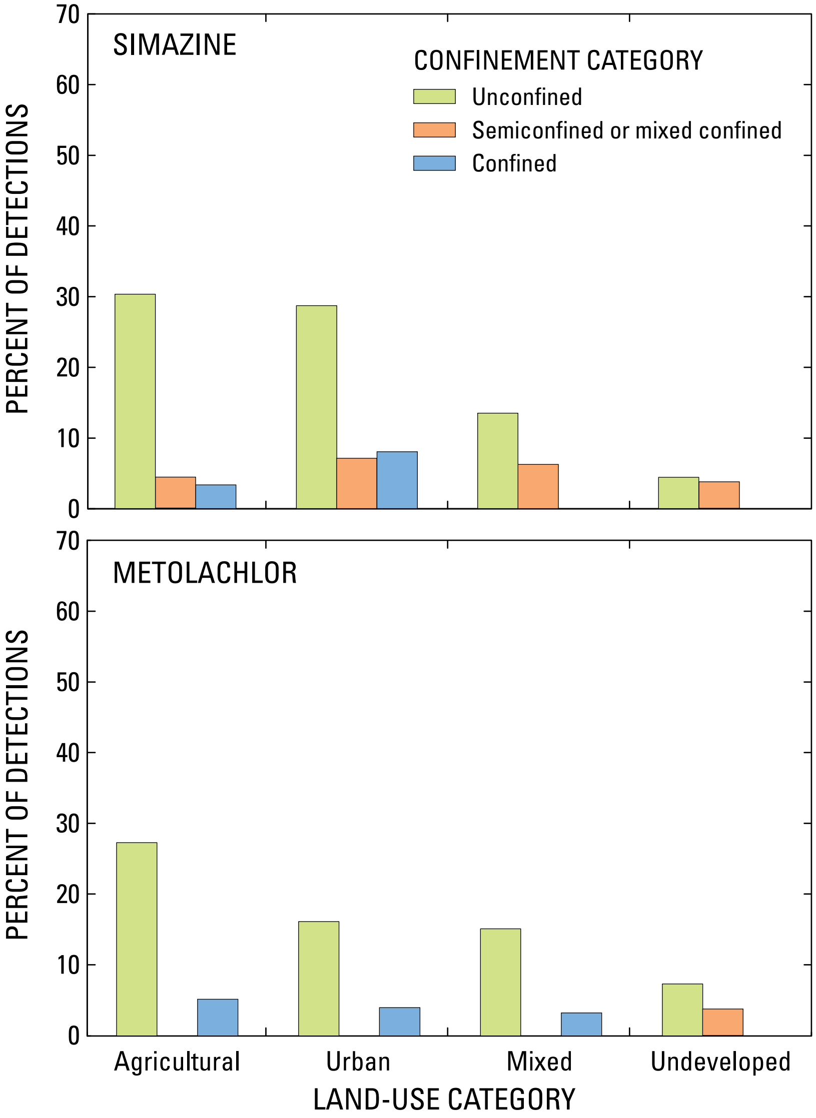
Agricultural: greater than 50 percent agricultural land use and less than 5 percent urban land use

Urban: greater than 25 percent urban land use and less than 25 percent agricultural land

Mixed land use: all other combinations

Undeveloped: less than 25 percent agricultural and less than 5 percent urban

Figure 34. Percent detections of atrazine and deethylatrazine by land use and confinement category in 12 carbonate aquifers or aquifer systems, 1993–2005 (assessment level, all detections).



LAND USE IN 1,640-FOOT RADIUS AROUND WELL

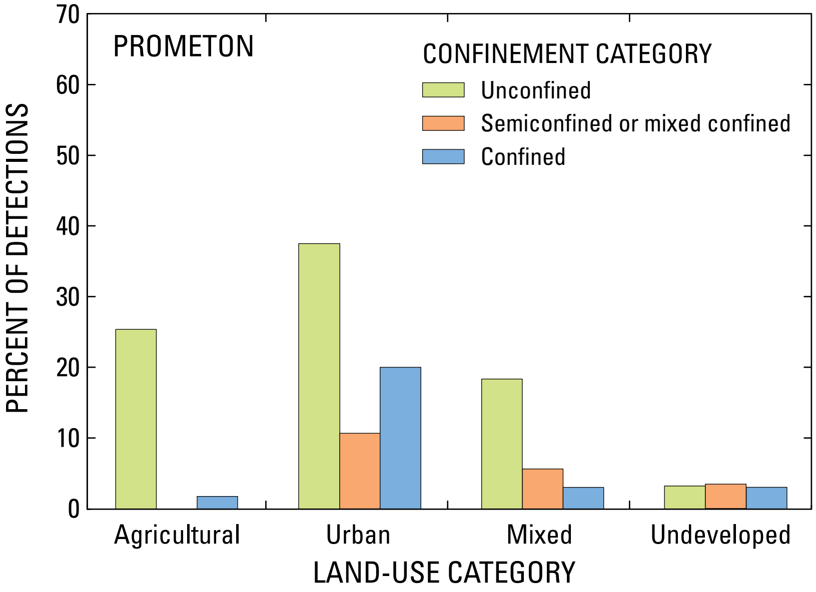
Agricultural: greater than 50 percent agricultural land use and less than 5 percent urban land use

Urban: greater than 25 percent urban land use and less than 25 percent agricultural land

Mixed land use: all other combinations

Undeveloped: less than 25 percent agricultural and less than 5 percent urban

Figure 35. Percent detections of metolachlor and simazine by land use and confinement category in 12 carbonate aquifers or aquifer systems, 1993–2005 (assessment level, all detections).



LAND USE IN 1,640-FOOT RADIUS AROUND WELL

Agricultural: greater than 50 percent agricultural land use and less than 5 percent urban land use

Urban: greater than 25 percent urban land use and less than 25 percent agricultural land

Mixed land use: all other combinations

Undeveloped: less than 25 percent agricultural and less than 5 percent urban

Figure 36. Percent detections of prometon by land use and confinement category in 12 carbonate aquifers or aquifer systems, 1993–2005 (assessment level, all detections).

carbon were also higher in the Silurian Devonian/Upper carbonate aquifer than in the Piedmont aquifer (fig. 16), which can affect the fate of pesticides. This more detailed comparison of two specific areas shows that transport factors sometimes must be combined with source factors to sufficiently explain the occurrence of atrazine or metolachlor. The aquifer characteristics that allow the pesticides to persist and move into the aquifer also must be present.

Logistic regression analysis is another way to determine the most significant factors affecting pesticide occurrence. Logistic regression analyzes the significance of multiple explanatory variables in determining whether the response variable exceeds a certain threshold, keeping only those variables that are statistically significant in the equation. The relative importance of the significant variables in the model is determined by the standardized estimate, which normalizes each variable so that the magnitude is relative to a common reference point. In the case of pesticides, the regression identifies those variables that are significant in determining the probability that a pesticide is likely to be detected above a selected threshold. Variables that were previously identified as having a significant individual correlation with the pesticide were used as the basis for the regression. Some variables were not included because missing data for one variable eliminates the entire case from the regression. The determination as to whether elimination of the variable or losing the missing cases was more important was done on a case-by-case basis. Well depth and depth to top of open interval were eliminated from the regression because of this. In some cases, explanatory variables were highly correlated with each other, such as soils and land use. In those cases, the variable that was considered more likely to be the determining variable was kept in the model. Percent agricultural land was too closely correlated with atrazine application rate to keep both variables in the model. The variable for degree of confinement was coded as a numeric group variable, with a value of 1 corresponding to confined aquifers, 2 corresponding to semiconfined/mixed confined, and 3 corresponding to unconfined aquifers; the same approach as was used for the logistic regression analysis for nitrate.

A logistic regression model was created to analyze the probability of atrazine exceeding 0.01 µg/L or greater. The predictor variables significant in this model were, in order of importance, atrazine application rate on agricultural land, degree of confinement, concentration of dissolved oxygen, percent urban land, population density, and recharge (table 26). All these factors had a positive relation with atrazine exceeding 0.01 µg/L. An alternate model using percent agricultural land instead of atrazine application rate was similar to but slightly weaker than the model selected. The model had a concordance of 87, an r-squared value of 0.30, and a maximum rescaled r-squared value of 0.45. The final model variables were checked for multicollinearity using the variance inflation factor (VIF), and the VIF for all variables was less than 2.5, indicating multicollinearity was not a major issue. This model was one of several that could be used to analyze atrazine occurrence. Model results differ somewhat depending on the threshold used for detection and the variables used as input for the model; however, most results were very similar to the results in table 26. Because logistic regression analyzes these variables simultaneously, the standardized estimate can be used as an indication of the importance of the variables relative to each other. Three of the four highest standardized estimates are related to either land use or degree of confinement. The variables of recharge and population density are statistically significant but less important in predicting atrazine occurrence.

The logistic regression model for deethylatrazine indicated the same general pattern of explanatory variables as the model for its parent pesticide, atrazine, with the exception that population density was not significant in this model (table 27). Similar to the results for atrazine, the model indicates that unconfined aquifers with high atrazine application rates on agricultural land and (or) a high percent of urban land use are likely to have deethylatrazine concentrations that exceed 0.01 µg/L. The model had a concordance of 87.8, an r-squared

Table 26. Results of logistic regression model predicting probability of atrazine being detected at a threshold of greater than 0.01 micrograms per liter in 12 carbonate aquifers or aquifer systems, 1993–2005.

[<, less than]

Parameter	Parameter estimate	Chi-square	p-value	Standardized estimate
Intercept	-6.6	92.3	< 0.0001	
Atrazine application rate	.11	96.9	< .0001	0.81
Aquifer-confinement category	1.06	19.9	< .0001	.42
Dissolved oxygen	.17	27.2	< .0001	.31
Urban land use	.01	10.8	.001	.24
Population density 1990	.001	9.0	.003	.19
Recharge	.08	8.8	.003	.16

Table 27. Results of logistic regression model predicting probability of deethylatrazine being detected at a threshold of greater than 0.01 micrograms per liter in 12 carbonate aquifers or aquifer systems, 1993–2005.

[<, less than]

Parameter	Parameter estimate	Chi-square	p-value	Standardized estimate
Intercept	-5.9	62.9	< 0.0001	
Atrazine application rate	.10	63.6	< .0001	0.69
Urban land use	.03	57.7	< .0001	.44
Aquifer-confinement category	1.07	18.9	< .0001	.43
Hydrologic group D soils	-.03	15.7	< .0001	-.34
Dissolved oxygen	.18	26.8	< .0001	.34
Dunne overland flow	-.23	14.3	.0002	-.29
Recharge	.11	10.5	.001	.21

value of 0.33, and a maximum rescaled r-squared value of 0.51.

The logistic regression models for simazine (table 28), metolachlor (table 29), and prometon (table 30) also had results generally similar to the models for atrazine. For simazine, urban and agricultural land uses were the most important variables, followed by degree of confinement. Several soil and hydrology related variables are statistically significant in this model, including Dunne overland flow (inversely correlated), the amount of moderately well-drained soils, and available water capacity. Although simazine was not strongly correlated with urban land use in the Spearman's rank correlation (table 22), urban land use was an important predictive variable in the logistic regression model. The model for simazine had a concordance of 90.6, an r-squared value of 0.21, and a maximum rescaled r-squared value of 0.45. The logistic regression model for metolachlor varies from the other models in that degree of confinement is not a significant variable, and the land-use-related variables are not among the strongest predictive variables. The model included an inverse association with poorly drained soils and a positive association with recharge, concentration of dissolved oxygen, metolachlor application rate, and population density as the significant variables (table 29). The model for metolachlor had a concordance of 82.2, an r-squared value of 0.10, and a maximum rescaled r-squared value of 0.24, indicating that this is one of the weaker models. The logistic regression model for prometon had results similar to the models for the other pesticides (table 30), with a positive relation to agricultural and urban land uses and degree of confinement and an inverse relation to poorly drained soils and calcium-magnesium ratio. The model for prometon had a concordance of 82.7, an r-squared value of 0.12, and a maximum rescaled r-squared value of 0.26, indicating that this is also one of the weaker models.

Overall, the logistic regression models show patterns for the individual pesticides that have recurring themes. The degree of aquifer confinement is one of the most important explanatory variables in all but one of the models. One or more source variables are significant in all the models. The source factor of application rate on agricultural land is significant for the four pesticides with use data, and land use variables of agricultural or urban land use are also significant for all models. Several other variables are statistically significant but typically less important in predicting pesticide occurrence. Population density is a significant variable in many of the models. Hydrology and soils variables were also significant. Recharge, a measure of the flux of water through the ground-water system, always had a positive relation to pesticide occurrence. The presence of well-drained soils tended to increase the probability of a pesticide exceeding the selected threshold, and poorly drained soils decreased the probability of a pesticide exceeding the threshold. Dunne overland flow represents runoff from saturated soils through which water can no longer infiltrate, thus resulting in overland flow, and is an inverse factor with respect to pesticide occurrence. These results indicate that a combination of source, fate, and transport factors affect the detections and concentrations of pesticides.

Volatile Organic Compounds

Water samples were collected for analysis of VOCs at 793 sites from the 12 carbonate aquifers—154 samples were analyzed for 54 VOCs from 1993 through 1995 (Rose and Schroeder, 1995) and 639 samples were analyzed for 86 VOCs from 1996 through 2005 (Connor and others, 1998). The results of VOC sampling for the 12 carbonate aquifers are analyzed with respect to the distribution of VOCs, a screening-level assessment of potential human-health concerns, and factors affecting the distribution of VOC detection frequencies. Table 31 lists all the VOCs analyzed for this study, the number of samples analyzed, the number of detections, and the detection frequencies for each VOC analyzed.

Table 28. Results of logistic regression model predicting probability of simazine being detected at a threshold of greater than 0.01 micrograms in 12 carbonate aquifers or aquifer systems, 1993–2005.

[<, less than]

Parameter	Parameter estimate	Chi-square	p-value	Standardized estimate
Intercept	-11.3	70.9	< 0.0001	
Percent urban land	.04	27.9	< .0001	0.72
Percent agricultural land	.04	20.7	< .0001	.71
Aquifer-confinement category	1.17	11.2	.0008	.47
Dunne overland flow	-.37	14.0	.0002	-.47
Dissolved oxygen	.17	15.2	< .0001	.32
Soil available water capacity	14.56	8.5	.0036	.29
Hydrologic group B soils	.02	6.5	.0111	.29
Simazine application rate	.13	23.0	< .0001	.24

Table 29. Results of logistic regression model predicting probability of metolachlor being detected at a threshold of greater than 0.01 micrograms per liter in 12 carbonate aquifers or aquifer systems, 1993–2005.

[<, less than]

Parameter	Parameter estimate	Chi-square	p-value	Standardized estimate
Intercept	-4.45	95.8	< 0.0001	
Hydrologic Group D soils	-.05	5.2	.022	-0.57
Dissolved oxygen	.15	11.6	.0006	.28
Recharge	.15	11.2	.0008	.28
Metolachlor application rate	.03	18.7	< .0001	.21
Population density 1990	.001	10.1	.0015	.20

Table 30. Results of logistic regression model predicting probability of prometon being detected at a threshold of greater than 0.01 micrograms per liter in 12 carbonate aquifers or aquifer systems, 1993–2005.

[<, less than]

Parameter	Parameter estimate	Chi-square	Probability	Standardized estimate
Intercept	-8.1	41.1	< 0.0001	
Percent agricultural land	.03	25.3	< .0001	0.65
Percent urban land	.04	32.8	< .001	.63
Aquifer-confinement category	1.34	12.1	.0005	.54
Hydrologic group D soils	-.04	5.9	.0144	-.45
Calcium-magnesium molar ratio	-.04	6.9	.009	-.25

Table 31. List of volatile organic compounds analyzed, number of detections greater than or equal to 0.2 micrograms per liter, and human-health-benchmark exceedances in 12 carbonate aquifers or aquifer systems, 1993-2005.

[DBP, disinfection by-product; FUM, fumigant-related compound; GAS, gasoline hydrocarbons, oxygenates, and oxygenate degradates; PC, personal care and domestic use product; REF, refrigerants and propellant; SOL, solvent; SYN, organic synthesis compound; µg/L, micrograms per liter; MCL, Maximum contaminant level; HBSL, Health-based screening level; N/A, not applicable]

Name	Type of compound	Number of detections greater than or equal to 0.2 µg/L	Percent detection greater than or equal to 0.2 µg/L	Number of detections at any concentration	Number of analyses	Maximum concentration (µg/L)	Benchmark level (µg/L)	Benchmark type[1]	Percent greater than benchmark	Percent detection at any concentration
Chloroform	DBP	57	7.2	229	793	61	[2]80	MCL	0	28.9
Tetrahydrofuran	SOL	22	3.4	23	639	1,430	NONE			3.6
Tetrachloroethene (PCE)	SOL	23	2.9	118	792	5.01	5	MCL	.1	14.9
Toluene[3]	GAS	18	2.3	81	793	12	1,000	MCL	0	10.2
Acetone	SOL	15	2.3	15	639	6.97	6,000	HBSL	0	2.3
Ethylmethylketone	SOL	14	2.2	17	639	17.6	NONE			2.7
Methyl tert-butyl ether (MTBE)	GAS	17	2.1	33	793	51	NONE			4.2
Trichloroethene (TCE)	SOL	15	1.9	38	793	7.48	5	MCL	.1	4.8
Xylene	GAS	3	1.9	3	154	41	10,000	MCL	0	1.9
1,1,1-Trichloroethane	SOL	11	1.4	35	793	3	200	MCL	0	4.4
1,2,4-Trimethylbenzene[4]	GAS	10	1.3	19	793	12	NONE			2.4
cis-1,2-Dichloroethene	SOL	10	1.3	28	793	4.4	NONE			3.5
Carbon disulfide	SYN	7	1.1	130	639	1.85	700	HBSL	0	20.3
Dichlorodifluoromethane (CFC-12)	REF	7	.9	17	793	2.0	1,000	HBSL	0	2.1
Tribromomethane	DBP	7	.9	17	793	3.09	[2]80	MCL	0	2.1
4-Isopropyltoluene	GAS	6	.8	18	793	3.0	NONE			2.3
Bromodichloromethane	DBP	5	.6	31	793	3.50	[2]80	MCL	0	3.9
Dibromochloromethane	DBP	5	.6	18	793	2.89	[2]80	MCL	0	2.3
1,1-Dichloroethane	SOL	4	.5	16	793	.58	NONE			2.0
Dichloromethane	SOL	4	.5	17	793	1.9	5	MCL	0	2.1
Naphthalene	GAS	4	.5	6	793	2.02	100	HBSL	0	.8
Benzene	GAS	3	.4	31	793	4.4	5	MCL	0	3.9
Carbon tetrachloride	SOL	3	.4	7	793	.60	5	MCL	0	.9
Trichlorofluoromethane (CFC-11)	REF	3	.4	14	793	1.57	2,000	HBSL	0	1.8
Diisopropyl ether (DIPE)	GAS	1	.3	2	610	2.07	NONE			.3
1,1-Dichloroethene	SOL	2	.3	16	793	1.00	7	MCL	0	2.0
1,2-Dichlorobenzene	SOL	2	.3	3	793	.27	NONE			.4
1,2-Dichloropropane	FUM	2	.3	22	793	6.4	5	MCL	.1	2.8
1,3,5-Trimethylbenzene	GAS	2	.3	5	793	4.00	NONE			.6
Chlorobenzene	SOL	2	.3	8	793	.53	100	MCL	0	1.0
1,1,2-Trichlorotrifluoroethane (CFC-113)	REF	2	.3	9	793	.30	200,000	HBSL	0	1.1
Ethylbenzene	GAS	2	.3	18	793	8.7	700	MCL	0	2.3
Isopropylbenzene	GAS	2	.3	9	793	1.94	700	HBSL	0	1.1
n-Butylbenzene	GAS	1	.3	2	793	.26	NONE			.3
n-Propylbenzene	SOL	2	.3	6	793	2.11	NONE			.8
sec-Butylbenzene	GAS	1	.3	2	793	.43	NONE			.3
Vinyl chloride	SYN	2	.3	3	793	4.68	2	MCL	0	.4
1,2,3-Trimethylbenzene	GAS	1	.2	4	639	1.32	NONE			.6

Table 31. List of volatile organic compounds analyzed, number of detections greater than or equal to 0.2 micrograms per liter, and human-health-benchmark exceedances in 12 carbonate aquifers or aquifer systems, 1993-2005.—Continued

[DBP, disinfection by-product; FUM, fumigant-related compound; GAS, gasoline hydrocarbons, oxygenates, and oxygenate degradates; PC, personal care and domestic use product; REF, refrigerants and propellant; SOL, solvent; SYN, organic synthesis compound; µg/L, micrograms per liter; MCL, Maximum contaminant level; HBSL, Health-based screening level; N/A, not applicable]

Name	Type of compound	Number of detections greater than or equal to 0.2 µg/L	Percent detection greater than or equal to 0.2 µg/L	Number of detections at any concentration	Number of analyses	Maximum concentration (µg/L)	Benchmark level (µg/L)	Benchmark type[1]	Percent greater than benchmark	Percent detection at any concentration
2-Ethyltoluene	GAS	1	0.2	5	639	2.07	NONE			0.8
Isobutylmethylketone	SOL	1	.2	3	639	.20	NONE			.5
m- + p-Xylene	GAS	1	.2	25	639	14.71	NONE			3.9
o-Xylene	GAS	1	.2	10	639	9.50	NONE			1.6
Prehnitene	GAS	1	.2	1	639	.25	NONE			.2
Styrene	GAS	1	.1	31	793	3.45	100	MCL	0	3.9
1,1-Dichloropropene	SYN	0	0	0	793	N/A	N/A			0
1,1,1,2-Tetrachloroethane	SOL	0	0	0	793	N/A	N/A			0
1,1,2-Trichloroethane	SOL	0	0	0	793	N/A	N/A			0
1,1,2,2-Tetrachloroethane	SOL	0	0	0	793	N/A	N/A			0
1,2-Dibromo-3-chloropropane (DBCP)	FUM	0	0	0	793	N/A	N/A			0
1,2-Dibromoethane (EDB)	FUM	0	0	0	793	N/A	N/A			0
1,2-Dichloroethane	SOL	0	0	1	793	.16	5	MCL	0	.1
1,2,3-Trichloropropane	SYN	0	0	0	793	N/A	N/A			0
1,2,3-Trichlorobenzene	SYN	0	0	0	793	N/A	N/A			0
1,2,4-Trichlorobenzene	SOL	0	0	0	793	N/A	N/A			0
1,3-Dichlorobenzene	SOL	0	0	2	793	.08	600	HBSL	0	.3
1,3-Dichloropropane	FUM	0	0	0	793	N/A	N/A			0
1,4-Dichlorobenzene	FUM	0	0	16	793	.5	NONE			2.0
3-Chloro-1-propene	SYN	0	0	0	639	N/A	N/A			0
2-Chlorotoluene	SOL	0	0	1	793	.13	NONE			.1
2-Hexanone	SOL	0	0	0	639	N/A	N/A			0
2-Methyl-2-propenitrile	SYN	0	0	0	639	N/A	N/A			0
2,2-Dichloropropane	FUM	0	0	0	793	N/A	N/A			0
4-Chlorotoluene	SOL	0	0	0	793	N/A	N/A			0
Acrolein	SYN	0	0	0	269	N/A	N/A			0
Acrylonitrile	SYN	0	0	0	639	N/A	N/A			0
Bromobenzene	SOL	0	0	1	793	0	NONE			.1
Bromochloromethane	PC	0	0	1	793	.02	90	HBSL	0	.1
Bromomethane	FUM	0	0	0	793	N/A	N/A			0
Chloroethane	SOL	0	0	1	793	.06	NONE			.1
Chloromethane	SYN	0	0	74	797	.10	NONE			9.3
cis-1,3-Dichloropropene	FUM	0	0	0	793	N/A	N/A			0
Dibromomethane	SOL	0	0	2	793	.05	NONE			.3
Diethyl ether	SOL	0	0	2	639	.06	NONE			.3
Ethyl methacrylate	SYN	0	0	0	639	N/A	N/A			0

Table 31. List of volatile organic compounds analyzed, number of detections greater than or equal to 0.2 micrograms per liter, and human-health-benchmark exceedances in 12 carbonate aquifers or aquifer systems, 1993-2005.—Continued

[DBP, disinfection by-product; FUM, fumigant-related compound; GAS, gasoline hydrocarbons, oxygenates, and oxygenate degradates; PC, personal care and domestic use product; REF, refrigerants and propellant; SOL, solvent; SYN, organic synthesis compound; µg/L, micrograms per liter; MCL, Maximum contaminant level; HBSL, Health-based screening level; N/A, not applicable]

Name	Type of compound	Number of detections greater than or equal to 0.2 µg/L	Percent detection greater than or equal to 0.2 µg/L	Number of detections at any concentration	Number of analyses	Maximum concentration (µg/L)	Benchmark level (µg/L)	Benchmark type[1]	Percent greater than benchmark	Percent detection at any concentration
Hexachloroethane	SOL	0	0	0	639	N/A	N/A			0
Hexachlorobutadiene	SYN	0	0	0	793	N/A	N/A			0
Methyl acrylate	SYN	0	0	0	639	N/A	N/A			0
Methyl methacrylate	SYN	0	0	0	639	N/A	N/A			0
Iodomethane	SYN	0	0	11	639	1.05	NONE			1.7
Isodurene	GAS	0	0	2	639	.10	NONE			.3
tert-Butylbenzene	GAS	0	0	0	793	N/A	N/A			0
tert-Butyl ethyl ether	GAS	0	0	2	639	.02	NONE			.3
tert-Pentyl methyl ether	GAS	0	0	2	639	.17	NONE			.3
trans-1,2-Dichloroethene	SOL	0	0	2	793	.03	100	MCL	0	.3
trans-1,3-Dichloropropene	FUM	0	0	0	793	N/A	N/A			0
trans-1,4-Dichloro-2-butene	SYN	0	0	0	639	N/A	N/A			0
Vinyl acetate	SYN	0	0	0	126	N/A	N/A			0
Vinyl bromide	SYN	0	0	0	545	N/A	N/A			0

[1] U.S. Environmental Protection Agency, 2006; Toccalino and others, 2007.

[2] Part of total trihalomethane maximum contaminant level of 80 µg/L.

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

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

Detection Levels and Data-Analysis Methods

Assessment levels are used to allow a common comparison among samples for the same VOC if the reporting level changed over time, or to allow comparisons among several VOCs that have different reporting levels. As stated previously, prior to 1996, the LRL was 0.2 µg/L for most compounds, so comparisons between data collected before 1996 (154 samples) and from 1996 through 2005 (639 samples) can only be made by comparing percent detections at the 0.2 µg/L assessment level. For these reasons, comparisons of the detection frequencies among the VOCs and the 12 aquifers throughout this section were computed for detections greater than or equal to 0.2 µg/L.

Occurrence and Distribution

Twenty percent of samples contained one or more VOCs at the 0.2 µg/L assessment level, about 8 percent of samples contained two or more VOC detections per sample, about 4 percent of samples contained three or more VOC detections, and about 2 percent contained four or more VOC detections per sample (fig. 37). The percent of samples in these carbonate aquifers containing one or more VOCs was similar to findings from national studies (which also include some of the data used in this report) where 19 percent of samples contained one or more VOCs at concentrations greater than or equal to 0.2 µg/L (Zogorski and others, 2006, p. 16). Among the aquifers, the percent of samples with one or more VOCs detected at the 0.2 µg/L assessment level ranged from 8 percent in the Basin and Range aquifer to 41 percent in the Castle-Hayne aquifer (fig. 38A). Altogether, seven of the carbonate aquifers or aquifer systems had more than 20 percent of samples with one or more VOCs per sample—Biscayne (34 percent), Castle Hayne (41 percent), Mississippian (21 percent) Ozark Plateaus (22 percent), Piedmont (27 percent), Silurian-Devonian/Upper carbonate (27 percent) and Valley and Ridge (24 percent) (fig. 38Aa).

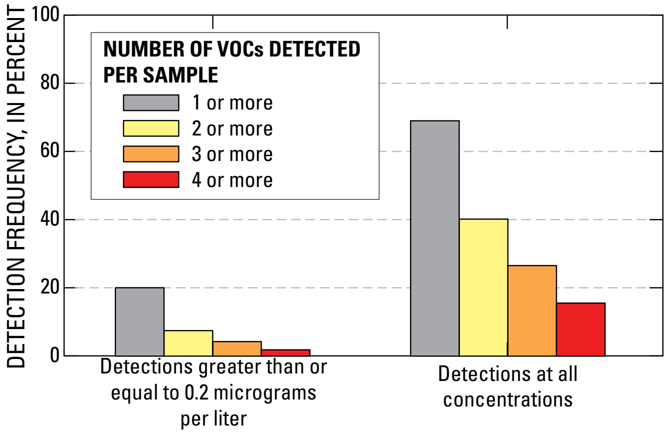


Figure 37. Detection frequency for samples with one or more, two or more, three or more, and four or more volatile organic compounds (VOCs) detected including all detections and at the 0.2 micrograms per liter assessment level in 12 carbonate aquifers or aquifer systems, 1993–2005.

A larger percent of VOC occurrence was evident for a subset of 639 samples that were collected during 1996–2005 and analyzed using the low-level analytical method. Sixty-nine percent of the 639 samples contained 1 or more VOC detections per sample, about 40 percent of samples contained 2 or more VOC detections, about 27 percent of samples contained 3 or more VOC detections, and about 16 percent contained 4 or more VOC detections (fig. 37). The percent of samples in these carbonate aquifers containing one or more VOCs was higher than the findings from national studies (which also include some of the data used in this report)—in the national studies about half of wells sampled contained one or more VOCs at an assessment level of 0.02 µg/L and 19 percent contained one or more VOCs at a level of 0.2 µg/L (Zogorski and others, 2006, p. 16). The finding that one or more VOCs were detected in nearly 70 percent of the samples analyzed using the low-level method demonstrates the vulnerability of many of the carbonate aquifers to low-level VOC contamination.

The percentage of samples with one or more VOC detections per sample did not vary by degree of confinement or redox status but did vary by land use. At the 0.2 µg/L assessment level, the percent of samples with one or more VOC detections was similar between unconfined (22 percent of samples) and confined areas (19 percent), with a lower percentage for semiconfined/mixed confined areas (13 percent) (fig. 38B). Similarly, the percent of sites with two or more VOC detections per sample was similar for unconfined (6 percent) and confined areas (8 percent) with a lower percentage for sites in semiconfined/mixed confined areas (1 percent). Less than 3 percent of sites contained four or more VOCs in any of the confinement categories at the 0.2 µg/L assessment level. The percentage of samples with one or more VOC detections per sample were similar for the three redox-status categories at the 0.2 µg/L assessment level—23 percent of the anoxic samples contained one or more VOC detections, 18 percent of mixed-source samples and 19 percent of oxic samples (fig. 38C). Fewer than 3 percent of samples contained four or more VOCs per sample in any of the redox-status categories. The lack of variability by redox status is likely due to the fact that some of the VOCs persist under oxic conditions, and others persist under anoxic conditions. Among land-use categories, the percentage of samples with one or more VOC detections was higher in sites categorized as urban (31 percent of samples) than in the mixed land use (21 percent), undeveloped (16 percent), or agricultural (13 percent) land-use areas (fig. 38D) at the 0.2 µg/L assessment level. Four percent of samples contained four or more VOCs per sample in the urban land-use category but fewer than 2 percent of samples contained four or more VOCs in the agricultural, mixed land use, or undeveloped land-use categories.

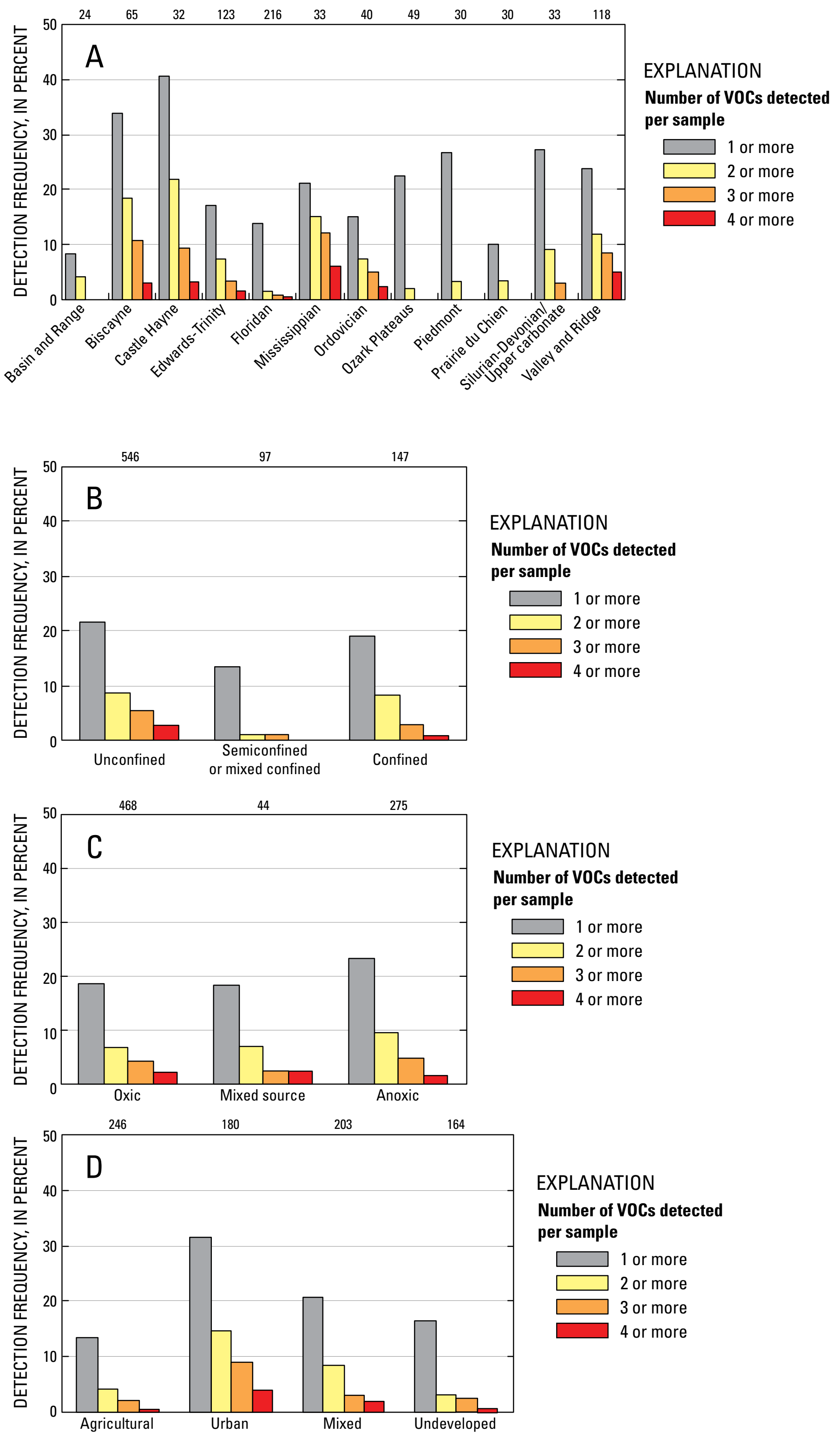


Figure 38. Detection frequency for samples with one or more, two or more, three or more, and four or more volatile organic compounds (VOCs) detected at the 0.2 micrograms per liter assessment level by A) aquifer, B) confinement category, C) redox status, and D) land-use category in 12 carbonate aquifers or aquifer systems, 1993–2005.

Thirteen VOCs were detected in 1 percent or more samples at the 0.2 µg/L assessment level, and detection frequencies were variable among the aquifers. Chloroform was the most frequently detected VOC and was detected in 7.2 percent of the samples from all 12 aquifers (fig. 39). Chloroform was detected most frequently in the Mississippian aquifer (18 percent of samples) and the Valley and Ridge aquifer (14 percent of samples) and it was not detected in any samples at the 0.2 µg/L assessment level in five aquifers—Basin and Range, Castle Hayne, Piedmont, Prairie du Chien, and Silurian-Devonian/Upper carbonate aquifers (fig. 40). Tetrahydrofuran was the second most frequently detected VOC at the 0.2 µg/L assessment level (3.4 percent in all 12 aquifers) and its occurrence was highly variable—it was detected in 30 percent of the samples in the Castle Hayne aquifer and in 3 percent or less of samples in the other aquifers. Tetrachloroethene (PCE) was detected in 2.9 percent of samples at the 0.2 µg/L assessment level—it was detected in 21 percent of the samples from the Silurian-Devonian/Upper carbonate aquifer, 9 percent of the Mississippian, 7 percent of the Valley and Ridge aquifer samples and less than 4 percent in the other aquifers at the 0.2 µg/L assessment level. PCE was not detected in any samples from the Basin and Range, Biscayne, Castle Hayne, Piedmont, or Prairie du Chien aquifers at the 0.2 µg/L assessment level (fig. 40). Toluene was detected in 2.3 percent of samples at the 0.2 µg/L assessment level—it was detected in 8 percent of samples from the Biscayne aquifer and about 6 percent of samples from the Castle Hayne, and Silurian-Devonian/Upper carbonate aquifers. Toluene was detected in less than 4 percent of samples from the other aquifers. Toluene was not detected in samples from the Basin and Range, Piedmont, and Prairie du Chien aquifers at the 0.2 µg/L assessment level (fig. 40).

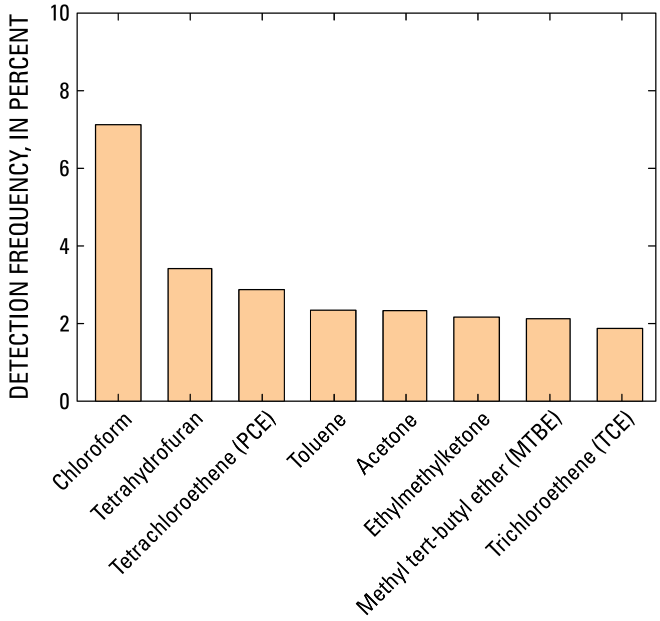


Figure 39. Detection frequencies of the eight most frequently detected volatile organic compounds at the 0.2 micrograms per liter assessment level in 12 carbonate aquifers or aquifer systems, 1993–2005.

Assessment of Potential Human-Health Significance

Concentrations of VOCs were compared to human-health benchmarks (MCLs and HBSLs) to determine the potential impacts of these compounds on human health. BQ values were calculated and represent the concentration of a given VOC divided by the MCL or HBSL (figs. 41–44). Although chloroform was the most frequently detected VOC (table 31), concentrations were all less than the human-health benchmarks. Chloroform concentrations were compared to the MCL for total trihalomethanes of 80 µg/L (U.S. Environmental Protection Agency, 2006) and no concentrations were found above this level—concentration of other trihalomethanes analyzed were less than 5 µg/L (table 31). Two samples in urban areas in the unconfined Valley and Ridge aquifer did have chloroform BQ values greater than 0.1 (fig. 41A), indicating the concentrations were within an order of magnitude of the MCL. The maximum concentration of chloroform was 61 µg/L in a monitoring well in an urban land-use area in the unconfined Valley and Ridge aquifer.

Four VOCs—vinyl chloride, PCE, trichloroethene (TCE), and 1,2-dichloropropane—were each detected at concentrations exceeding an MCL. Each of these exceedances occurred in drinking-water supplies. Vinyl chloride was detected in two samples from the unconfined Biscayne aquifer at concentrations of 4.7 and 3.2 µg/L, which exceeded the MCL of 2 µg/L. Both of the sites where vinyl chloride was detected were in anoxic samples in urban areas. PCE, TCE, and 1,2-dichloropropane had one sample each in unconfined areas of the Mississippian aquifer with a concentration greater than the MCL—the MCL is 5 µg/L for each of these VOCs (U.S. Environmental Protection Agency, 2006) (figs. 42–44). PCE was detected at a concentration of 5.01 µg/L in one sample from a public supply well in a predominantly urban area, TCE was detected at a concentration of 7.5 µg/L in one sample from a domestic supply well in an agricultural area (fig. 43), and 1,2,-dichloropropane was detected at a concentration of 6.4 µg/L in one sample from a spring in an agricultural area that is used for domestic supply (fig. 44). Nine samples had PCE concentrations within an order of magnitude of the MCL (fig. 42), eight samples had TCE concentrations within an order of magnitude of the MCL (fig. 43), and two samples had 1,2-dichloropropane concentrations within an order of magnitude of the MCL (fig. 44). These occurrences of concentrations within an order of magnitude of the MCL occurred in agricultural, urban, and mixed land-use areas (figs. 42–44), but all were in samples from unconfined areas. About 70 percent of the 793 samples with VOC analyses were categorized as unconfined, so the higher numbers of VOC occurrences in this category are not surprising.

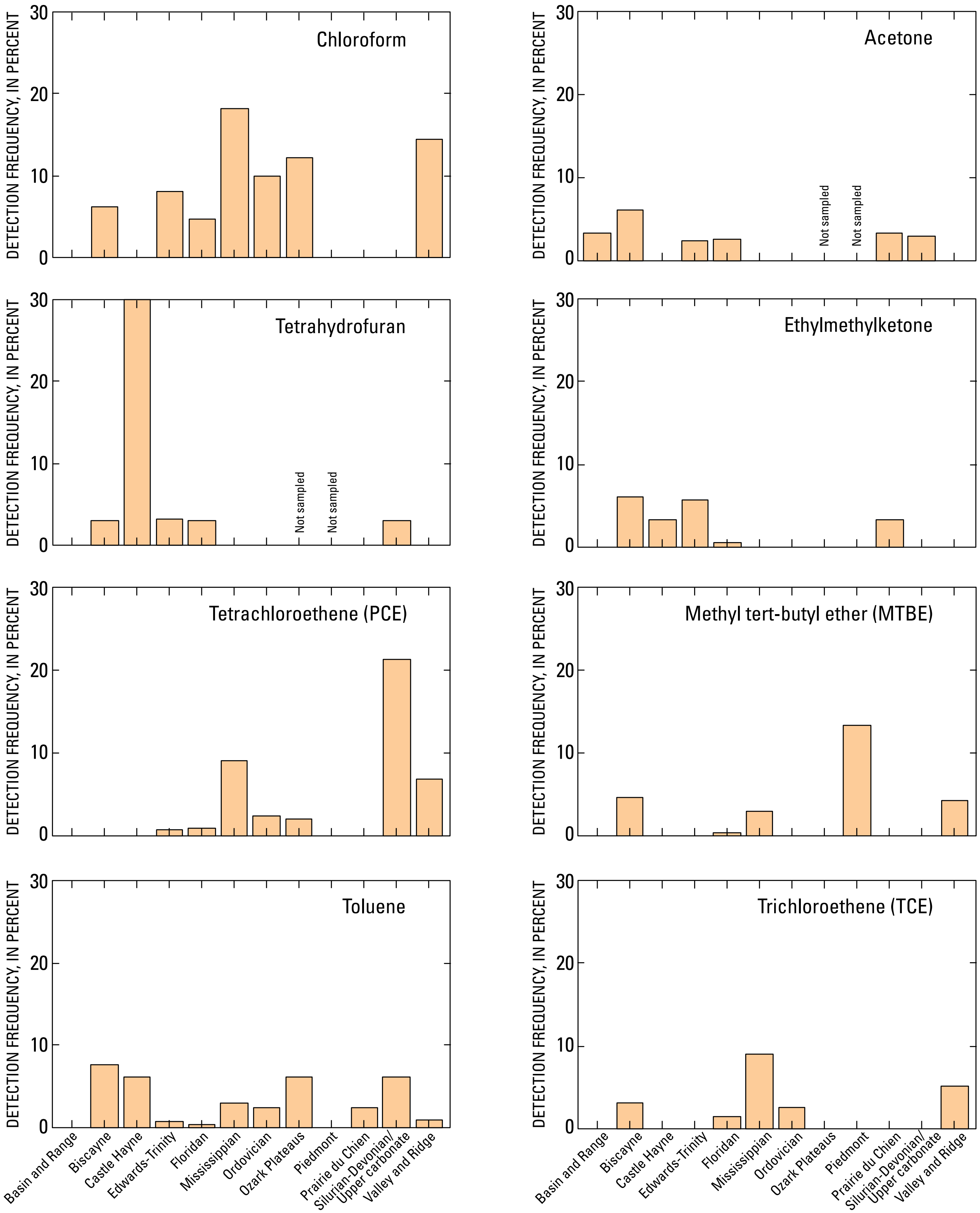
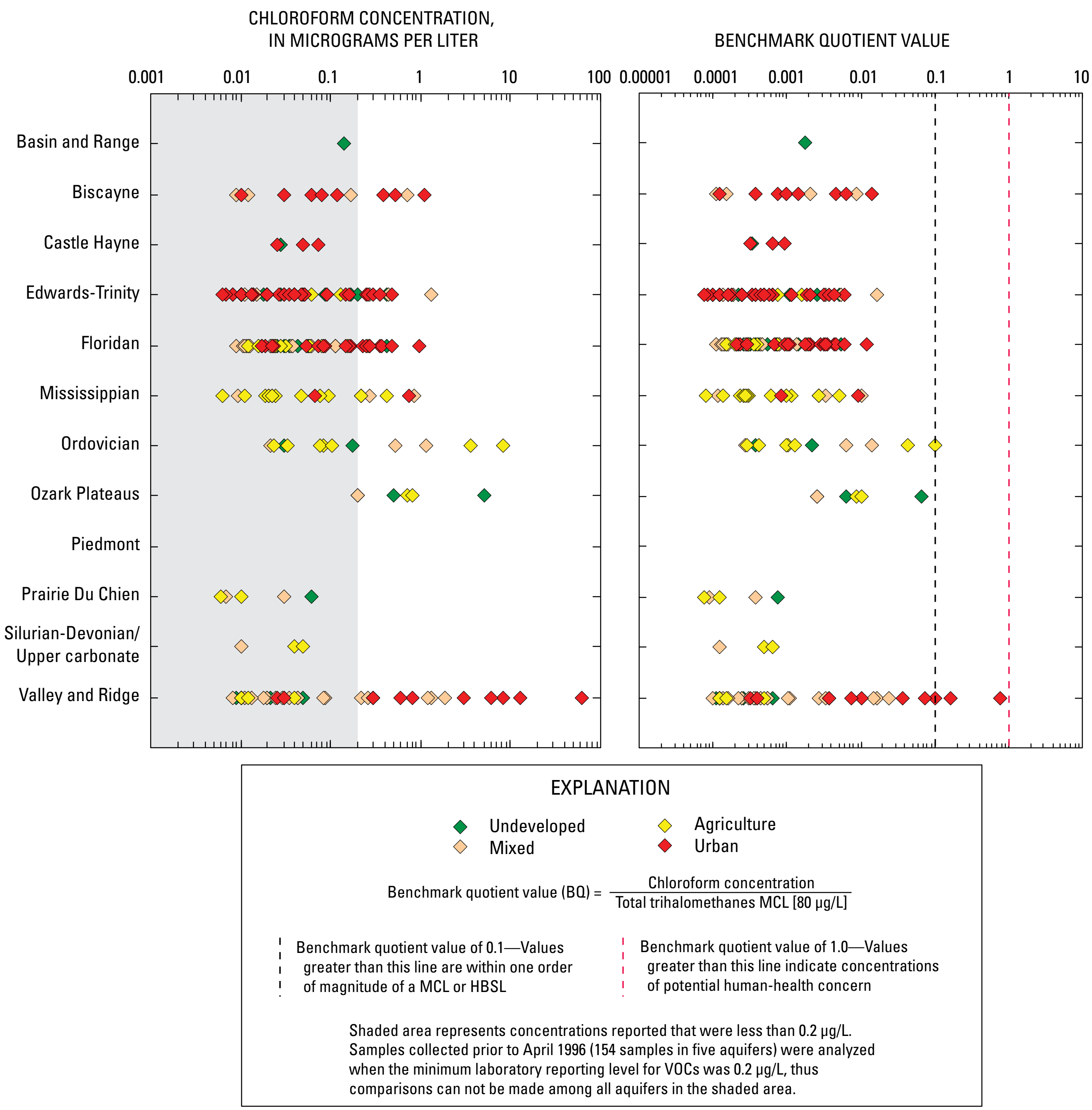


Figure 40. Detection frequencies of the eight most frequently detected volatile organic compounds in each aquifer at the 0.2 micrograms per liter assessment level in 12 carbonate aquifers or aquifer systems, 1993–2005.



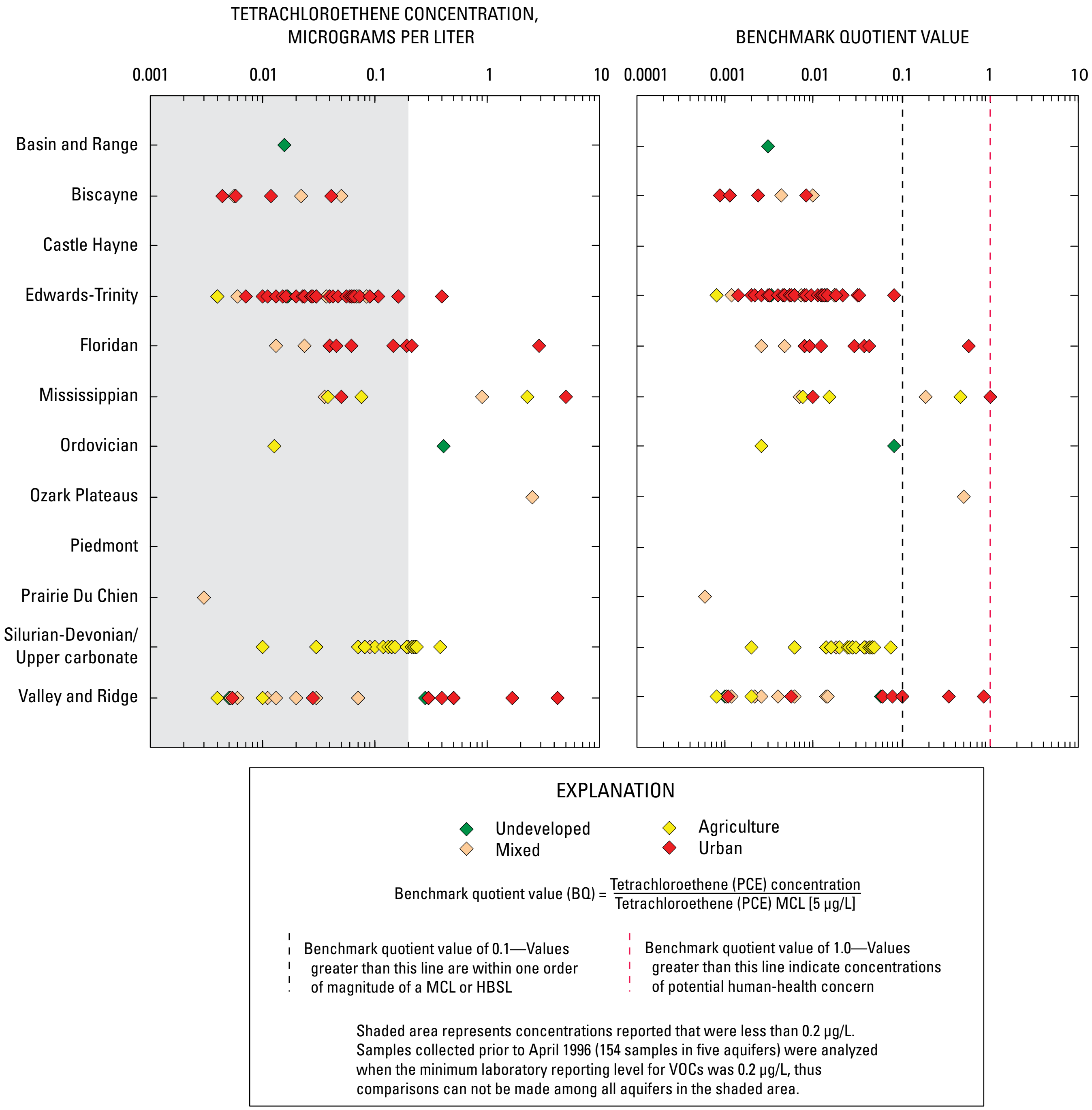
Benchmark quotient value (BQ) = $\frac{\text{Chloroform concentration}}{\text{Total trihalomethanes MCL [80 µg/L]}}$

Benchmark quotient value of 0.1—Values greater than this line are within one order of magnitude of a MCL or HBSL

Benchmark quotient value of 1.0—Values greater than this line indicate concentrations of potential human-health concern

Shaded area represents concentrations reported that were less than 0.2 µg/L. Samples collected prior to April 1996 (154 samples in five aquifers) were analyzed when the minimum laboratory reporting level for VOCs was 0.2 µg/L, thus comparisons can not be made among all aquifers in the shaded area.

Figure 41. Concentrations and human-health benchmark quotient values for chloroform by land-use category in 12 carbonate aquifers or aquifer systems, 1993–2005.



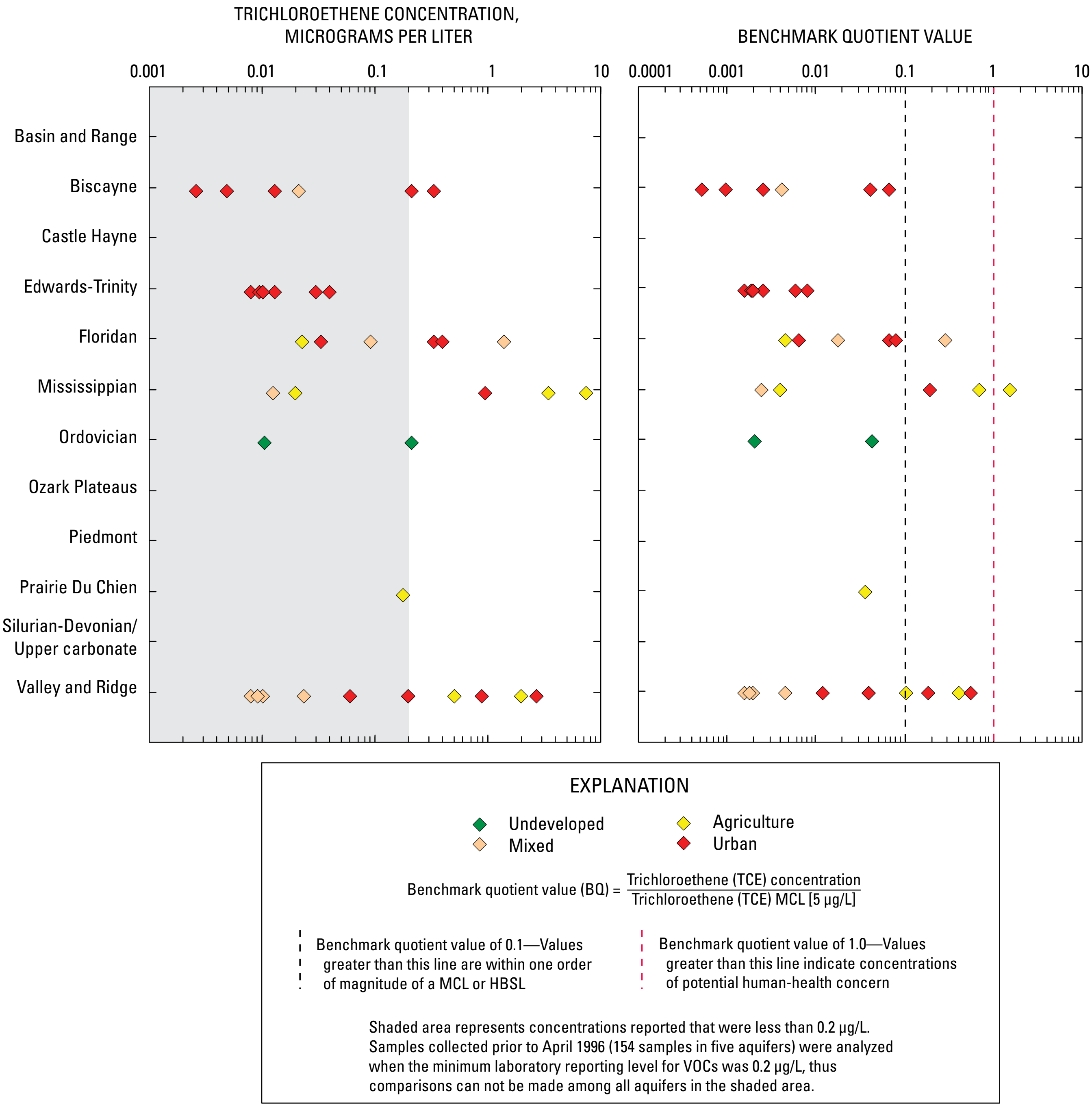
Benchmark quotient value (BQ) = $\frac{\text{Tetrachloroethene (PCE) concentration}}{\text{Tetrachloroethene (PCE) MCL [5 µg/L]}}$

Benchmark quotient value of 0.1—Values greater than this line are within one order of magnitude of a MCL or HBSL

Benchmark quotient value of 1.0—Values greater than this line indicate concentrations of potential human-health concern

Shaded area represents concentrations reported that were less than 0.2 µg/L. Samples collected prior to April 1996 (154 samples in five aquifers) were analyzed when the minimum laboratory reporting level for VOCs was 0.2 µg/L, thus comparisons can not be made among all aquifers in the shaded area.

Figure 42. Concentrations and human-health benchmark quotient values of tetrachloroethene (PCE) by land-use category in 12 carbonate aquifers or aquifer systems, 1993–2005.



Benchmark quotient value (BQ) = $\frac{\text{Trichloroethene (TCE) concentration}}{\text{Trichloroethene (TCE) MCL [5 µg/L]}}$

Benchmark quotient value of 0.1—Values greater than this line are within one order of magnitude of a MCL or HBSL

Benchmark quotient value of 1.0—Values greater than this line indicate concentrations of potential human-health concern

Shaded area represents concentrations reported that were less than 0.2 µg/L. Samples collected prior to April 1996 (154 samples in five aquifers) were analyzed when the minimum laboratory reporting level for VOCs was 0.2 µg/L, thus comparisons can not be made among all aquifers in the shaded area.

Figure 43. Concentrations and human-health benchmark quotient values of trichloroethene (TCE) by land-use category in 12 carbonate aquifers or aquifer systems, 1993–2005.

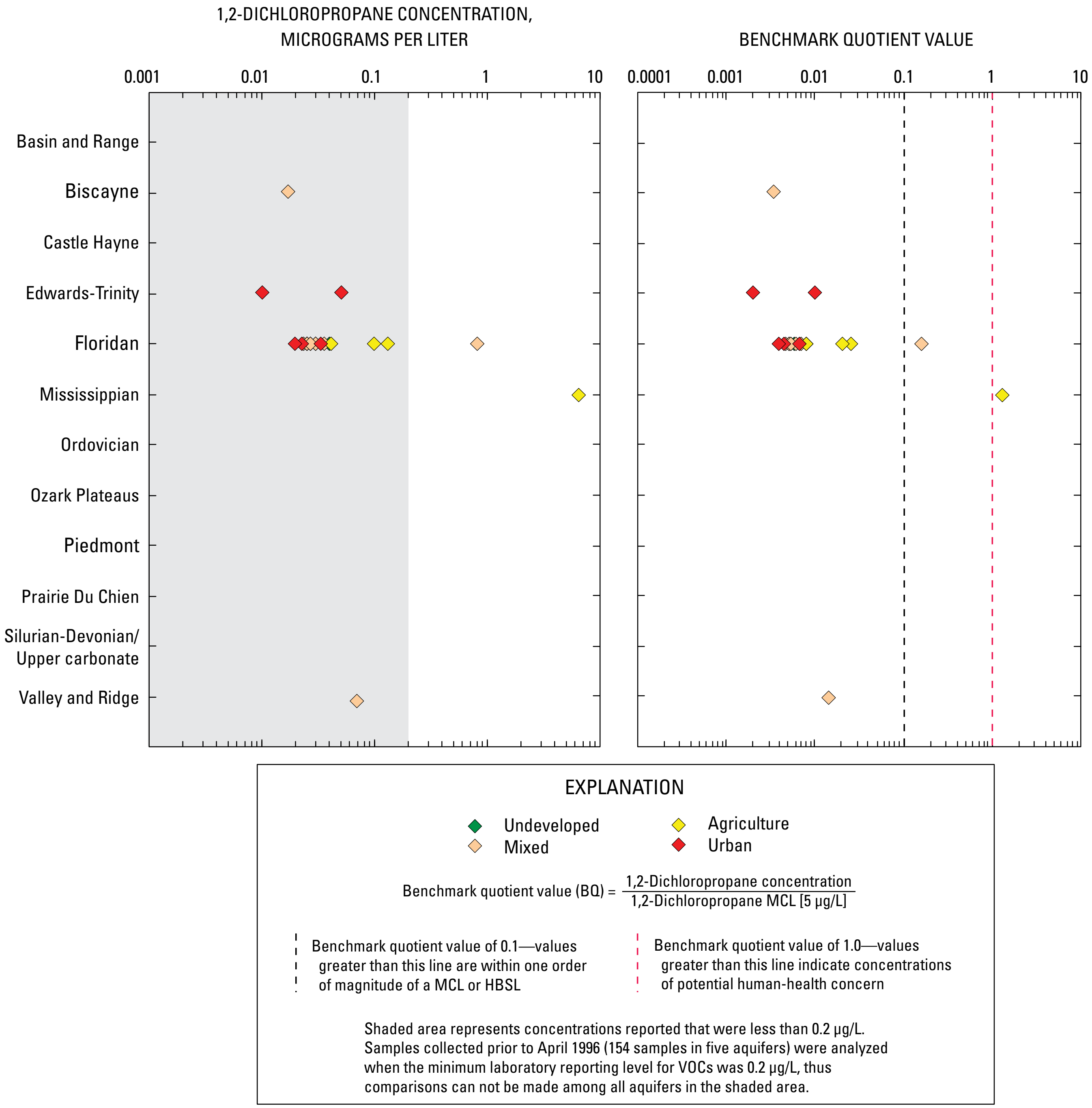


Figure 44. Concentrations and human-health benchmark quotient values of 1,2-dichloropropane by land-use category in 12 carbonate aquifers or aquifer systems, 1993–2005.

Factors Affecting Occurrence of Frequently Detected Volatile Organic Compounds

The eight most frequently detected VOCs—chloroform, tetrahydrofuran, PCE, toluene, acetone, ethylmethylketone, methyl tert-butyl ether (MTBE), and TCE—differed in their detection frequencies among the carbonate aquifers studied and these differences are likely related to various natural and anthropogenic factors, including hydrogeology, water chemistry, and land use. Comparison of the detection frequencies of the eight most frequently detected VOCs among categories of confinement and land use at the sampling site, as well as redox status of the water sample, were used to assess the importance of the factors affecting VOC occurrence in the 12 carbonate aquifers. Previous national studies have shown that VOC occurrence in ground water was associated with natural and anthropogenic factors, the most common of which is dissolved oxygen concentration—other factors include urban land use, hazardous-waste facilities, gasoline storage sites, septic systems, climate, well characteristics, and soil characteristics (Zogorski and others, 2006). In this study, similarities and differences were seen in the factors associated with the occurrence of different types of VOCs, including trihalomethanes (including disinfection by-products such as chloroform), solvents (PCE, TCE, and chloromethane) and gasoline hydrocarbons and oxygenates (toluene and MTBE).

Differences in the detection frequencies by degree of confinement, redox status, and land use demonstrate that the occurrence of the eight most frequently detected VOCs—chloroform, tetrahydrofuran, toluene, PCE, acetone, ethylmethylketone, MTBE, TCE—are associated with different land uses and are affected differently by degree of confinement and redox status in ground water. Chloroform was detected most frequently at the 0.2 μg/L assessment level in sites categorized as unconfined (10 percent), in oxic samples (11 percent), and from areas where the predominant land use was urban (14 percent) (fig. 45A, B, and C), indicating that these settings are the most vulnerable to contamination from chloroform. The occurrence of chloroform has been associated with oxygenated waters, the percentage of urban land, the number of hazardous-waste facilities, and septic-tank density near the well sites (Squillace and Moran, 2006; Zogorski and others, 2006).

Five of the eight most frequently detected VOCs were solvents—tetrahydrofuran, PCE, acetone, ethylmethylketone, and TCE. Although detection frequencies were low in each category (most were less than 5 percent) some similarities and differences were noted among the five solvents (figs. 45A, B, and C). The five solvents were most frequently detected in urban land-use settings, except for acetone, which was detected most frequently in urban and mixed land-use settings (fig. 45C). Tetrahydrofuran, acetone, and ethylmethylketone were detected most frequently in anoxic water (fig. 45B) and in confined or semiconfined/mixed confined areas (fig. 45A). The greater frequency of detection in anoxic water may indicate these three VOCs are more persistent under anoxic conditions. If tetrahydrofuran does persist under anoxic conditions, this may explain the high detection frequency of that compound in the Castle-Hayne aquifer, which has low concentrations of dissolved oxygen and no wells in the ‘oxic’ redox-status category. PCE was detected at similar frequencies in confined areas and unconfined areas and TCE was detected most frequently in unconfined areas. PCE was detected more frequently in mixed source and oxic samples than in anoxic samples and TCE was detected most frequently in oxic samples. The findings are similar to the results of the analysis of national VOC data (Zogorski and others, 2006), which showed that the occurrence of PCE and TCE were associated with septic system density, the percentage of urban land use, and oxic water (which includes the mixed source redox category used in this report).

The gasoline hydrocarbon, toluene, and the gasoline oxygenate, MTBE, showed different occurrence patterns among the categories of confinement, redox status, and land use. Toluene was detected most frequently in confined areas, in anoxic samples, and in undeveloped and urban land-use settings, whereas MTBE was detected most frequently in unconfined areas, in oxic samples, and in urban land-use settings (fig. 45A, B, and C). This is also similar to the results of the analysis of national VOC data (Zogorski and others, 2006), which showed that toluene was more persistent in anoxic water, and MTBE was more persistent in oxic water. The high detection frequency of toluene in undeveloped areas may be because many of the detections were in confined areas, where the predominant land use near the well may be different than the predominant land use in the recharge area.

Summary

Carbonate aquifers provide an abundant supply of water to a large percentage of the population of the United States. The USGS National Water-Quality Assessment (NAWQA) Program has collected water-quality samples from 1993 through 2005 at 1,042 sites in 12 of the principal carbonate aquifers of the United States. These aquifers/aquifer systems include the Basin and Range, Biscayne, Castle Hayne, Edwards-Trinity, Floridan, Mississippian, Ordovician, Ozark Plateaus, Piedmont, Prairie du Chien (part of the Cambrian-Ordovician aquifer), Silurian-Devonian/Upper carbonate (the Upper carbonate aquifer is a small carbonate aquifer lumped with the Silurian-Devonian aquifer for this study), and the Valley and Ridge. Some of these aquifers contain other lithologic units such as sandstone, but only wells completed in the carbonate parts of the aquifers were included in this study. These carbonate aquifers share the common characteristic of carbonate lithology, but otherwise, the hydrogeologic characteristics of these aquifers vary widely.

Most of the aquifers have fracture permeability, with varying degrees of solutional enlargement that increases transmissivity; thus, all these aquifers are referred to as karst

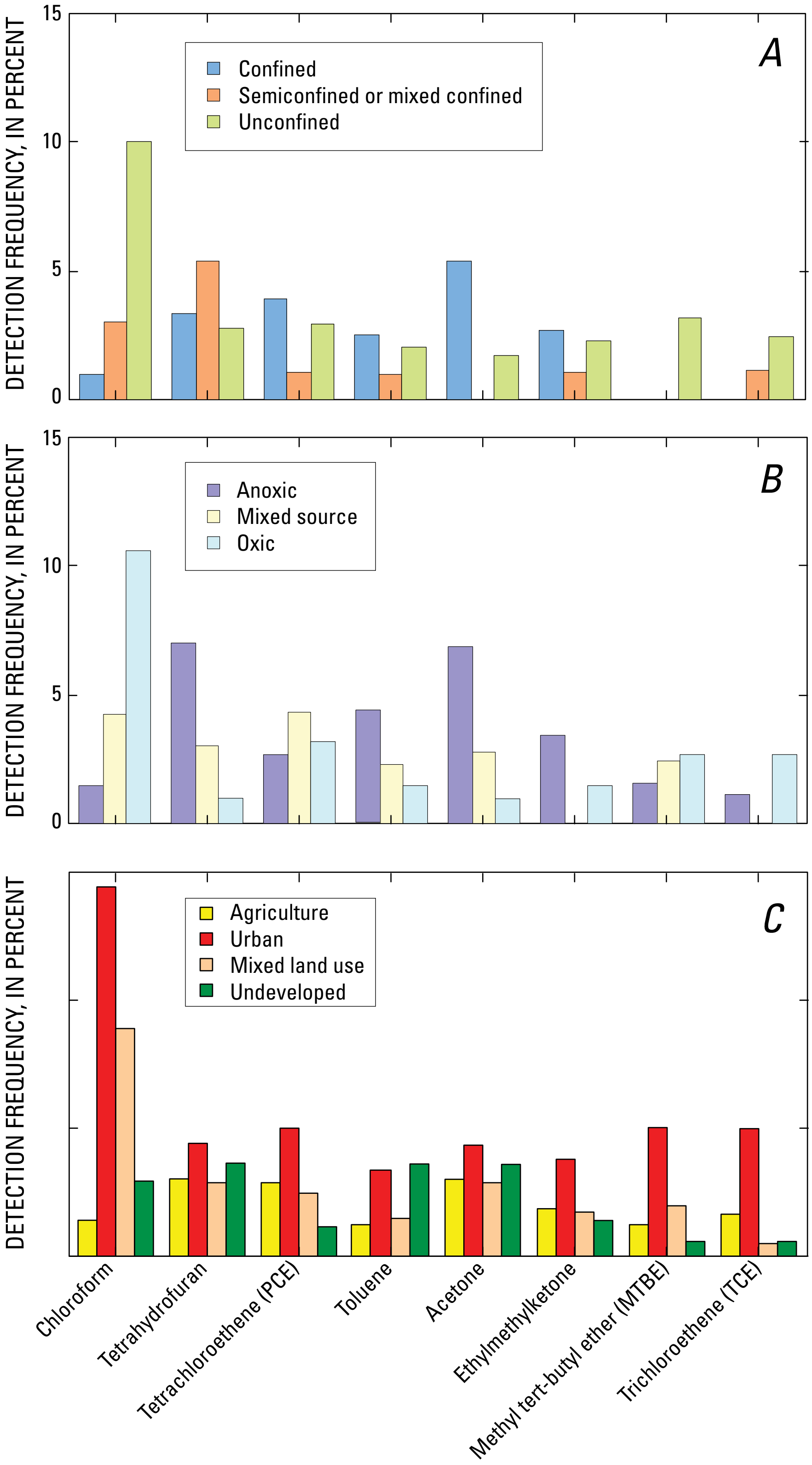


Figure 45. Detection frequencies of the eight most frequently detected volatile organic compounds at the 0.2 micrograms per liter assessment level by A) confinement category, B) redox status, and C) land use in 12 carbonate aquifers or aquifer systems, 1993–2005.

aquifers. Some aquifers, however, such as the Biscayne, also have a significant component of primary porosity in the rock matrix. Karst-feature development also varies among these aquifers; sinkholes, caverns, and springs are common in most of the aquifers. These features play an important role in the recharge, transport, and discharge of water and contaminants in the aquifers.

The physical characteristics of the natural and anthropogenic features in the carbonate aquifers have an effect on water quality. The climate varies from an arid environment in the southwest, to subtropical in the southeast, to temperate in the central and northeastern parts of the United States. This variation affects the recharge and flux of water through the systems. The carbonate aquifers can be unconfined, sometimes with bedrock exposed at the land surface. In other areas, the carbonate aquifers are confined by layers of materials of varying thickness and permeability. The nature and thickness of these materials provide a variable level of protection for the aquifer from contaminants. These characteristics affect the typical construction of wells drilled in each aquifer. Wells in these aquifers range from very shallow in the Biscayne aquifer (tens of feet) to thousands of feet deep in several of the other aquifers. The land use overlying these aquifers is also highly variable, ranging from urban to agricultural, to forested and shrub land. The type and intensity of human activity at the land surface also has a potential effect on the quality of water in the aquifer.

Geochemical analysis of the water indicated that most waters had a near-neutral pH; the median was 7.1. Water from shallower aquifers that were thought to have a shorter residence time had lower pH, and pH had a strong positive correlation with well depth. Major ions and dissolved solids also showed positive correlations with increasing well depth, and these constituents are indicators of ground-water residence time, which is a controlling factor in aquifer geochemistry. Dominant major ions were calcium, magnesium, and bicarbonate. The relation between molar concentrations of calcium plus magnesium and bicarbonate indicated that calcite and dolomite dissolution were the dominant processes controlling major-ion composition. Saturation indices were calculated for numerous minerals. Most samples were considered to be at equilibrium with respect to calcite and undersaturated with respect to dolomite. The exceptions to this were that the Mississippian and Ordovician aquifers were undersaturated with respect to calcite, and the Prairie du Chien and Basin and Range aquifers were at equilibrium with respect to dolomite.

The oxidation-reduction (redox) status was highly variable; the Biscayne, Castle Hayne, Floridan, Prairie du Chien, and Silurian-Devonian/Upper carbonate aquifers/aquifer systems had median concentration of dissolved oxygen less than 1.0 mg/L. In most cases, wells in confined aquifers had lower concentrations of dissolved oxygen than wells in unconfined aquifers. Differences in concentrations of dissolved oxygen are likely related to timing and amounts of recharge, presence of karst features such as sinkholes and large conduits, and presence of dissolved organic carbon. Median concentrations of dissolved organic carbon were highest in the Biscayne (11 mg/L), Castle Hayne (2.51 mg/L), and Silurian-Devonian/Upper carbonate (1.2 mg/L) aquifers—the three aquifers with the lowest median concentrations of dissolved oxygen—organic carbon is likely enhancing the rate of oxygen consumption in the ground water in these systems.

The median radon concentration for all samples in carbonate aquifers was 360 pCi/L. Most radon concentrations in water from the Basin and Range, Biscayne, Mississippian, Piedmont, and Prairie du Chien aquifers were greater than the USEPA-proposed maximum contaminant level (MCL) of 300 pCi/L. Radon concentrations were highest in the water from wells in unconfined aquifers. Several geochemical measures or indicators were found to be important explanatory variables for the anthropogenic contaminants. These include factors directly related to fate such as concentrations of dissolved oxygen (or redox status) and dissolved organic carbon, as well as indicators of residence time, such as calcite S.I., dolomite S.I., and the calcium-magnesium ratio.

Nitrate was detected in 793 of 1,037 samples (76 percent). Concentrations ranged from below the detection limit of 0.06 mg/L to 25 mg/L. Nitrate concentrations exceeded the USEPA MCL of 10 mg/L in 54 samples (5 percent). The majority of the sites with concentrations exceeding the MCL were in the Valley and Ridge and Piedmont aquifers. The rate of exceedance of the MCL in the remaining 10 aquifers was about 1 percent. Median concentrations of nitrate were highest in the Piedmont and Valley and Ridge aquifers and lowest in the Biscayne, Castle Hayne, and Silurian-Devonian/Upper carbonate aquifers. Nitrate concentrations were related to source factors and transport factors.

Agricultural land use and the total nitrogen input from atmospheric deposition, fertilizer, manure, and septic systems were the source factors with the strongest positive correlation with nitrate concentrations. Ground-water age was a significant factor affecting nitrate concentration. Water recharged prior to 1953 had significantly lower median concentrations of nitrate than water recharged in 1953 or later. In addition, water from wells in confined aquifers and semiconfined/mixed confined aquifers had statistically significant lower nitrate concentrations than water from wells in unconfined aquifers. Dissolved oxygen concentration had a strong positive correlation with nitrate concentration, indicating that redox processes in the aquifer play an important role in the fate and transport of nitrate. Among waters with recharge dates later than 1953, a comparison of oxic and anoxic waters with a gradient of land-use types showed that oxic water in the area with the lowest potential nitrogen source (undeveloped) had greater nitrate concentrations than anoxic water with the highest potential nitrogen source (agricultural). This indicates that the redox status of the water is a more important controlling factor affecting nitrate concentration than land use. Nitrate concentrations were positively correlated with calcium-magnesium ratios and inversely correlated with calcite or dolomite S.I., which are indicators of longer residence time in the aquifer. Dissolved organic carbon concentration had an inverse correlation with nitrate concentrations and dissolved oxygen concentrations, indicating the importance of carbon in the nitrogen cycle.

Any single source or transport factor is not likely to control the concentration of nitrate. The Silurian-Devonian/Upper carbonate aquifer had the second-highest loadings of nitrogen but had the second-lowest median concentration of nitrate. A combination of the degree of aquifer confinement and land use provides a good explanation of the distribution of the concentrations of nitrate in the carbonate aquifers. A logistic regression model was built to assess the interaction of the source and transport variables. The variables that were significant in this model were the percent of soils in hydrologic group D (soils with a high runoff potential, an inverse relation), concentration of dissolved oxygen, percent forested land (inverse relation), calcium-magnesium ratio (inverse relation), and the input of nitrogen from all sources.

Pesticide samples were collected at 1,027 sites in the carbonate aquifers. At least 1 pesticide out of a schedule of 47 pesticides analyzed was detected at 509 of the sites (50 percent). Multiple pesticides were frequently detected; 39 percent of the samples had two or more pesticides detected in the same sample, and 4 percent of the samples had six or more pesticides detected.

Only two pesticides were detected at a concentration that exceeded a human-health benchmark. Dieldrin was detected at 20 sites at a concentration greater than the value for the HBSL of 0.002 µg/L; 9 of these sites were used as drinking-water sources. The maximum concentration of dieldrin detected was 0.81 mg/L. Diazinon was detected at a concentration greater than the HBSL of 1 µg/L at a single well used for domestic supply.

The most frequently detected pesticides were atrazine, deethylatrazine, simazine, metolachlor, and prometon. When comparing the concentrations of these pesticides to a threshold of 10 percent of the human-health benchmark, only 41 atrazine samples (4 percent) and 1 simazine sample (0.1 percent) exceeded that threshold. For these five compounds, the Biscayne, Mississippian, Piedmont, and Valley and Ridge aquifers had the highest detection frequencies; at least one of the pesticides was detected in 30 percent of the wells in those four aquifers. The Basin and Range, Castle Hayne, Floridan, and Ozark Plateaus aquifers/aquifer systems had the lowest detection rates for these five pesticides; less than 10 percent of the wells in those aquifers had one or more of the five most frequently occurring pesticides detected. All the frequently detected pesticides had positive correlations with agricultural land use and the application rate of the pesticide, if it was available. Atrazine, simazine, and prometon had a positive correlation with urban land use. The detections of pesticides were related to ground-water age and degree of confinement; samples of younger water and water from unconfined aquifers had a statistically significant higher rate of pesticide detection than samples of older water and water from aquifers with mixed confinement or confined aquifers. Dissolved oxygen concentration had a positive correlation with pesticide concentration. This is likely because well-oxygenated waters are young rather than any direct cause-and-effect relation because the degradation processes of some of these pesticides require oxygen. Dissolved organic carbon had an inverse correlation with pesticide concentrations in some aquifers, and a positive correlation in others. In the cases where the correlation was positive, it is likely that the correlation was a result of land use and not concentration of dissolved organic carbon. Several of the pesticides showed positive correlations with calcium-magnesium ratios and inverse correlations with calcite or dolomite S.I., which are indicators of longer residence time in the aquifer.

Analysis of the interaction of source, transport, and fate factors showed that a combination of land use and degree of confinement explained the patterns of detections of pesticides. Wells in unconfined areas with urban, mixed land use, or agricultural land use had a higher frequency of pesticide detection than confined aquifers with other land-use types. The detections in the unconfined areas with these land-use types make up 71 percent of the samples, but nearly 90 percent of the detections of the frequently detected pesticides. The logistic regression models built for each of the five frequently occurring pesticides also showed the importance of land use and degree of confinement; one of the land-use variables was significant in each of the regression models, and degree of confinement was significant in all but one of the regression models.

VOCs were detected in 20 percent of samples at concentrations greater than or equal to 0.2 µg/L (159 of 793 samples). About 8 percent of samples contained two or more VOC detections per sample, about 4 percent of samples contained three or more VOC detections, and about 2 percent of samples contained four or more VOC detections. VOCs were detected in a larger percent of samples when all concentrations were included for a subset of 639 samples that were analyzed using a low-level analytical method. Sixty-nine percent of the 639 samples contained 1 or more VOCs, about 40 percent of samples contained 2 or more VOC detection per sample, about 27 percent of samples contained 3 or more VOC detections, and about 16 percent contained 4 or more VOC detections. Detection frequencies for VOCs were slightly higher for samples in areas with urban or mixed land use than in areas with agricultural or undeveloped land use, but did not vary significantly among confinement categories or redox-status categories. Thirteen VOCs were detected in 1 percent or more samples at the 0.2 µg/L assessment level, and detection frequencies were variable among the aquifers. The most frequently detected VOCs at the 0.2 µg/L assessment level were chloroform (detected in 7.2 percent of samples), tetrahydrofuran (3.4 percent), PCE (2.9 percent), toluene (2.3 percent), acetone (2.3 percent), ethylmethylketone (2.2 percent), MTBE (2.1 percent), and TCE (1.9 percent). These VOCs differed in their detection frequencies among the carbonate aquifers studied and these differences are likely related to various natural and anthropogenic factors, including hydrogeology, water chemistry, and land use.

Chloroform was detected most frequently at the 0.2 μg/L assessment level in sites categorized as unconfined (10 percent), in oxic samples (11 percent), and from areas where the predominant land use was urban (14 percent). Detection frequencies for five solvents—tetrahydrofuran, PCE, acetone, ethylmethylketone, and TCE—were lower in each category (most were less than 5 percent). These VOCs were most frequently detected in urban land-use settings but detection frequencies varied among the redox status and confinement categories. Tetrahydrofuran, acetone, and ethylmethylketone were detected most frequently in anoxic water and in confined or semiconfined/mixed confined areas. PCE was detected at similar frequencies in confined areas and unconfined areas, and TCE was detected most frequently in unconfined areas. PCE was detected more frequently in mixed source and oxic samples than in anoxic samples and TCE was detected most frequently in oxic samples. The gasoline hydrocarbon, toluene, and the gasoline oxygenate, MTBE, showed different occurrence patterns among the categories of confinement, redox status, and land use. Toluene was detected most frequently in confined areas, in anoxic samples, and in undeveloped and urban land-use settings. MTBE was detected most frequently in unconfined areas, in oxic samples, and in urban land-use settings.

Four VOCs—vinyl chloride, PCE, TCE, and 1,2-dichloropropane—were each detected at concentrations exceeding an MCL in a small number of samples. Vinyl chloride concentrations exceeded the MCL of 2 μg/L in two samples—the samples were anoxic and from urban areas in the unconfined Biscayne aquifer. Three samples exceeded MCLs for PCE, TCE, and 1,2-dichloropropane (MCL for each is 5 mg/L) in unconfined areas of the Mississippian aquifer.

This study of water quality in carbonate aquifers provided an opportunity to compare and contrast the factors affecting the concentrations and occurrence of anthropogenic contaminants. The study used a combination of networks with variations in land use, degree of confinement, and target depths, which affected the comparisons among aquifers. This range of characteristics, however, allowed the identification of several important factors that affect water quality in carbonate aquifers. These findings can be used to help those involved in the protection and management of these important aquifers.

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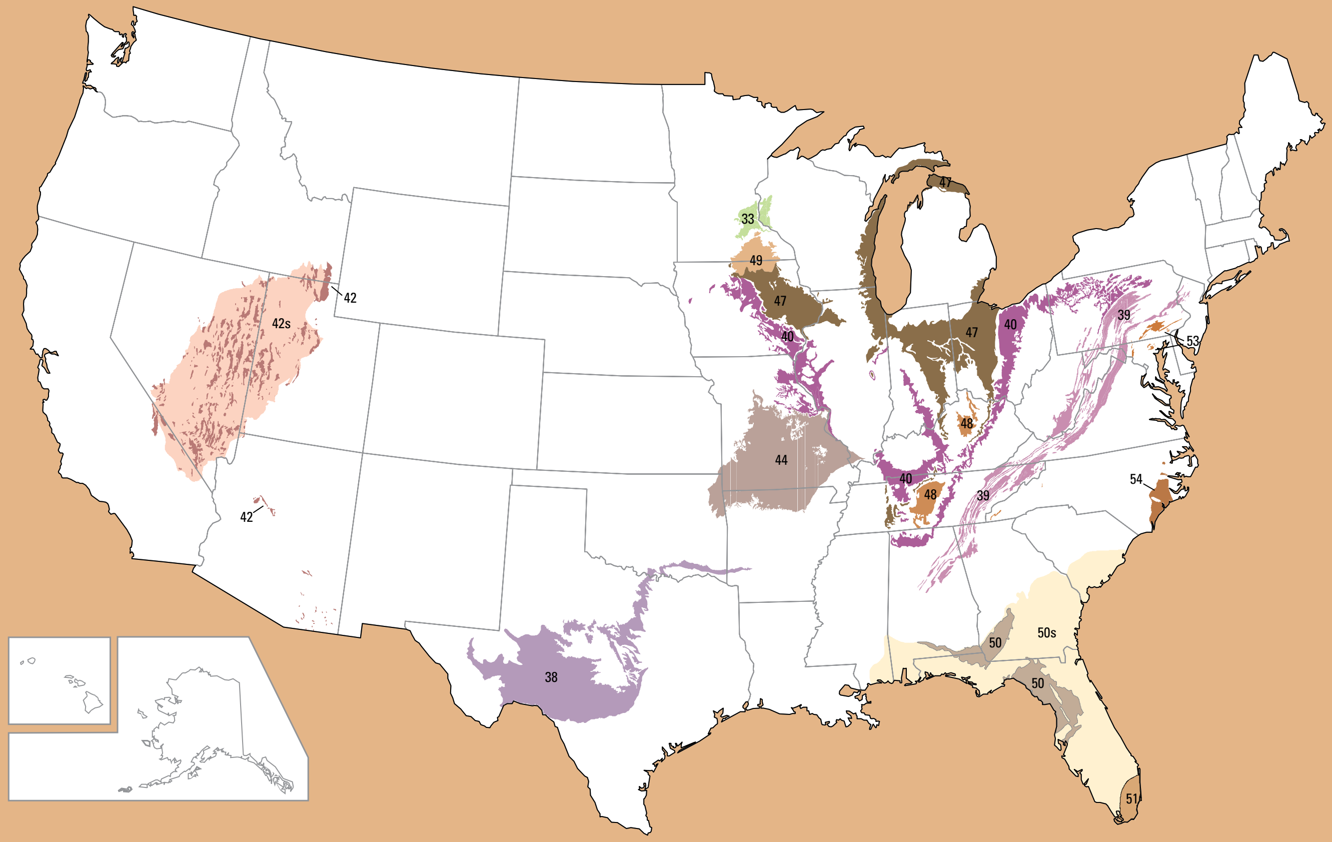

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