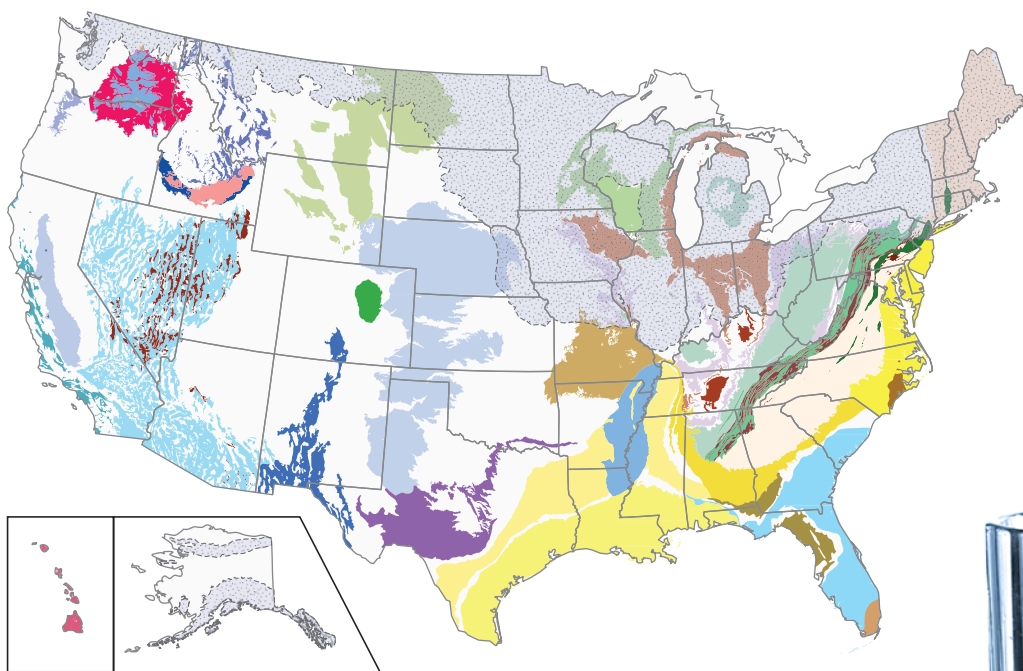


Water Quality in Principal Aquifers of the United States, 1991–2010



National Water-Quality Assessment Program

Circular 1360

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

Front cover. Map showing Principal Aquifers of the United States that are included in this study. Image of pitcher and glass copyright istockphoto.com.

Back cover. USGS scientists collecting and processing samples from monitoring, domestic, and public-supply wells for this study. Photographs by USGS.

The Quality of Our Nation's Waters

Water Quality in Principal Aquifers of the United States, 1991–2010

By Leslie A. DeSimone, Peter B. McMahon, and Michael R. Rosen

National Water-Quality Assessment Program

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

U.S. Department of the Interior

SALLY JEWELL, Secretary

U.S. Geological Survey

Suzette M. Kimball, Acting Director

U.S. Geological Survey, Reston, Virginia: 2014

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Foreword

The United States has made major investments in assessing, managing, regulating, and conserving natural resources, such as water and a variety of ecosystems. Sustaining the quality of the Nation's water resources and the health of our diverse ecosystems depends on the availability of sound water-resources data and information to develop effective, science-based policies. Effective management of water resources also brings more certainty and efficiency to important economic sectors. Taken together, these actions lead to immediate and long-term economic, social, and environmental benefits that make a difference to the lives of millions of people (<http://water.usgs.gov/nawqa/applications/>).

Two decades ago, Congress established the U.S. Geological Survey's National Water-Quality Assessment (NAWQA) Program to meet this need. Since then NAWQA has served as a primary source of nationally consistent information on the quality of the Nation's streams and groundwater, on ways in which water quality changes over time, and on the natural features and human activities affecting the quality of streams and groundwater. Objective and reliable data, systematic scientific studies, and models are used to characterize where, when, and why the Nation's water quality is degraded—and what can be done to improve and protect the water for human and ecosystem needs. This information is critical to our future because the Nation faces an increasingly complex and growing need for clean water to support people, economic growth, and healthy ecosystems. For example, NAWQA findings for public-supply wells, which provide water to about 105 million people, showed that 22 percent of source-water samples contained at least one contaminant at levels of potential health concern. Similarly, 23 percent of samples from domestic (or privately owned) wells, which supply untreated water to an additional 43 million people, also had contaminant levels of potential concern.

This report is one of a collection of publications that describe water-quality conditions in selected Principal Aquifers of the United States (<http://water.usgs.gov/nawqa/studies/praq/>). The collection is part of the series "The Quality of Our Nation's Waters," which describes major findings of the NAWQA Program on water-quality issues of regional and national concern and which provides science-based information for assessing and managing the quality of our groundwater resources. Other reports in this series focus on occurrence and distribution of nutrients, pesticides, and volatile organic compounds in streams and groundwater, the effects of contaminants and streamflow alteration on the condition of aquatic communities in streams, and the quality of untreated water from private domestic and public-supply wells. Each report builds toward a more comprehensive understanding of the quality of regional and national water resources (http://water.usgs.gov/nawqa/nawqa_sumr.html). All NAWQA reports are available online at <http://water.usgs.gov/nawqa/bib/>.

The information in this series primarily is intended for those interested or involved in resource management and protection, conservation, regulation, and policymaking at regional and national levels. In addition, the information should be of interest to those at a local level who wish to know more about the general quality of streams and groundwater in areas near where they live and how that quality compares with other areas across the Nation. We hope this 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.

Jerad Bales
Acting Associate Director for Water
U.S. Geological Survey



NAWQA

National Water-Quality Assessment Program

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Introduction to Principal Aquifers and to This Report

This report contains the major findings of national and regional assessments of the quality of groundwater in the Principal Aquifers of the United States. The Principal Aquifers, more than 60 in number, are regionally extensive aquifers that supply most of the groundwater pumped across the Nation for drinking water, irrigation, and other uses. The aquifers are composed of rocks and sediment such as unconsolidated sand and gravel, carbonate rock (limestone), granite, or volcanic rock. The aquifers extend across State boundaries and lie beneath diverse land uses. Water-quality conditions in the Principal Aquifers are summarized in this report and compared to selected national benchmarks, such as those for drinking-water quality.

This is one of a series of reports by the U.S. Geological Survey that present major findings for the Principal Aquifers. This report specifically focuses on water-quality conditions at the national scale and summarizes findings about groundwater quality from nine regional assessments of selected Principal Aquifers or groups of aquifers. Water-quality conditions in selected Principal Aquifers are discussed in greater detail in companion U.S. Geological Survey circulars to this report and in other reports listed in the references. Detailed technical information, data and analysis, sample collection, and analytical methodology, models, graphs, and maps that support the findings presented in this report, in addition to the companion reports in this series, can be accessed from the National Water-Quality Assessment Program (NAWQA) Web site (<http://water.usgs.gov/nawqa>).

Chapter 1: *Overview of Major Findings and Implications*



About 130 million people in the United States rely on groundwater for drinking water, and the need for high-quality drinking-water supplies becomes more urgent as our population grows. Although groundwater is a safe, reliable source of drinking water for millions of people nationwide, high concentrations of some chemical constituents can pose potential human-health concerns. Some of these contaminants come from the rocks and sediments of the aquifers themselves, and others are chemicals that we use in agriculture, industry, and day-to-day life. When groundwater supplies are contaminated, millions of dollars can be required for treatment so that the supplies can be usable. Contaminants in groundwater can also affect the health of our streams and valuable coastal waters. By knowing where contaminants occur in groundwater, what factors control contaminant concentrations, and what kinds of changes in groundwater quality might be expected in the future, we can ensure the availability and quality of this vital natural resource in the future.



Photographs: Chesapeake Bay Program; copyright istockphoto.com, copyright 1980 by W.H. Mullins and published with permission

National Findings

1 Contaminants from geologic or manmade sources were a potential human-health concern in one of every five wells sampled in the parts of aquifers used for drinking water

Groundwater from 22 percent of sampled wells—more than one in five—contained at least one chemical constituent at a concentration greater than a U.S. Environmental Protection Agency Maximum Contaminant Level (MCL) or other human-health benchmark for concentrations in drinking water. Most of these contaminants were from geologic sources—for example, arsenic, manganese, radon, and uranium. Nitrate was the only constituent from manmade sources that exceeded its human-health benchmark in more than 1 percent of wells.

2 Differences in geology, hydrology, geochemistry, and chemical use explain how and why aquifer vulnerability and concentrations of contaminants vary across the Nation

The geologic and manmade sources of contaminants that are present, how groundwater moves through an aquifer, and geochemical conditions within aquifers all affect concentrations of contaminants in groundwater. Because these factors differ among Principal Aquifers, different contaminants occur more—or less—frequently in some aquifers than in others. An understanding of how geology, hydrology, geochemistry, and chemical use affect the concentrations of individual contaminants is essential to explaining how and why groundwater quality varies across the Nation. In-depth regional assessments, based on comprehensive sampling of 6,600 wells and ancillary data, provided this understanding for the major contaminants in each Principal Aquifer and, in some cases, have allowed us to predict concentrations across wide areas. This information also can be used to assess aquifer vulnerability and design efficient and effective programs for monitoring the Nation's groundwater resources.

3 Changes to groundwater flow have also altered groundwater quality

People's use of water, through irrigation, pumping, artificial recharge, and drainage, has drastically changed how water moves through some aquifers. In some parts of the western United States, the amount of water that flows through aquifers has doubled, tripled, or increased by even more. Such large changes have affected contaminants from both manmade and geologic sources. Irrigation and pumping have made the deep parts of some aquifers, which are used for drinking water, more vulnerable to contamination by nitrate, pesticides, and other manmade chemicals. Irrigation and other sources of artificial recharge have increased concentrations of dissolved solids in some shallow aquifers in dry climates. Irrigation, pumping, and artificial recharge, by mixing waters of different chemistry, have sometimes had the unexpected consequence of releasing contaminants, such as uranium, selenium, or radium, from aquifer rocks and sediment into the groundwater.

4 Our actions today are determining groundwater quality for decades to come

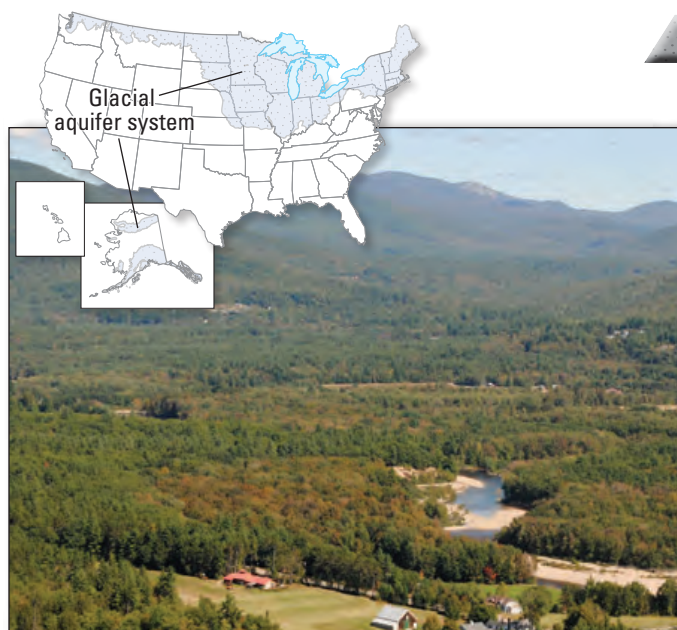
Groundwater quality changes slowly. However, indicators of human influence on groundwater quality are increasing across the Nation, even over the relatively short time periods of single decades. Concentrations of dissolved solids, chloride, and (or) nitrate in groundwater increased in two-thirds of groundwater well networks that were sampled at 10-year intervals between the early 1990s and 2010. People's influence on groundwater quality also is apparent in the concentrations of nitrate, pesticides, and other manmade chemicals found in shallow groundwater beneath agricultural and urban land. Concentrations of these chemicals exceeded human-health benchmarks two to four times more frequently in shallow groundwater beneath agricultural and urban land than in groundwater from the deeper parts of aquifers currently used for drinking water. Over time, the changes that we see in shallow groundwater are likely to appear in the deeper parts of aquifers, as the shallow groundwater moves downward. This change in quality of deeper aquifers is a concern for the future because the restoration of groundwater supplies that have become contaminated is difficult, is costly, and can take decades. In parts of many aquifers, we are still seeing the effects of contaminant inputs from more than 30 years ago; similarly, our actions today are determining groundwater quality for decades to come.

Groundwater—The Invisible and Vital Resource

- 80,000,000,000** Gallons of groundwater pumped each day
- 130,000,000** People who use groundwater for drinking water
- 43,000,000** People who use groundwater from private wells for drinking water
- 1,300,000** Chemical analyses performed in this study
- 6,600** Wells sampled for this study
- 62** Principal Aquifers in the United States



Findings From the Regional Principal Aquifer Assessments



Photograph by Kelly Warner, USGS

Glacial Aquifer System

One-sixth of the Nation's population relies on groundwater from the sands and gravels of the glacial aquifer system, in the northern United States, for drinking water. Contaminants from geologic sources—including arsenic and manganese, in more than 10 percent of sampled wells—were present in some areas at concentrations of potential concern for human health, especially in oxygen-depleted groundwater, which is more common in this aquifer than in many others. Agriculture, especially in the upper Midwest, is a source of nitrate and pesticides to groundwater, but low-permeability soils and artificial drainage reduce the aquifer's vulnerability to contamination in some areas.

USGS Circular 1352, available at <http://pubs.usgs.gov/circ/1352/>

Western Volcanics

Groundwater is hundreds of feet below the land surface in many parts of the volcanic-rock aquifers, located in the northwestern United States and Hawaii, but the high permeability of these aquifers allows contaminants from agriculture and other manmade sources to reach the water table. Nitrate is the most common contaminant, but concentrations of several pesticides and volatile organic compounds also exceeded human-health benchmarks, especially on Oahu, Hawaii. Use of some of these chemicals has been banned for decades, yet they continue to be detected in groundwater.

USGS Circular 1359, available at <http://pubs.usgs.gov/circ/1359/>



Photograph by Michael Rupert, USGS

Southwest Basin-Fill Aquifers

Contaminants from geologic sources are more common in the Southwest basin-fill aquifers than in many other aquifers in the Nation because of the hot and dry climate, long groundwater flow paths, and types of rocks and sediments present. Irrigation and pumping have greatly altered natural flow systems in some areas, increasing concentrations of dissolved solids and carrying manmade contaminants down to shallow and deep groundwater. Arsenic, dissolved solids, and nitrate are some of the contaminants of concern for drinking-water quality; their concentrations in groundwater throughout the Southwest basin-fill aquifers can be predicted on the basis of geology, climate, hydrology, and other natural and manmade factors.

USGS Circular 1358, available at <http://pubs.usgs.gov/circ/1358/>



Photograph by Susan Thiros, USGS



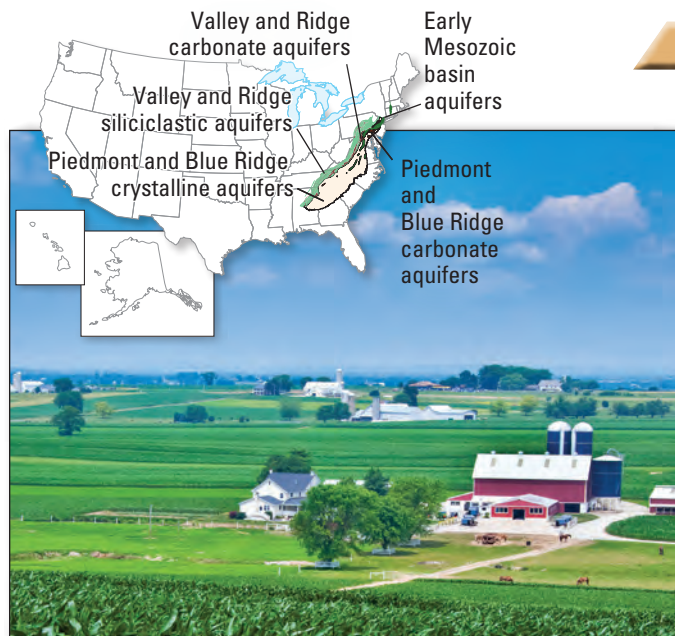
Photograph by Steve W. Krull, copyright istockphoto.com

Denver Basin Aquifer System

Groundwater in the deep sandstone layers of this aquifer system provides high-quality drinking water to the Front Range urban corridor of Colorado, but shallow groundwater quality has been degraded by irrigation and other human activities. Dissolved solids are relatively high in the shallow aquifer, and irrigation water has mobilized contaminants, such as uranium, from geologic sources. The shallow groundwater can migrate into deep aquifer layers, increasing the vulnerability of drinking-water supplies to contamination.

USGS Circular 1357, available at <http://pubs.usgs.gov/circ/1357/>

Findings From the Regional Principal Aquifer Assessments



Photograph copyright istockphoto.com

Piedmont, Blue Ridge, and Valley and Ridge Aquifers

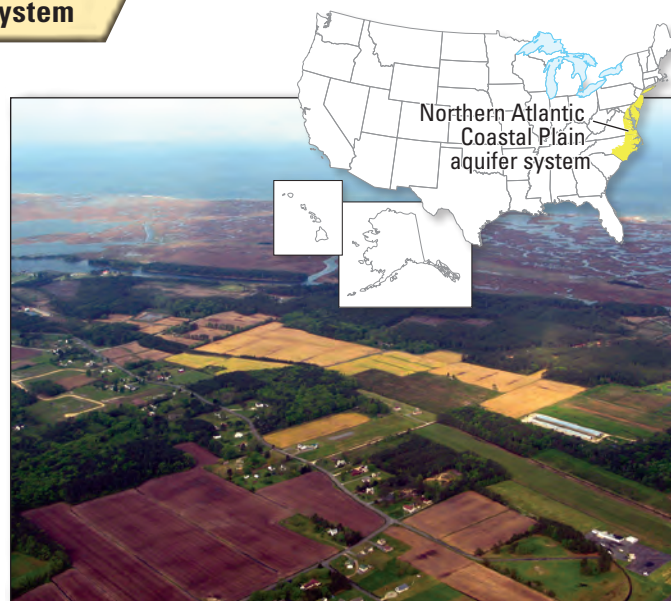
Geology largely determines where contaminants occur in these aquifers, which supply a large suburban and rural population in the eastern United States with drinking water. Radon, arsenic, and manganese occur in the crystalline-rock or siliciclastic (sandstone, siltstone, or shale) aquifers. The carbonate-rock aquifers, in contrast, are particularly susceptible to contamination from human activities at land surface because of karst (solution) features. Concentrations of nitrate in the carbonate-rock aquifers were among the highest in the Nation. Fecal-indicator bacteria were detected in half of the drinking-water sources sampled in the Piedmont, Blue Ridge, and Valley and Ridge aquifers.

USGS Circular 1354, available at <http://pubs.usgs.gov/circ/1354/>

Northern Atlantic Coastal Plain Surficial Aquifer System

Manmade contaminants—nitrate, pesticides, and volatile organic compounds—move readily through the sandy, permeable sediments of the Northern Atlantic Coastal Plain surficial aquifer system, located along the east coast of the United States; the areas of intense agriculture or dense population centers are particularly vulnerable. Radium from geologic sources is a concern because the natural acidity of the groundwater causes radium to be released from aquifer sediments into the groundwater. Groundwater from the shallow aquifer drains to streams and supplies nitrate that contributes to the ecological degradation of estuaries along the Atlantic coast.

USGS Circular 1353, available at <http://pubs.usgs.gov/circ/1353/>



Photograph by Emily Nauman, Integration and Application Network, University of Maryland Center for Environmental Science (IAN, UMCES)

Upper Floridan Aquifer and Overlying Surficial Aquifers

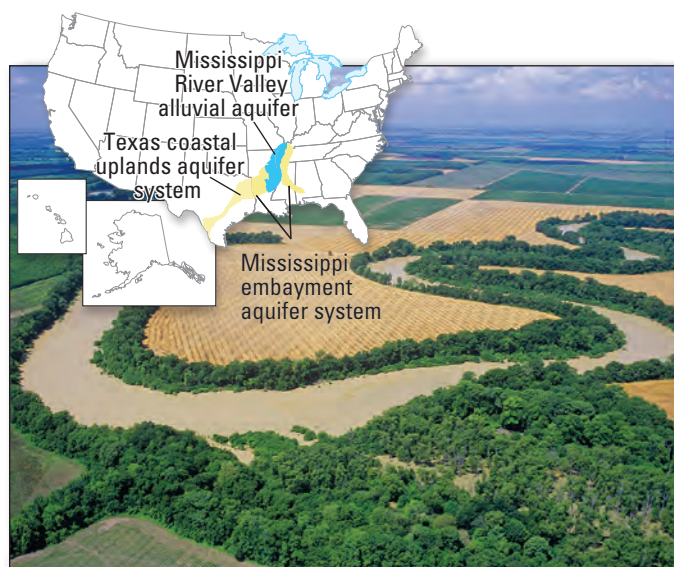
Groundwater in the Upper Floridan carbonate-rock aquifer, in the southeastern United States, has few contaminants from geologic sources and, in many areas, is protected from manmade contaminants by a low-permeability confining layer that inhibits downward flow. In some areas, where the confining unit is thin or absent, sinkholes and other karst features allow nitrate and pesticides from the land surface to move rapidly into and through the aquifer. Pumping of supply wells can enhance aquifer vulnerability to contamination by drawing shallow groundwater into the deep aquifer.

USGS Circular 1355, available at <http://pubs.usgs.gov/circ/1355/>



Photograph by Alan M. Cressler, USGS

Mississippi Embayment–Texas Coastal Uplands Aquifer System and Mississippi River Valley Alluvial Aquifer



Photograph by Jim Wark, Airphoto North America

These sandy aquifers in the southeastern and south-central United States are pumped heavily for irrigation and public supply, but have few manmade contaminants. Manganese and arsenic, which are derived from the aquifer sediments, are the most common contaminants. Concentrations of nitrate are low despite large fertilizer applications because of low recharge rates and natural attenuation in the oxygen-depleted groundwater. Pumping of supply wells has drawn deep, saline water up into the freshwater aquifer in some areas.

USGS Circular 1356, available at <http://pubs.usgs.gov/circ/1356/>

Findings From the Regional Principal Aquifer Assessments

High Plains Aquifer



Photograph courtesy of John Charlton, Kansas Geological Survey

The thick, extensive sediments of the High Plains aquifer, in the central United States, supply one-third of the groundwater pumped for irrigation in the Nation and are used for public and private supplies. Recently recharged shallow groundwater, especially beneath irrigated cropland, has higher concentrations of dissolved solids and nitrate than deep groundwater that was recharged thousands of years ago. The aquifer has little natural capacity to attenuate nitrate because even deep, old groundwater commonly contains dissolved oxygen. High-capacity pumping wells with long screens can cause shallow and deep groundwater to mix, drawing manmade contaminants into deeper parts of the aquifer and altering groundwater geochemistry.

USGS Circular 1337, available at <http://pubs.usgs.gov/circ/1337/>

Chapter 2: *Principal Aquifers and NAWQA Approach to Assessing Groundwater Quality*

The Principal Aquifers extend beneath vast and diverse areas of forests, plains, and deserts; they also lie beneath our agricultural lands and residential neighborhoods. How was the groundwater quality in such extensive and diverse areas assessed? The U.S. Geological Survey (USGS) National Water-Quality Assessment (NAWQA) Program used different types of groundwater studies, located across the United States, in which networks of wells were sampled for a comprehensive suite of water-quality constituents (appendix 1) using nationally consistent methods. A consistent study design means that results can be analyzed at multiple spatial scales, from the local scale of individual groundwater studies to the regional scale of Principal Aquifers (fig. 2–1) and, more broadly, to the national scale where NAWQA provides a unique perspective on the Nation’s groundwater quality. In addition to the chemical data, a wide range of information about the wells, the aquifer, and the surrounding environment was collected (see sidebar, NAWQA assessments use a wide range of geochemical data and site information, p. 16); these data are used to understand the factors that affect groundwater quality.

This chapter summarizes the study design used to investigate water quality in the Principal Aquifers.

Water samples were collected from domestic wells, public-supply wells, and monitoring wells. More than 6,000 wells were sampled.



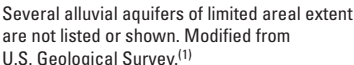
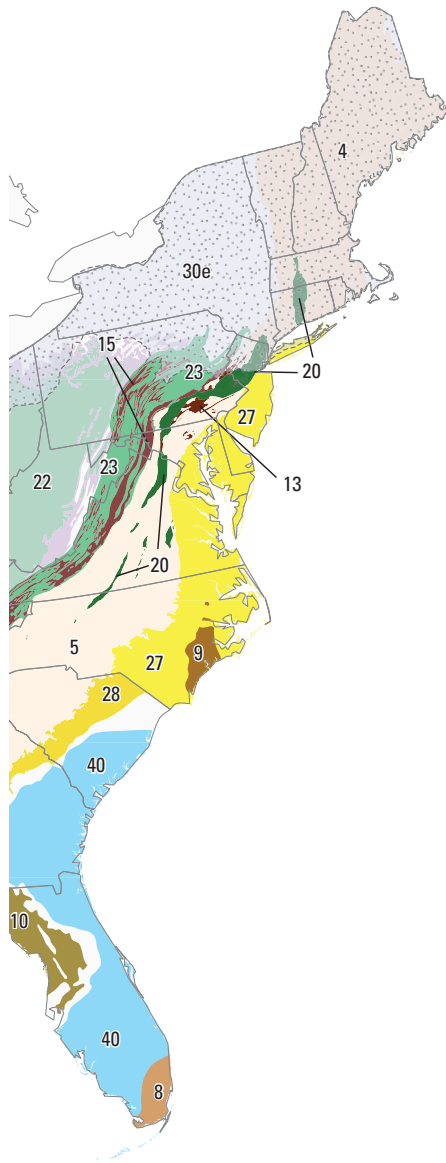


Figure 2-1. The quality of groundwater in about 40 of the Nation's Principal Aquifers is described in this circular, based on groundwater samples hydrogeology. The map shows the uppermost regional aquifer in an area; parts of some aquifers are buried beneath other aquifers or geologic units. and more than half of the water supplied by private domestic wells nationally.



EXPLANATION

Basalt and volcanic-rock aquifers

- 1 Columbia Plateau basaltic-rock aquifers
- 2 Hawaiian volcanic-rock aquifers
- 3 Snake River Plain basaltic-rock aquifers

Crystalline-rock aquifers

- 4 New England crystalline-rock aquifers
- 5 Piedmont and Blue Ridge crystalline-rock aquifers
- 6 Rocky Mountain Front Range crystalline-rock aquifers (not shown)

Carbonate-rock aquifers

- 7 Basin and Range carbonate-rock aquifers
- 8 Biscayne aquifer
- 9 Castle Hayne aquifer
- 10 Upper Floridan aquifer
- 11 Ordovician aquifers
- 12 Ozark Plateaus aquifer system
- 13 Piedmont and Blue Ridge carbonate-rock aquifers
- 14 Silurian-Devonian aquifers
- 15 Valley and Ridge carbonate-rock aquifers

Sandstone and carbonate-rock aquifers

- 16 Edwards-Trinity aquifer system
- 17 Mississippian aquifer

Sandstone aquifers

- 18 Cambrian-Ordovician aquifer system
- 19 Denver Basin aquifer system
- 20 Early Mesozoic basin aquifers
- 21 Lower Tertiary aquifers
- 22 Pennsylvanian aquifers
- 23 Valley and Ridge siliciclastic-rock aquifers
- 24 Woodbine aquifer (not shown)

Semiconsolidated sand and gravel aquifers

- 25 Coastal lowlands aquifer system
- 26 Mississippi embayment aquifer system
- 27 Northern Atlantic Coastal Plain aquifer system
- 28 Southeastern Coastal Plain aquifer system
- 29 Texas coastal uplands aquifer system

Glacial aquifer system—Aquifers are discontinuous in area shown

- 30w Western glacial aquifers
- 30wc West central glacial aquifers
- 30c Central glacial aquifers
- 30e Eastern glacial aquifers

Unconsolidated sand and gravel aquifers (nonglacial)

- 31 Basin and Range basin-fill aquifers
- 32 California Coastal Basin aquifers
- 33 Central Valley aquifer system
- 34 Columbia Plateau basin-fill aquifers
- 35 High Plains aquifer
- 36 Mississippi River Valley alluvial aquifer
- 37 Northern Rocky Mountain Intermontane Basins aquifers
- 38 Rio Grande aquifer system
- 39 Snake River Plain basin-fill aquifers
- 40 Surficial aquifers
- 41 Willamette Lowland basin-fill aquifers

collected between 1991 and 2010. The aquifers are grouped here according to rock or sediment type into categories with broadly similar
The Principal Aquifers shown here, which are included in this circular, provide about 90 percent of the groundwater pumped for public supply

Groundwater Studies

Groundwater studies, each based on a sampling network of 20 to 30 wells, are the building blocks of the Principal Aquifer assessments.

Groundwater studies are the building blocks of the Principal Aquifer water-quality assessments. There were three main types of studies, each with a different focus on groundwater quality and the natural and human-related factors that influence it (table 2–1).

Aquifer studies were designed to broadly assess water-quality conditions in the parts of aquifers used for drinking-water supply. For each study, 20 to 30 randomly located supply wells, mostly privately owned household (domestic) wells, were selected for sampling. The study areas were based on aquifer hydrogeology without regard to the overlying land use. This was the primary type of groundwater study used to assess water quality in the Principal Aquifers.

Agricultural and urban land-use studies were designed to characterize the quality of recently recharged groundwater in these land-use settings by sampling groundwater near the water table, mostly from shallow monitoring wells installed by the USGS. Most (86 percent) of the wells in land-use studies tapped groundwater from within 50 feet (ft) of the water table, and the median depth of the land-use study wells was 16 ft below the water table. Diverse types of agricultural areas were studied—areas with fields of wheat and other grains, mixed row crops and poultry, and rangeland. The areas sampled in urban settings primarily were residential, typically with low to medium population densities (300 to 5,600 people per square mile).

Results from more than 200 groundwater studies, each based on a sampling network of 20 to 30 wells, are synthesized in this circular (fig. 2–2). The studies were conducted between 1991 and 2010. Most wells were sampled only once during this time; for wells that were sampled repeatedly, data from the most recent samples were used to characterize the groundwater quality. More than 6,000 wells were sampled in total (fig. 2–2).

Table 2–1. The water-quality assessments summarized in this circular use data from three types of groundwater studies.

Characteristic	Type of groundwater study		
	Aquifer study	Agricultural land-use study	Urban land-use study
Study design objective	Assess quality of water in the parts of aquifers used for drinking-water supply	Assess quality of shallow groundwater beneath agricultural land	Assess quality of shallow groundwater beneath urban land
Land use in study area	Mixed	Agricultural	Residential and commercial
Number of studies	123	64	46
Total number of wells	3,669	1,793	1,158
Type of well	Mostly existing domestic wells; also some other types of supply wells	Mostly monitoring wells, installed for NAWQA	Mostly monitoring wells, installed for NAWQA
Number of wells per sampling network (typical)	20–30	20–30	20–30
Well selection method	Random	Random	Random
Number of aquifers with studies of this type	41	22	22

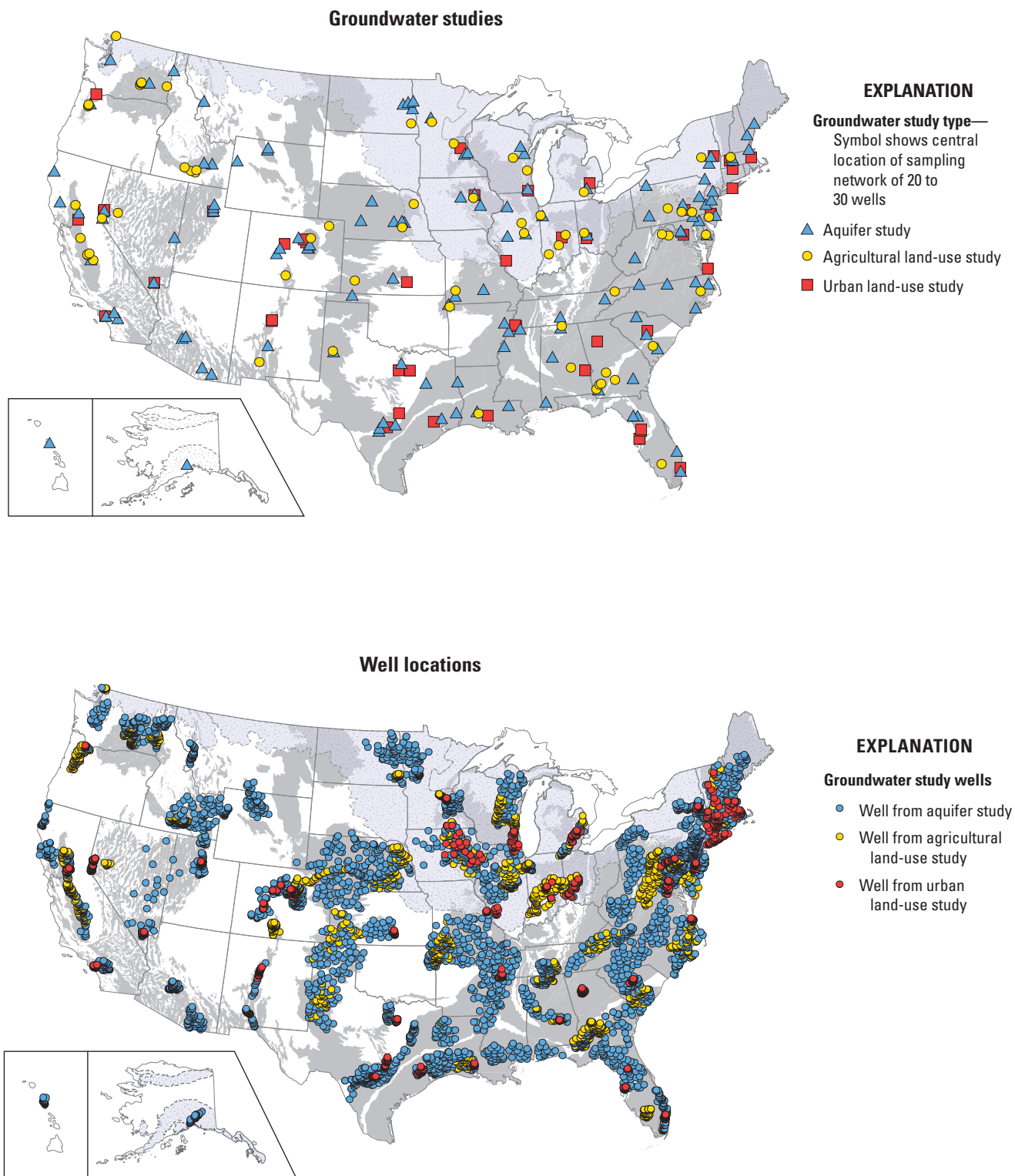


Figure 2–2. Each of the 233 groundwater studies (top map) in this water-quality assessment is based on a sampling network of 20 to 30 wells. More than 6,000 wells (bottom map) were sampled in total. About half of the studies focused on the parts of aquifers used for drinking water (aquifer studies); the remainder were studies of shallow groundwater beneath agricultural or urban land (land-use studies).

What types of wells were sampled, and how might that affect the water quality measured?

Two types of wells that supply drinking water were sampled: domestic (private) wells and public-supply wells. Domestic wells are usually shallower than public-supply wells and, therefore, pump water that is nearer to sources of manmade contaminants, such as fertilizers and pesticides, at the land surface. They commonly are located in rural areas and so are more likely than public-supply wells to be vulnerable to contamination from agricultural chemicals.

Public-supply wells pump larger volumes of water than domestic wells, from deeper in the aquifer. They have larger pumps and longer screened intervals, and are pumped for longer periods of time than domestic wells. Because they are commonly located in suburban and urban areas, public-supply wells are more likely than domestic wells to be vulnerable to contamination from chemicals associated with urban activities; because they pump water from deeper in the aquifer, public-supply wells may be more likely to have high concentrations of constituents from geologic sources than domestic wells. The larger capture zones of public-supply wells also means that they are more vulnerable than domestic

wells to manmade contamination from distant sources. If the amount of water withdrawn is large enough, it can change the flow direction and velocity of the groundwater, which can, in turn, affect the groundwater geochemistry of the constituents contained. Water from public-supply wells is required to be tested by the well operator on a routine basis to help assure that the water provided to consumers meets Federal and State water-quality standards. Routine testing of water from domestic wells is not required. Homeowners are responsible for testing, maintenance, or treatment of the water from their domestic well.

Groundwater samples also were collected from wells that supply water for purposes other than drinking, such as irrigation, livestock, recreational facilities, and commercial or industrial uses. These wells can have pumping rates comparable to public-supply or domestic wells; they might be pumped every day or only during spring and summer. Depending on their depth, location, and pumping rate, these supply wells may be more or less vulnerable to contaminants associated with agriculture or urban activities.



Public-supply well



Domestic well



Monitoring well

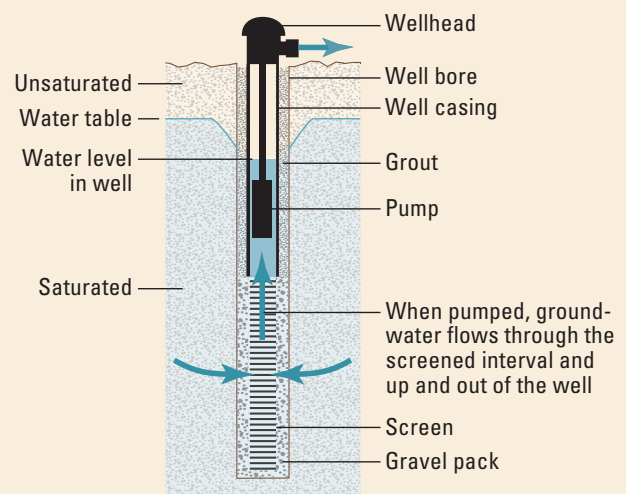
Understanding study results

Important aspects of the NAWQA Principal Aquifer assessments:

- Water samples were collected at the wellhead prior to any treatment. They represent the quality of the groundwater resource but not necessarily the quality of tap water.
- The focus of the assessments is the condition of the total resource, including groundwater in a wide range of hydrologic and land-use settings across the Nation, rather than conditions at specific sites with known water-quality concerns.
- A wide range of constituents and properties are measured, including many that are not measured in programs that monitor water quality for compliance with drinking-water regulations. These data, along with ancillary information about the aquifer and surrounding environment (See sidebar, NAWQA assessments use a wide range of geochemical data and site information, p. 16), allow scientists to understand the sources and processes that affect groundwater quality.
- The assessments are guided by a nationally consistent study design, and all assessments use the same methods of sampling and analysis. Findings apply to water quality of a particular aquifer but also contribute to the larger picture of how and why water quality varies regionally and nationally. This consistent approach helps to determine if a water-quality issue is isolated or widespread. (See <http://water.usgs.gov/nawqa/about.html> for more information.)
- The assessments focused on aquifers used for water supply or on shallow groundwater that underlies a particular type of land use. Because NAWQA groundwater study areas do not cover the full spatial extent of the targeted Principal Aquifer, the findings might not represent the effects of the full range of geology, climate, and land use present.
- Analytical methods used by USGS chemists for assessments of water quality in Principal Aquifers are designed to measure constituents at as low a concentration as feasible. As a result, constituents frequently are detected at concentrations far below human-health benchmarks (see sidebar, Human-health benchmarks and other guidelines used in this assessment, p. 38). Low-level detections allow scientists to identify and evaluate emerging issues and to track contaminant levels over time.

Anatomy of a well

A well is simply a hole in the ground (well bore or borehole) from which water can be removed. The well bore is lined with a well casing, such as a pipe, to prevent the well bore from collapsing. The casing, along with a sealant (called grout), also prevents water from flowing into the well from the land surface or from parts of the aquifer where the water quality may be less desirable. The casing can be open at the bottom or perforated at a specific depth with a screen, to allow water to flow into the well where it can be pumped to the surface. Coarse sand or gravel (called sand pack or gravel pack) can be placed around the well screen to help improve the flow of water into the well. Some wells are cased only near the land surface, allowing water to flow into the well from nearly the entire length of the well bore.



NAWQA assessments use a wide range of geochemical data and site information

Constituents measured in samples from most wells	
Constituent group	Examples
Water-quality properties	pH, specific conductance, dissolved oxygen, temperature
Major ions (filtered)	Bromide, calcium, chloride, magnesium, sodium, sulfate
Trace elements (filtered)	Arsenic, boron, iron, manganese, selenium, uranium
Nutrients (filtered)	Ammonia, nitrate, phosphorus
Pesticides (filtered)	Herbicides, insecticides, fungicides
Volatile organic compounds	Solvents, gasoline hydrocarbons, refrigerants, trihalomethanes, fumigants
Organic carbon (filtered)	
Additional constituents measured in samples from some wells	
Constituent group	Examples
Radionuclides	Radon
Groundwater age tracers	Tritium, chlorofluorocarbons
Stable isotopes	Oxygen-18, hydrogen-2
Microorganisms	<i>Escherichia coli</i> and total coliforms
Additional site information	
Use of well	Land-surface elevation at well
Well depth	Land use within a 500-meter (1,640-foot) radius buffer
Depth to water	Estimates of nutrient inputs
Well-construction data	Estimates of pesticide use
Principal Aquifer	



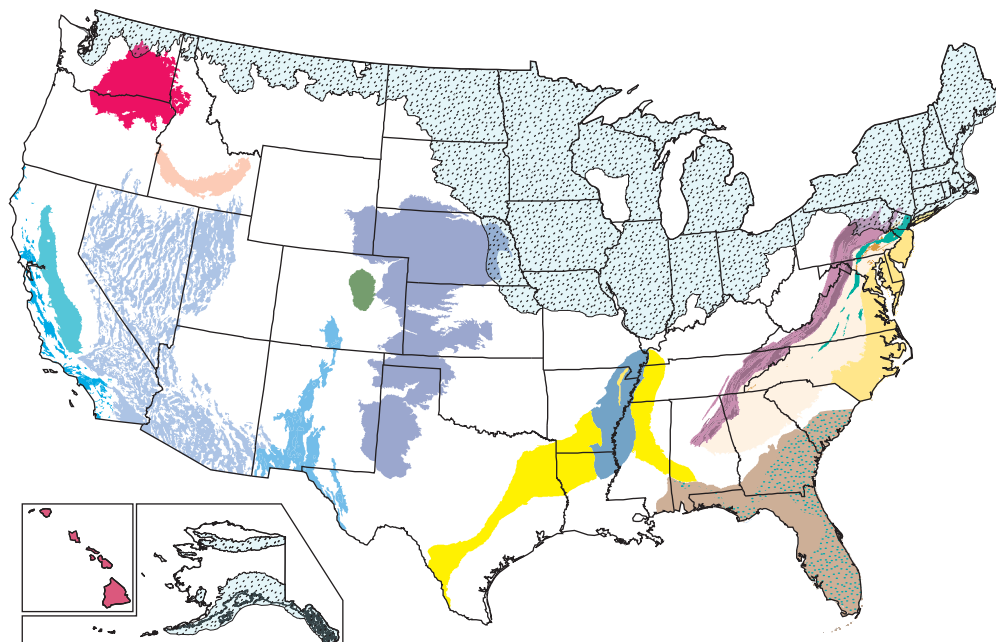
Chemists at the USGS National Water Quality Laboratory analyze groundwater samples using an array of sophisticated techniques.



Additional information (often called “ancillary information”) about the well and the surrounding environment complements the chemical data measured. This additional information often is key to making sense of the chemical data. For example, the information might be used to determine that shallow groundwater is more (or less) vulnerable to contamination than deep groundwater, that domestic wells are more (or less) vulnerable to contamination than public-supply wells, or that urban land use is associated with different types of groundwater contamination than is agricultural land use. Chemical data without accompanying ancillary data are much less useful for understanding factors that affect groundwater quality.

Regional Assessments of Principal Aquifers

About half of the Principal Aquifers included in this circular received in-depth study as part of regional water-quality assessments (fig. 2–3). These aquifers included many of the most heavily used aquifers, supplying water for drinking and for irrigation across the Nation. Findings from the regional Principal Aquifer assessments are summarized in this circular and are fully described in nine companion circulars (<http://water.usgs.gov/nawqa/studies/praq/>).



In-depth Regional Assessments

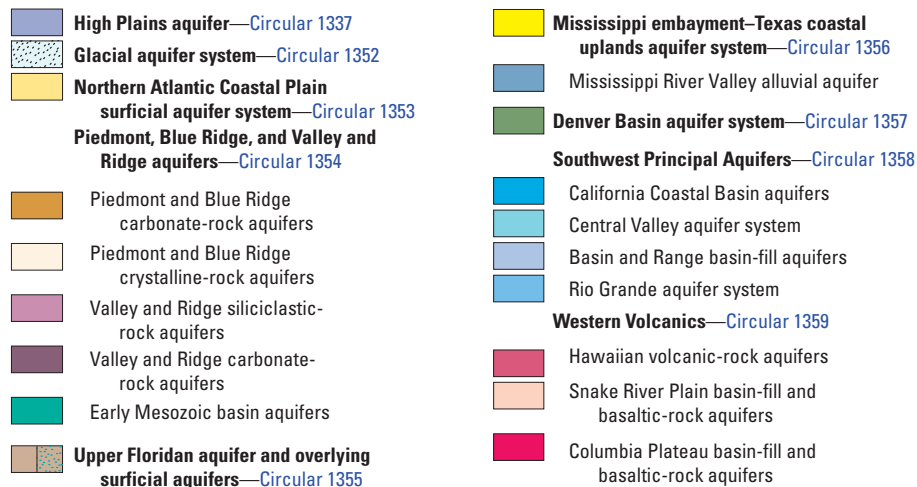


Figure 2–3. In-depth, regional-scale assessments of groundwater quality focus on the most heavily used Principal Aquifers in the Nation. Groundwater quality in these aquifers is described in nine U.S. Geological Survey circulars.

Decadal Trends

How is groundwater quality changing? To address this question, well networks in some groundwater study areas are being revisited at 10-year intervals for repeated sampling. Samples from 1,295 wells in 56 groundwater studies have been analyzed to date.^(2, 3) About one-third of the studies were aquifer studies, and the rest were land-use studies. Well networks that were initially sampled from 1988 through 2000 were resampled 10 years later from 2001 through 2010. The two sets of samples from each well network were compared, and the changes were analyzed to determine whether concentrations in the groundwater study area generally increased, decreased, or remained the same over the 10-year period. This approach aggregates local-scale changes in water quality at individual wells and provides a statistically based, broad overview of changes in water quality across the Nation.

Some wells are sampled repeatedly, at 10-year intervals, to monitor changes in groundwater quality.



Photograph by Patrick C. Mills, USGS

Chapter 3: *Aquifers and Processes That Affect Groundwater Quality*

What is an aquifer? An aquifer is defined as saturated, permeable geologic material (rock or sediment) that will yield a useful quantity of water to a well (see sidebar, Anatomy of an aquifer, this page). Regionally extensive aquifers and aquifer systems⁽¹⁾ have been mapped as the Nation's Principal Aquifers (fig. 2–1). Aquifers can be made up of a variety of geologic materials, such as sand, gravel, limestone, basalt, or sandstone. Aquifers commonly are characterized by their geologic materials (see sidebar, Principal Aquifer rock types, p. 20) because rock type is directly related to an aquifer's capacity to transmit water—its permeability—and to other hydrogeologic characteristics.

This chapter includes information about the Principal Aquifers, such as rock type, water use, and land use, and describes physical, chemical, and biological processes affecting groundwater quality.

Anatomy of an aquifer

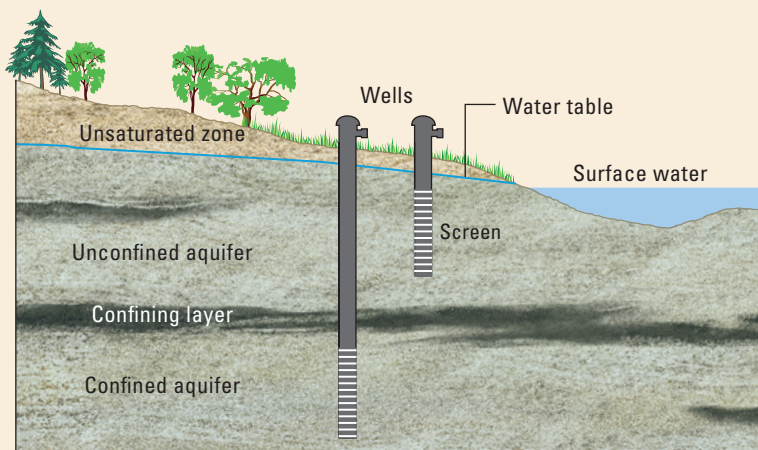
The **unsaturated zone** is the area below the land surface and above an aquifer. In addition to soil, rocks, and air, it contains water from the land surface (such as rain) that is slowly moving downward to the water table of the aquifer.

The **water table** is the upper surface of the saturated zone. In the saturated zone, void spaces are completely filled with water

An **unconfined aquifer** is bounded at its top by the water table, below which water fills all the pore spaces in the rock. Water from the land surface can move down into an unconfined aquifer.

A **confining layer** is a layer of material (commonly clay) through which water does not easily flow, creating a boundary between aquifers.

A **confined aquifer** is bounded at its top by a confining layer. Water enters or “recharges” confined aquifers where the confining layer is not present. Where the confining layer is not continuous or is breached (for example, by a well), flow between the unconfined and confined aquifer can occur.



Sedimentary aquifer

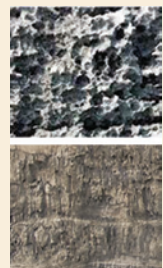
Groundwater storage and flow between grains of sediment

Carbonate aquifer

Groundwater storage and flow in solution cavities or fractures

Bedrock aquifer

Groundwater storage and flow in fractures



Principal Aquifer rock types

The Nation's Principal Aquifers are made up of a variety of geologic materials (rock types), ranging from hard, consolidated bedrock like basalt and granite to unconsolidated sand and gravel. The photographs show examples of these rock types, and the maps show the areal extent of aquifers of each rock type included in this circular.



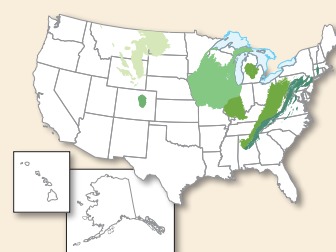
Volcanic-rock aquifers are made up of basaltic lava flows, ash, and other volcanic rocks. In basaltic rocks, groundwater flows through pore spaces that have formed as the lava solidified. Volcanic-rock aquifers are widespread in several western States and Hawaii. Thin-bedded basalt flows from the island of Hawaii are shown.



Crystalline-rock aquifers can be composed of granite, gneiss, schist, or other igneous and metamorphic rocks. These rocks are permeable only where they are fractured. Crystalline-rock aquifers extend beneath large areas of the eastern United States and are the only water-supply source in some areas. Rocks from the New England crystalline-rock aquifers in southern New Hampshire are shown; groundwater flowing from fractures has frozen on the outcrop.



Sandstone aquifers are rocks of cemented sandy deposits. Sandstone aquifers transmit water primarily along bedding planes and fractures, and they can be layered with other sedimentary rocks, such as siltstones and shales. Sandstone aquifers are present across the Nation, sometimes partly buried beneath other aquifers or geologic units. Sandstone layers from the Denver Basin aquifer system in Colorado are shown; these sandstones are geologically young and are not well consolidated.



Limestone and other sedimentary rocks made up of carbonate minerals form the **carbonate-rock aquifers**. Carbonate rocks are more soluble in groundwater than most other rocks, leading to the creation of cavities—caverns, conduits, and sinkholes—that can greatly enhance the rock's ability to transmit water. Carbonate-rock aquifers are most extensive in the eastern United States. Limestone beds from a carbonate-rock aquifer in the Delaware Valley of New Jersey are shown.



Photographs from top to bottom: Clifford Voss, USGS; Sarah Flanagan, USGS; Suzanne Paschke, USGS; New Jersey Geological and Water Survey



Carbonate rocks and permeable sandstone rocks are interbedded (layered) in about equal amounts in the **sandstone and carbonate-rock aquifers**. The carbonate layers usually yield more water than the sandstones in these systems. Sandstone and carbonate-rock aquifers are in several parts of the United States. Springs discharge groundwater from the Edwards-Trinity aquifer to the river shown here in the Hill Country of south-central Texas.



Semiconsolidated sand aquifers are made up of variably cemented sand layered with silt, clay, and, in some places, carbonate rocks. These aquifers were deposited as sediments from rivers or in tidal water. They underlie the coastal plain along the Atlantic Ocean and Gulf of Mexico and form a thick wedge that dips toward the coast. Water flows through pores between sand grains, and aquifer productivity can be high. Shown are sediments from the Northern Atlantic Coastal Plain in New Jersey.



The **glacial aquifers** contain unconsolidated sand, gravel, silt, and clay that was deposited primarily by meltwater from the continental ice sheets. They are widespread, though discontinuous, across the northern United States in river valleys, buried bedrock valleys, and broad lenses. Glacial aquifers also are buried beneath less permeable material in some places. Coarse-grained glacial deposits are widely used for public water supplies where present. A sand quarry in the glacial aquifer system in central Illinois is shown.



Unconsolidated sand and gravel aquifers that are not of glacial origin fill low-lying areas between mountains in the west, form blanket-like sedimentary deposits in the High Plains, and overlie carbonate-rock aquifers in the southeast. These aquifers also underlie stream valleys throughout the United States. Their sediments were deposited by wind or water. The unconsolidated sand and gravel aquifers include large regional aquifers as well as important local aquifers. Deposits of coarse sand and gravel overlying fine-grained lakebed sediments near Great Salt Lake, Utah, are shown.



Photographs from top to bottom: USGS; USGS; Brandon Curry, Illinois State Geological Survey; USGS

Water Use

Each day, about 80 billion gallons of water is pumped from the Nation’s aquifers. This water is used for drinking water, to irrigate crops and lawns, in industry, for aquaculture and livestock, in mining, to cool power plants, and for many other purposes.⁽⁴⁾ Groundwater provides one-third of the water that is pumped by public-supply systems to provide the water used in homes, schools, and businesses in cities and towns. Use of groundwater for public supply has quadrupled during the past 60 years, as the population has steadily increased and cities and suburbs have expanded (fig. 3–1). Groundwater also is used for drinking water by rural homeowners with privately owned household (domestic) wells. Overall, about 130 million people currently get their drinking water from groundwater sources in the United States.

The Principal Aquifers assessed in this circular provide about 90 percent of the groundwater pumped for public supply, irrigation, and other uses nationally.^(5, 6) The largest withdrawals are from the unconsolidated sand and gravel aquifers, and most of this water is used for irrigation (fig. 3–2). Public supply is the largest use of water pumped from the glacial aquifers and from most carbonate-rock, sandstone, and semiconsolidated sand aquifers. Water

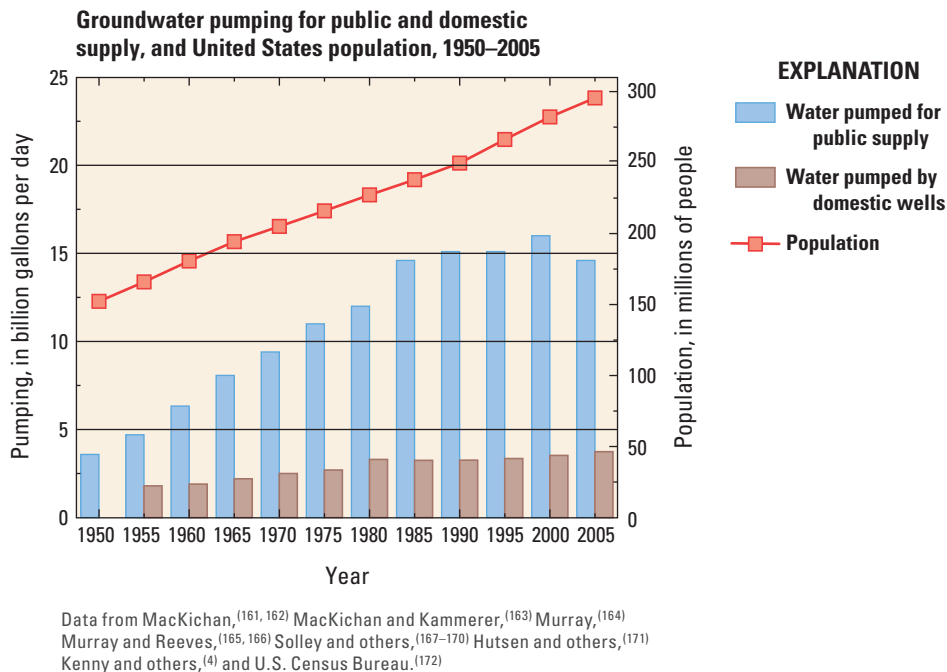


Figure 3–1. The volume of groundwater pumped for public supply has quadrupled in the past 60 years, while the population of the United States has about doubled. The volume of groundwater pumped by privately owned household (domestic) wells has increased more slowly. Water pumped for public supply is used for drinking in homes, schools, and businesses, as well as for other uses in urban and suburban areas.

withdrawals for domestic supply are small compared with other withdrawals for public supply and irrigation in nearly all aquifers. However, about 43 million people, or 15 percent of the total population of the United States, rely on private wells for their drinking water. Many of these people live in rural areas where there is no other source of drinking water available. Groundwater quality is of particular concern for domestic well users because there are no regulations that require routine testing or treatment for contaminants in domestic wells in most States.

In parts of the Nation where the population is growing, the demand for water is increasing. Groundwater will become an increasingly important water source, especially in areas where supplies of water withdrawals from lakes, rivers, and reservoirs are limited. For example, new communities in the Denver Basin area that are without available surface water rely on groundwater sources, and withdrawals from the deep sandstone aquifers have tracked population growth.⁽⁷⁾ In the upper Midwest, new water withdrawals from the Great Lakes, which supply water to large population centers, are limited to communities within the watershed; suburban communities outside the watershed rely on groundwater supplies to support their growing water demand.⁽⁸⁾ Groundwater sources of sufficient quality to meet these existing and future water needs are critical for economic development and human health.

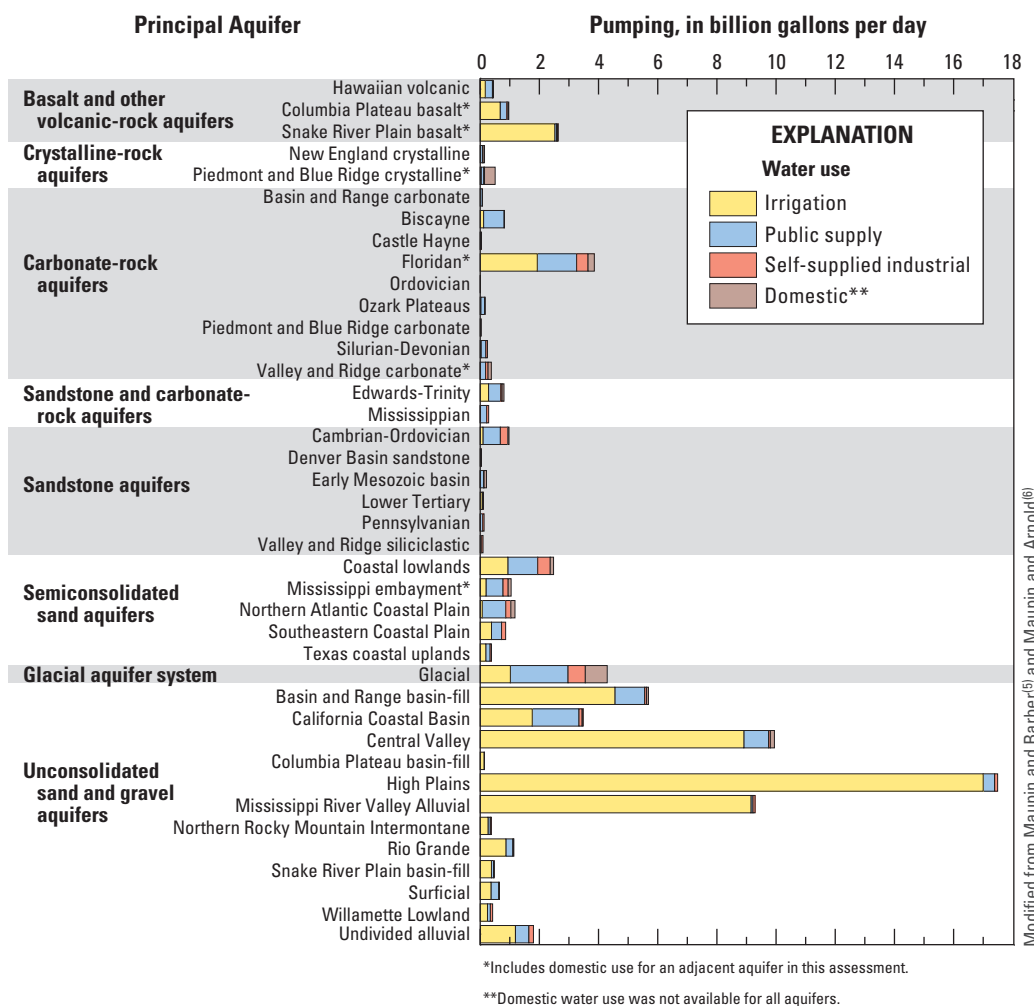


Figure 3-2. Irrigation, public supply, industrial use, and domestic use are major uses of the groundwater that is pumped from the Nation's Principal Aquifers. Some of the largest withdrawals are from the unconsolidated sand and gravel aquifers in the western United States, and most of this water is used for irrigation. Altogether, the Principal Aquifers included in this study provide about 90 percent of the 80 billion gallons of groundwater that is pumped on average each day in the United States.

Land Use

The Principal Aquifers lie underneath diverse types of land use. These land uses can affect the quality of water that infiltrates from the land surface and recharges groundwater. To study the effects of human activities on groundwater, NAWQA studies of shallow groundwater were located in areas of agricultural and urban land uses; these types of land use can result in large alterations of the land surface. Nationally, agricultural land use is most common in the central United States, and urban land use is most common in the East (fig. 3–3). However, parts of all aquifers across the Nation are overlain by some agricultural and urban land use (fig. 3–4).

Land use changes with time and these changes can affect water quality (fig. 3–5). Nationally, the amount of developed land in the United States increased by nearly 43 million acres, or 60 percent, between 1982 and 2010, mostly from conversion of forest and agricultural land; this increase is an area roughly the size of Oklahoma.⁽⁹⁾ Chemical use, waste disposal, and irrigation that can accompany the new development in urban and suburban areas are sources of contaminants to the underlying aquifer. When suburbs and cities expand into cropland, fertilizers and pesticides used in agriculture can be replaced with chemicals associated with residential activities, such as volatile organic compounds (VOCs) or deicing chemicals, as potential contaminants to underlying groundwater.

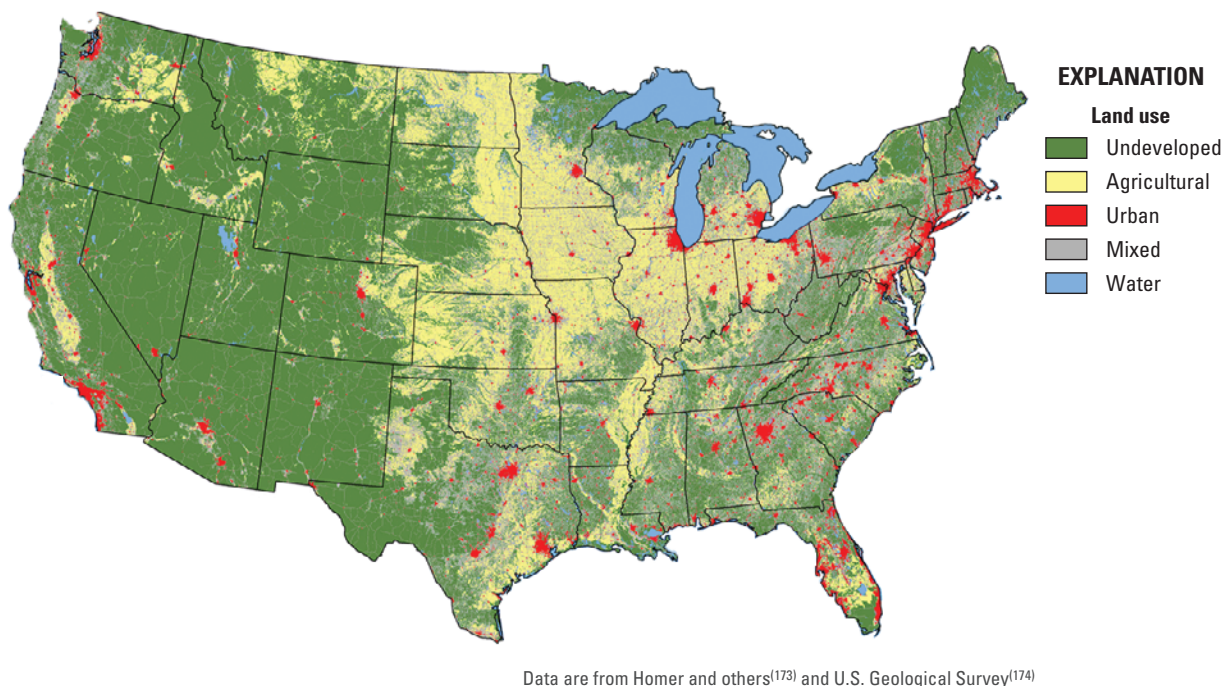


Figure 3–3. Areas of agricultural and urban land were the focus of groundwater studies to investigate the effects of human activities on groundwater quality.

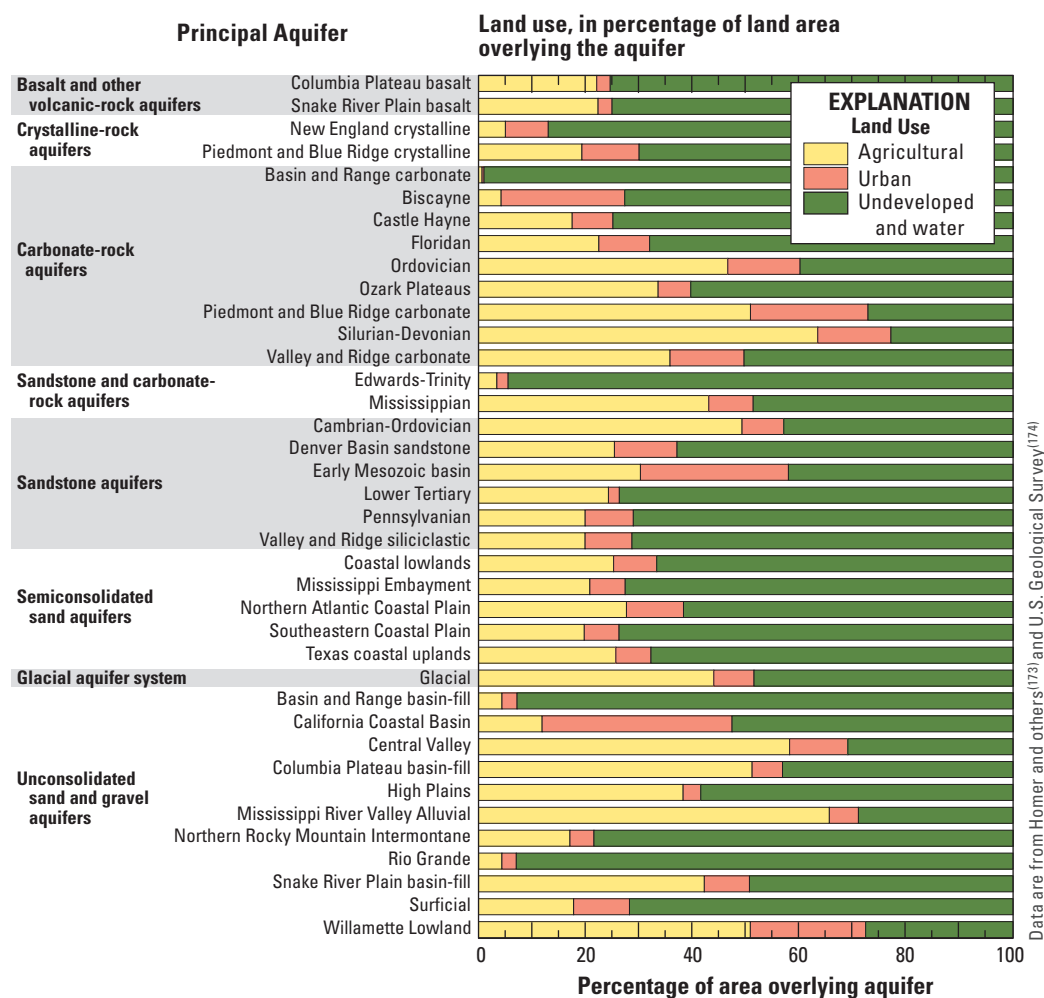
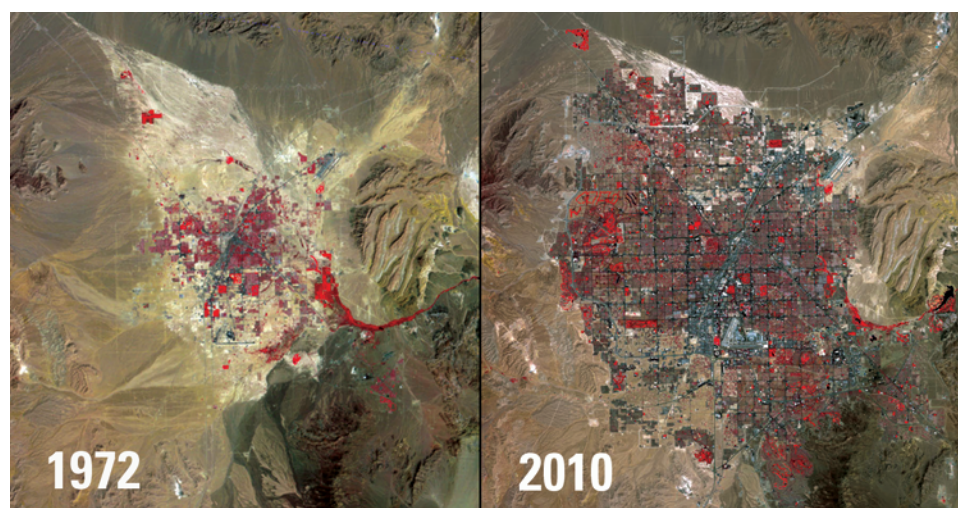


Figure 3–4. All aquifers are overlain by some areas of agricultural and urban land use. Many of the potential sources of manmade contaminants to groundwater are associated with these broad land-use categories. Areas are shown in figure 3–3.

Changing land use in the Las Vegas Valley, Nevada



USGS Earth Explorer by the NASA/Goddard Space Flight Center

Figure 3–5. Changes in land use from undeveloped or agricultural to urban or suburban can be accompanied by changes in the underlying groundwater quality. For example, urban expansion in Las Vegas, Nevada, increased the population from 273,000 people in 1972 to more than 2 million in 2010. Effects on the quality of shallow groundwater include higher concentrations of nitrate and dissolved solids and more frequent detections of pesticides and VOCs than in shallow groundwater beneath undeveloped areas. Areas of irrigated vegetation are shown in red and impervious surfaces, such as rooftops and roads, are shown in gray on these Landsat satellite images.

Groundwater Flow

Groundwater is not static but moves through aquifers, and the paths that it takes and rates at which it flows affect water quality. On a broad scale, groundwater flows from areas of recharge, where it enters the aquifer, to discharge areas, where it leaves the aquifer (fig. 3–6). The driving force behind groundwater flow is hydraulic head—a combination of elevation and water pressure.⁽¹⁰⁾ Natural groundwater recharge occurs wherever rain and snowmelt percolate through the unsaturated zone to reach the water table. Recharge is less than total precipitation because some water from rainfall and snowmelt runs off directly to streams or returns to the

Northern Atlantic Coastal Plain surficial aquifer system

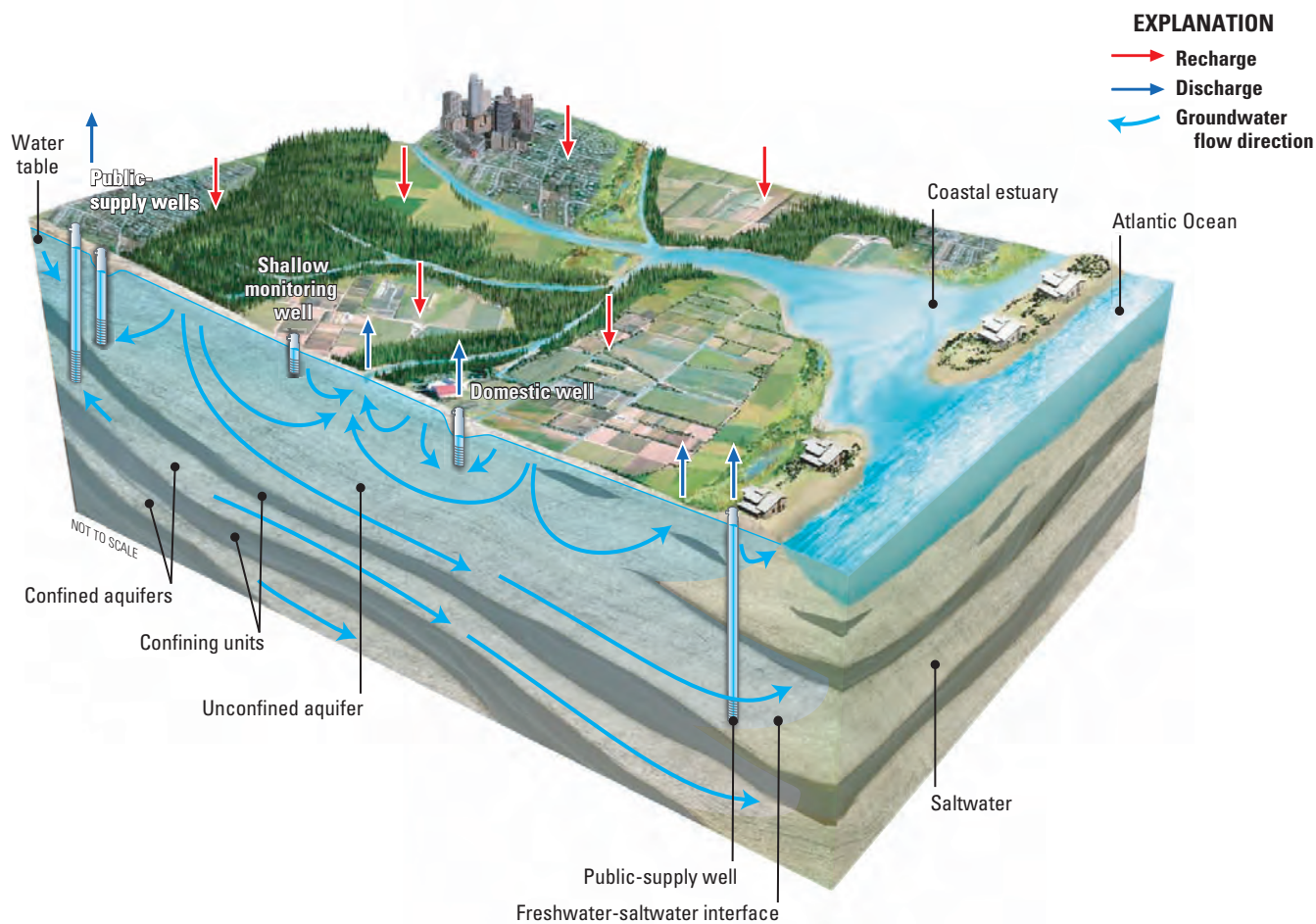
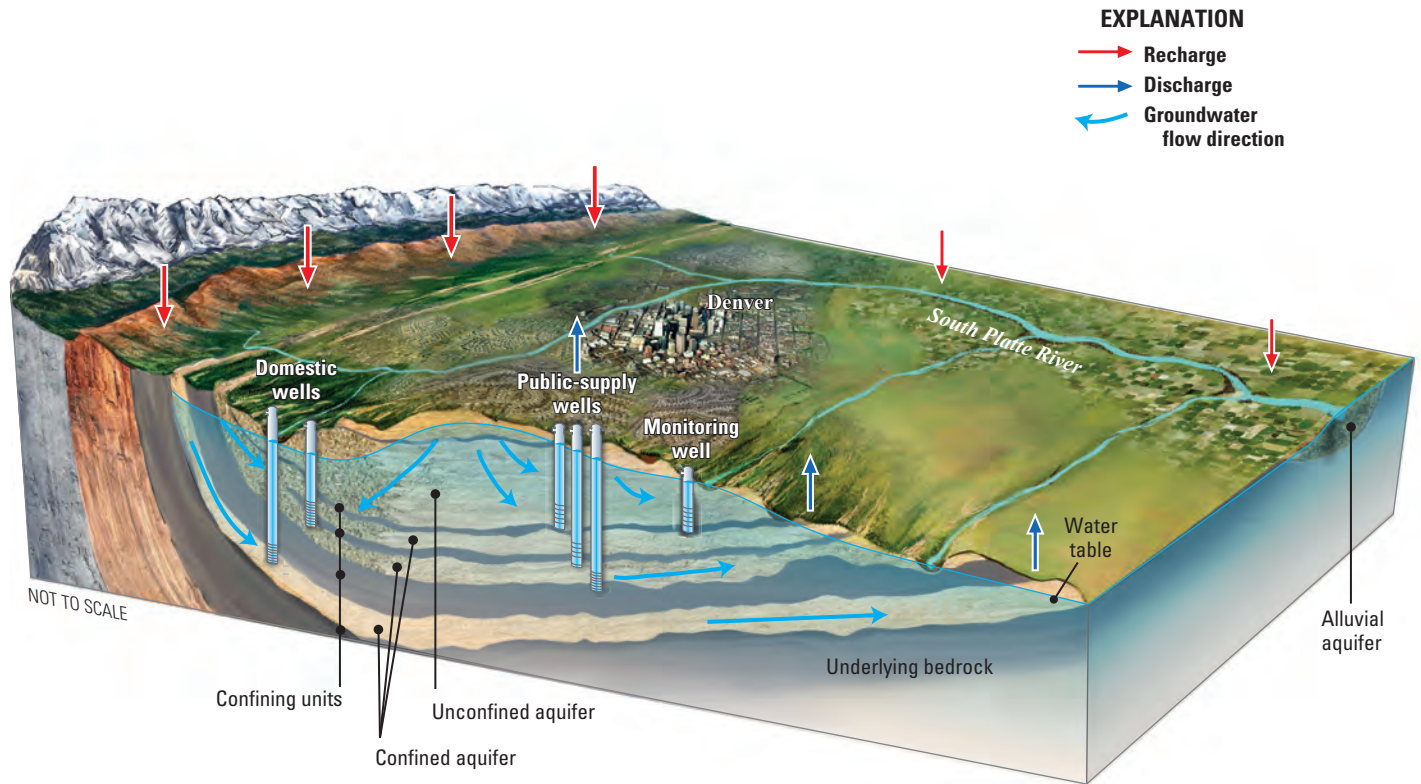


Figure 3–6. Groundwater flows through aquifers from recharge areas to discharge areas. Where precipitation is abundant and aquifers are shallow. In dry climates, such as in the Denver Basin aquifer system (right), recharge may occur primarily at mountain fronts or from leakage from streams.

atmosphere through evapotranspiration. Some aquifers also are recharged by flow across confining layers, by inflow from adjacent aquifers, or by seepage from streams or lakes. Water discharges from an aquifer when it flows into a stream, to a pumping well, or to the ocean, or when it is evaporated at the land surface. A groundwater flow path is the route that the water takes through the aquifer from recharge to discharge. Contaminants from manmade or geologic sources in the area where the water is recharged (the capture zone) and in the aquifer along the groundwater flow path can affect the quality of the groundwater pumped from a well or discharged to a stream.

Denver Basin aquifer system



and unconfined, such as in the Northern Atlantic Coastal Plain surficial aquifer system (left), recharge typically occurs across the landscape. Discharge from aquifers can be to streams, coastal waters, pumping wells, or directly to plants or the atmosphere where the water table is shallow.

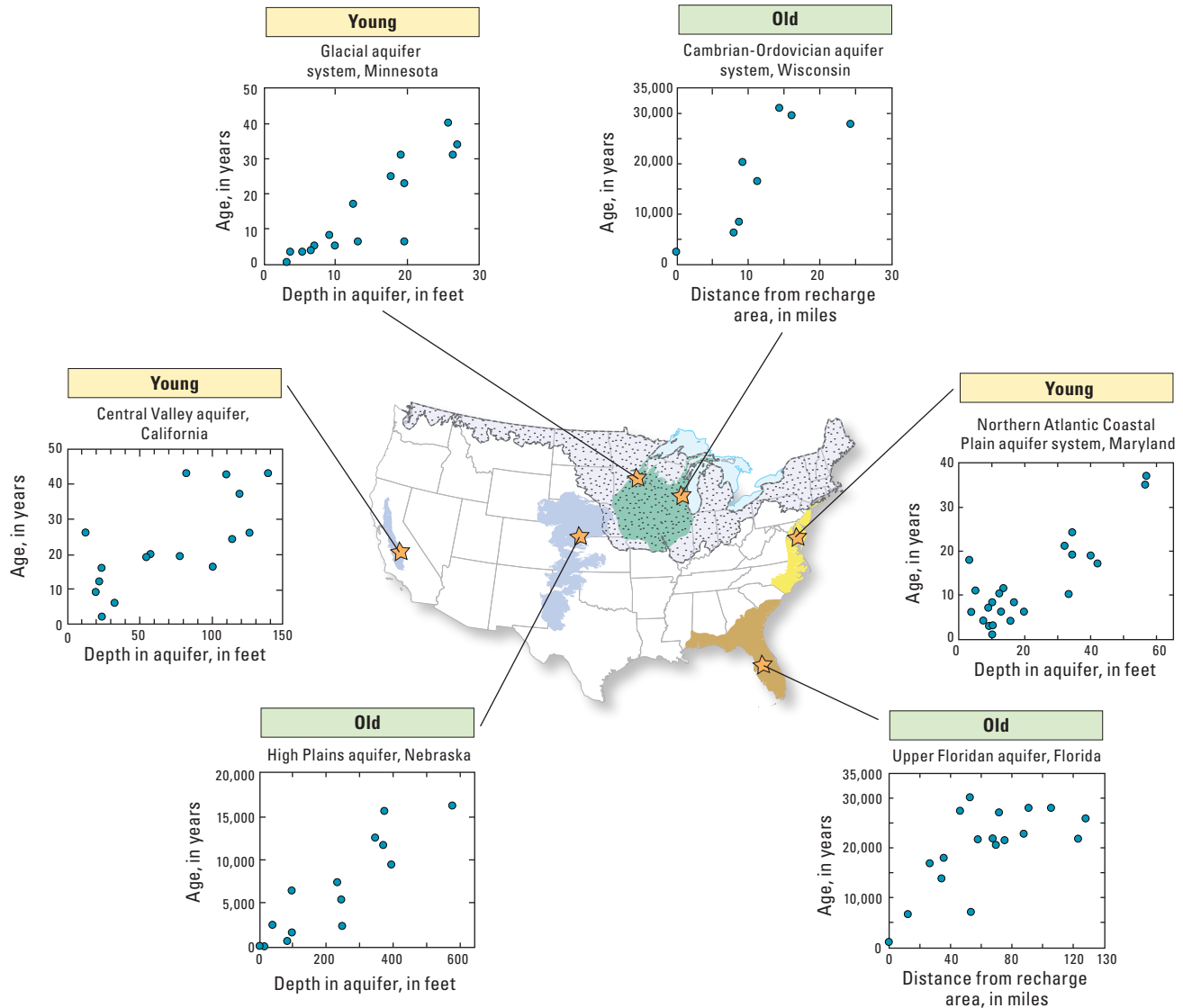
Groundwater moves slowly and can take tens, hundreds, or even thousands of years to travel through aquifers.

Groundwater moves slowly—a flow rate of 1 foot per day is fast for groundwater, and flow rates can be as low as 1 foot per year or 1 foot per decade.⁽¹¹⁾ Consequently, it can take tens, hundreds, or even thousands of years for groundwater to travel through aquifers. The length of time that water remains in an aquifer before it discharges is called the groundwater residence time. Groundwater age, a related concept, is the time that has elapsed since groundwater was recharged. Groundwater that is deep and far from the aquifer’s recharge area typically is older than groundwater that is shallow and near the recharge area. Consequently, all aquifers contain groundwater of different ages (fig. 3–7). Flow rates and residence times depend on the aquifer’s size, shape, permeability, recharge rates, and hydraulic-head gradients.

Knowledge of how water moves through aquifers can help us interpret some of the groundwater-quality characteristics that we observe. For example, older groundwater that has traveled a long distance through an aquifer has had more time to interact with the aquifer rocks and sediments than younger groundwater and is likely to have higher concentrations of constituents from geologic sources as a result. In contrast, younger or shallower groundwater is more likely than older or deeper groundwater to have contaminants from manmade sources. Young groundwater in aquifers with low recharge rates also can have relatively high concentrations of constituents from geologic sources because there has been little dilution of these constituents in the unsaturated zone as compared with aquifers with high recharge rates in areas of abundant precipitation. Human activities that change how water moves through aquifers, such as pumping (which removes water from aquifers) and irrigation (which adds water to aquifers), can affect groundwater quality by mixing older and younger water or otherwise changing the distribution of chemical constituents in groundwater.

Groundwater that is deep and far from the aquifer recharge area typically is older than groundwater that is shallow and near the recharge area.

Groundwater age at selected locations in Principal Aquifers



Modified from, upper left clockwise: Delin and others⁽¹⁷⁵⁾ and Böhlke and others;⁽⁶²⁾ Klump and others;⁽¹⁷⁶⁾ Dunkle and others⁽¹⁷⁷⁾ and Böhlke and Denver;⁽¹⁷⁸⁾ Plummer and Sprinkle;⁽⁶⁸⁾ McMahon and others;⁽⁵⁶⁾ Burrow and others⁽⁹⁶⁾

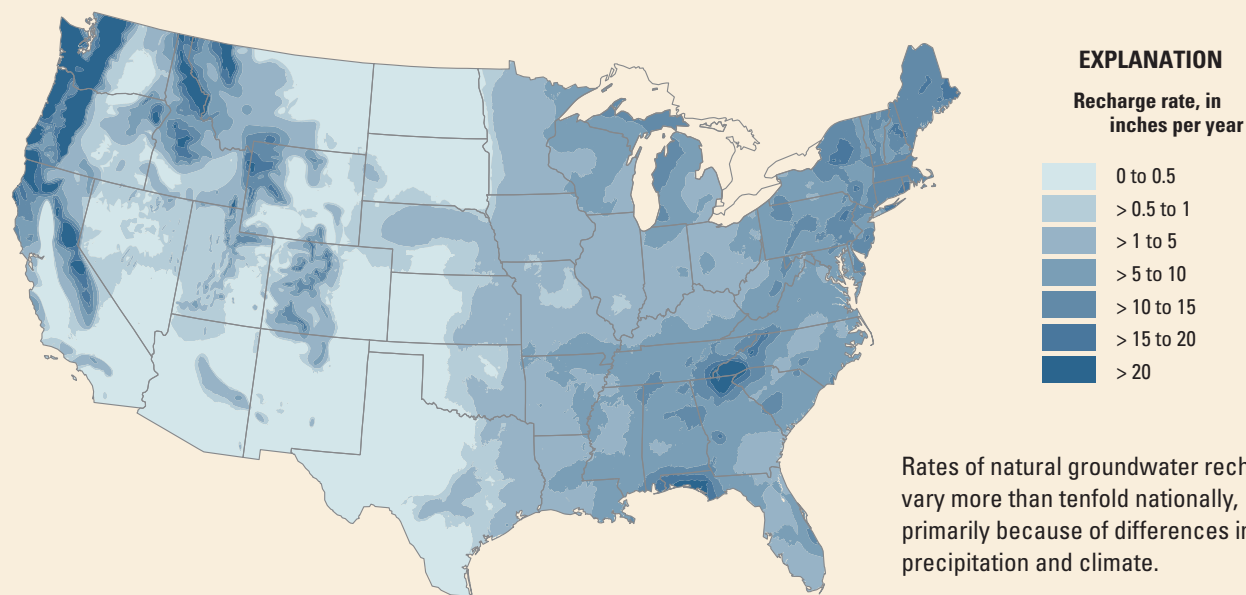
Figure 3-7. Groundwater can be thousands of years old in some confined aquifers and in thick unconfined aquifers where recharge rates are low, such as the High Plains aquifer, Upper Floridan aquifer, and the Cambrian-Ordovician aquifer system. Groundwater is younger—often only a few decades old—in shallow, unconfined aquifers with high recharge rates, such as the glacial aquifer system and the uppermost layers of the Northern Atlantic Coastal Plain aquifer system. Old groundwater may be more likely to have contaminants from geologic sources because it has had longer to react with aquifer rocks and minerals, and may be less likely to have contaminants from recent manmade sources.

Recharge rates

Natural groundwater recharge rates vary among and within Principal Aquifers because of regional differences in climate, soil type, vegetation, and topography. In general, recharge rates are higher where there is more rain and snow and are lower in hotter climates. Aquifers in the East, Northwest, and mountainous regions of the western United States have relatively high natural recharge

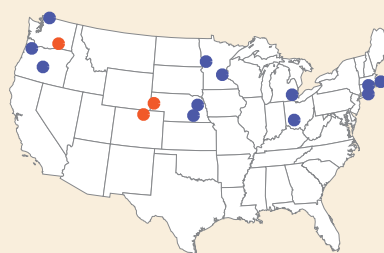
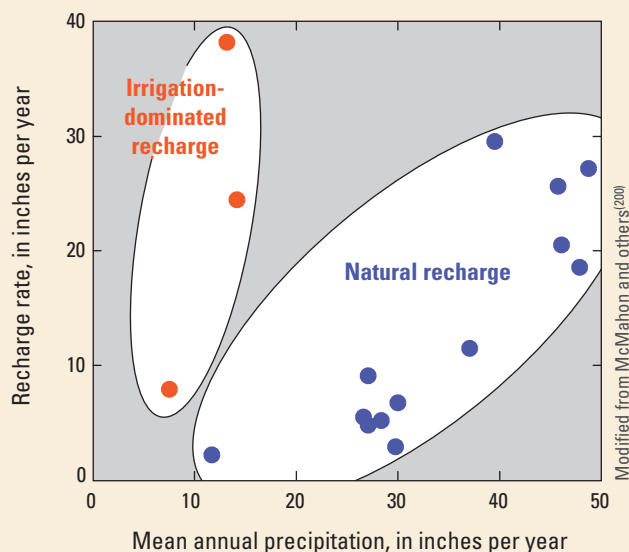
rates compared with aquifers in the High Plains and southwestern United States. Recharge rate is one of the factors that influence the rate at which groundwater flows through an aquifer—groundwater moves very slowly through aquifers that receive only a few inches per year of recharge. Groundwater recharge can be greatly increased by human activities such as irrigation.

Natural groundwater recharge rates



Modified from Wolock⁽¹²⁶⁾

Irrigation-dominated and natural recharge rates



Natural recharge rates increase as precipitation increases, but irrigation can greatly augment natural recharge in dry areas.

Geochemical Conditions and Processes

Geochemical conditions—pH, alkalinity, and reduction-oxidation (redox)—strongly affect the mobility and persistence of many chemical constituents in groundwater, including some that are of concern for human health. Geochemical conditions, together with constituent properties, control the reaction processes—dissolution and precipitation, sorption and desorption, redox processes, and biodegradation (table 3–1)—that affect constituent concentrations in groundwater. Geochemical conditions determine whether chemical constituents from geologic sources are released from the aquifer rocks and sediments or remain immobile in aquifer solids. Geochemical conditions also determine whether constituents from manmade sources travel with the groundwater, react with the aquifer material, or degrade into other chemicals along the groundwater flow path.

Groundwater pH can affect the concentrations of many trace elements because pH influences the sorption characteristics of aquifer rocks and sediments and, along with redox conditions, controls the solubility of some minerals. Trace elements that commonly exist as positively charged ions, including cadmium, cobalt, copper, lead, nickel, and zinc, are more likely to sorb onto aquifer rocks and sediments at higher pH. This is because, as pH increases, the surface charge of the metal oxide coatings and clay minerals in aquifer rocks and sediments becomes more negative, attracting the positively charged trace elements and decreasing their concentrations in groundwater.⁽¹²⁾ Conversely, negatively charged trace elements, such as arsenic, chromium, selenium, and molybdenum, are more likely to be desorbed from aquifer rocks and sediments as pH increases, resulting in higher concentrations of these trace elements in groundwater.

Table 3–1. Definitions of geochemical conditions and processes

Geochemical conditions	
Alkalinity	The capacity of the dissolved substances in water to react with and neutralize acid. Bicarbonate is an example of a dissolved substance that contributes to alkalinity.
pH	Concentration of hydrogen ion in a solution, a measure of the acidity of the solution. Water with low pH (less than 7) is acidic and water with high pH (greater than 7) is alkaline; a pH of 7 is neutral.
Redox conditions	Defined by the dominant type of redox reaction occurring in the water. Water is “oxic” when it contains dissolved oxygen and “anoxic” when dissolved oxygen is absent.
Geochemical processes	
Biodegradation	Transformation of a substance into new compounds through biochemical reactions or the actions of microorganisms such as bacteria.
Dissolution and precipitation	Processes by which minerals, or parts of minerals, pass into solution to become dissolved substances (dissolution) or come out of solution to form solids (precipitation). Halite (rock salt) is an example of a mineral that is easily dissolved; quartz (sand) is an example of a mineral that is not easily dissolved.
Reduction and oxidation (redox)	Chemical reactions that involve the transfer of electrons from one chemical species to another, resulting in a change in the valence state of the species. Redox processes in groundwater often are microbially facilitated.
Sorption and desorption	Processes by which dissolved substances such as ions become attached (sorption) or detached (desorption) to the surfaces of solid material. The actions of a household water softener are an example of sorption and desorption reactions, in which calcium and magnesium ions that cause hardness in water are exchanged for sodium.

The pH of groundwater varies among aquifer rock types (fig. 3–8). Rates and types of weathering processes—chemical reactions that dissolve or otherwise break down rock-forming minerals—vary among rock types and can alter pH. Natural waters that are in contact with the atmosphere and biological activity are slightly acidic because they contain dissolved carbon dioxide. Dissolution of carbonate minerals consumes dissolved carbon dioxide and results in an increase in the pH of the water. Thus, groundwater in the carbonate-rock aquifers and unconsolidated aquifers with carbonate sediments commonly has near-neutral or alkaline pH (fig. 3–8). Weathering of silicate minerals, which are major components of many rock types and sediments, also consumes acidity, but silicate mineral weathering proceeds more slowly than carbonate dissolution. Weathering of silicate minerals in source rocks and in aquifers with long groundwater residence times is one reason why alkaline groundwater is prevalent in the unconsolidated sand and gravel aquifers and volcanic-rock aquifers in the western United States. In contrast, aquifers with abundant quartz sand, such as parts of the semiconsolidated sand aquifers of the Atlantic and Gulf of Mexico coastal plains, are relatively resistant to weathering reactions that neutralize acidity and more commonly have acidic groundwater than aquifers of other rock types.

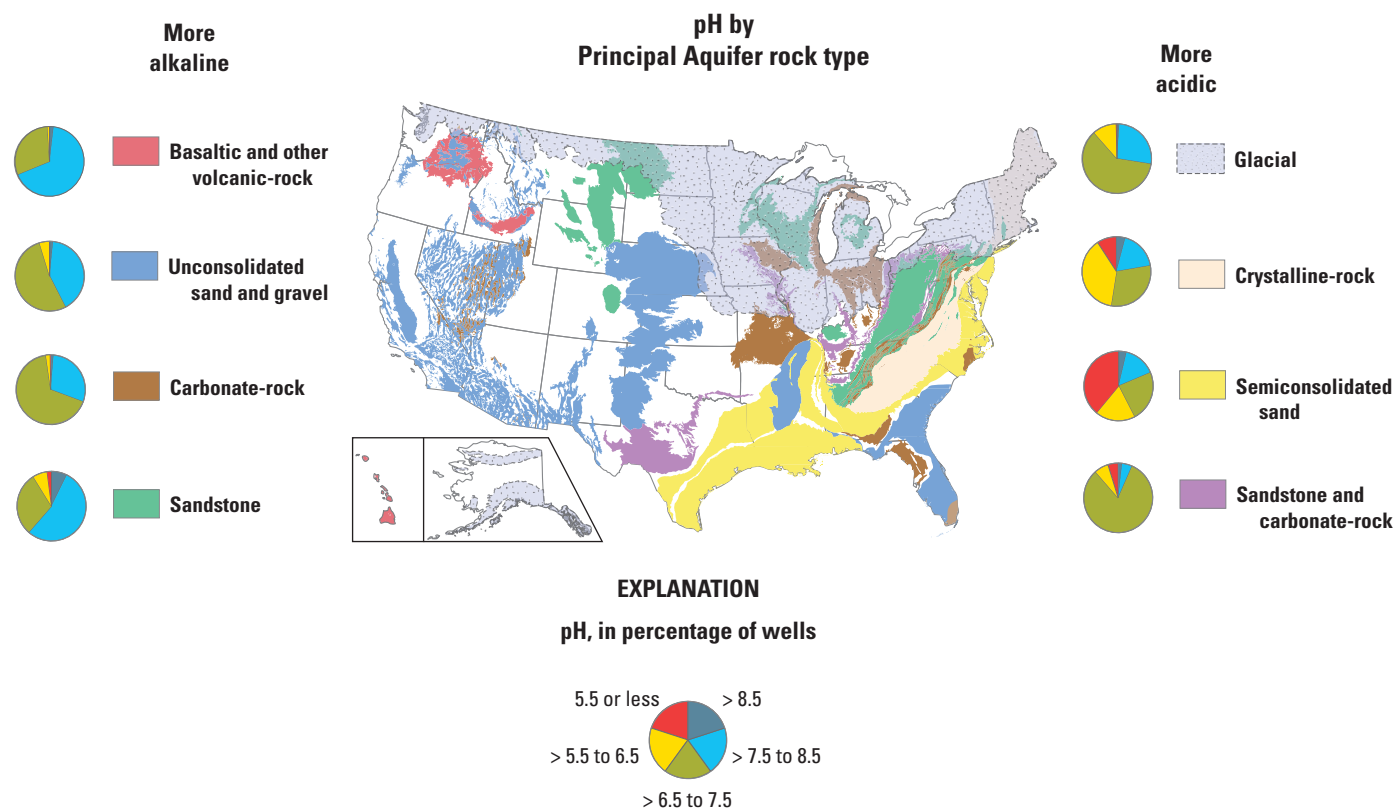


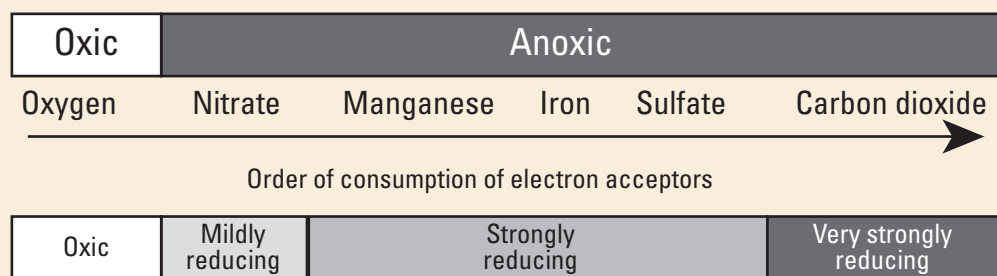
Figure 3–8. Alkaline groundwater is more common in the carbonate-rock and sandstone aquifers where weathering reactions increase pH than in aquifers of other rock types. Acidic groundwater is especially prevalent in the semiconsolidated sand aquifers of the Atlantic and Gulf of Mexico coastal plains; these aquifers have little capacity to reduce the acidity of precipitation through weathering reactions. pH is an important control on the sorption and dissolution processes that affect the concentrations of some contaminants, such as arsenic, in groundwater.

Redox conditions are important for groundwater quality because many chemical constituents can exist in several oxidation states that behave differently in aquifers. The redox condition of the groundwater—whether oxic (oxygen present) or anoxic (oxygen absent)—strongly influences the oxidation state of a chemical in the groundwater. Redox conditions influence sorption characteristics of aquifer materials because metal oxide coatings on rock and sediment surfaces, to which dissolved ions sorb, are stable under oxic conditions but can dissolve under anoxic conditions. Redox conditions influence the degradation processes that can transform contaminants, including nitrate and some manmade contaminants such as solvents and some pesticides.^(13, 14)

Older groundwater is more likely to be anoxic than younger groundwater because there has been more time for chemical reactions that consume dissolved oxygen to occur in older groundwater.

How do redox reactions work?

Reduction/oxidation (redox) processes require one chemical species that donates electrons and another chemical species that accepts those electrons. As a chemical species donates electrons it is “oxidized,” and as the other species accepts electrons it is “reduced.” Redox processes typically are facilitated by microbes (bacteria), which use the energy produced by the processes. In groundwater, organic carbon is the most common electron donor. If dissolved oxygen is present, it is the preferred electron acceptor because reduction of dissolved oxygen produces more energy than reduction of other chemical species that commonly occur in groundwater. The atmosphere is the source of the dissolved oxygen, so the redox conditions in an aquifer near where recharge occurs usually are oxic (defined here as having a concentration of dissolved oxygen of at least 0.5 mg/L).



From a water quality perspective, denitrification—the microbially driven reduction of nitrate (NO_3^-) to nitrogen gas (N_2) under anoxic conditions—is one of the most important redox processes that occurs in groundwater. Nitrate is a concern for human health and, where it discharges to surface water, can impair aquatic communities. Conversion of nitrate by denitrification to harmless nitrogen gas, the same gas that we breathe in the atmosphere, is the primary way that nitrate is removed from water. Similar to other redox processes, the reduction of nitrate is paired with the oxidation of some other chemical, such as organic carbon, which also must be present for denitrification to occur. Bicarbonate and carbon dioxide also are formed and raise the pH (make the water more alkaline).

Redox conditions vary among aquifers and along groundwater flow paths because of differences in the chemical compositions of aquifer rocks and sediments and differences in groundwater age. Oxidic conditions are dominant in the unconsolidated sand and gravel and the basaltic-rock aquifers, which are found mostly in the western United States (fig. 3–9); organic carbon and other electron donors that would consume the dissolved oxygen in recharging groundwater are typically not abundant in these aquifers⁽¹⁵⁾ (see sidebar, How do redox conditions work?, p. 33). Oxidic conditions also are prevalent in the crystalline-rock aquifers and the layered sandstone and carbonate aquifers, which are mostly in the eastern and central United States. Anoxic conditions are more common in the glacial, sandstone, carbonate-rock, and semiconsolidated coastal plain aquifers, which are mostly in the East. Wood fragments in glacial sediments or the remains of marine life in sedimentary rocks are examples of the organic-carbon-rich material that is likely to be more abundant in these aquifers and that depletes the oxygen dissolved in groundwater recharge.

In most aquifers, older groundwater is more likely to be anoxic than younger groundwater because there has been more time for chemical reactions that consume dissolved oxygen to occur in older groundwater. However, redox conditions can be quite variable across short distances because of small-scale variability in aquifers—the irregular distribution of organic-rich layers or the presence of reduced minerals along fractures, for example. Differences in the environments and soils in the recharge area also can cause small-scale differences in redox conditions that are carried with the groundwater as it travels through the aquifer.

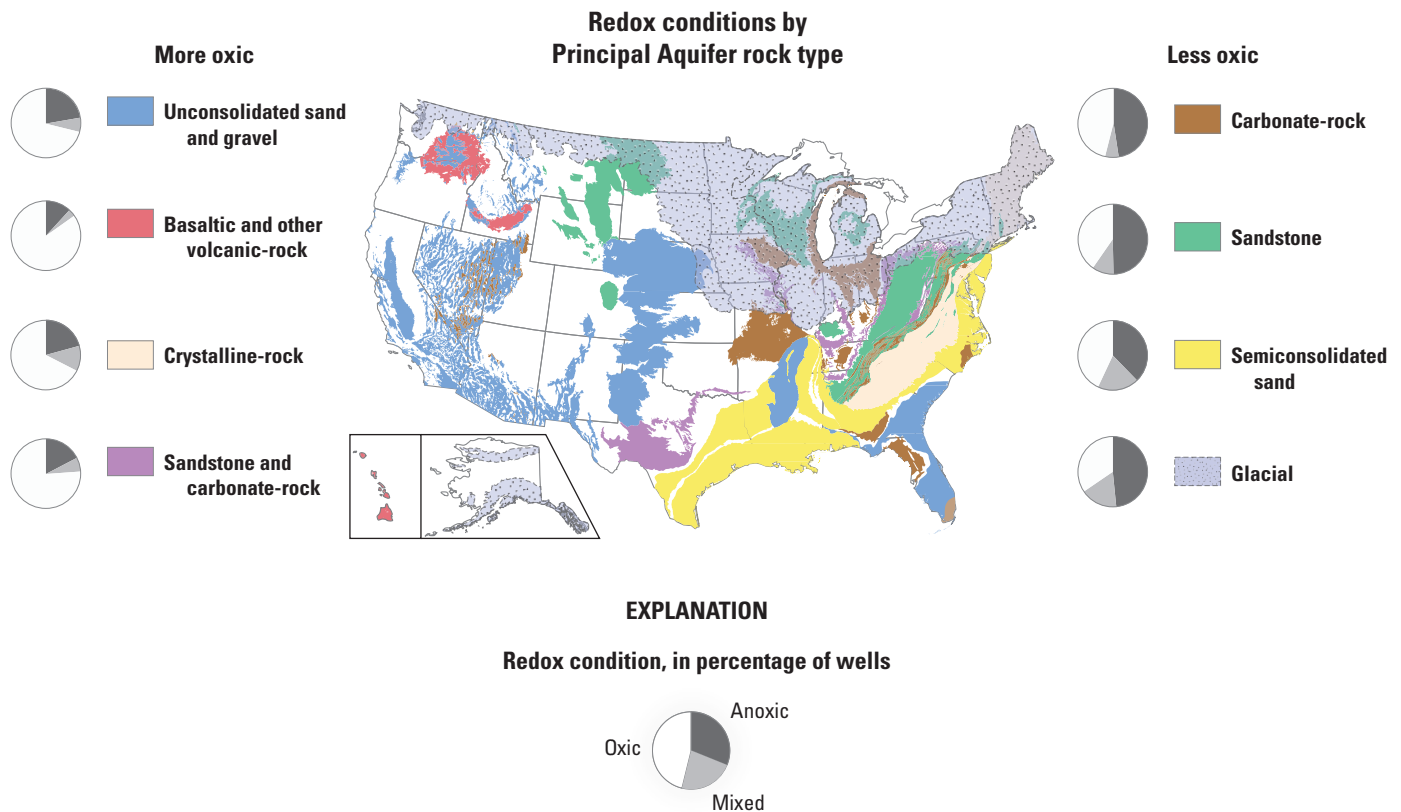
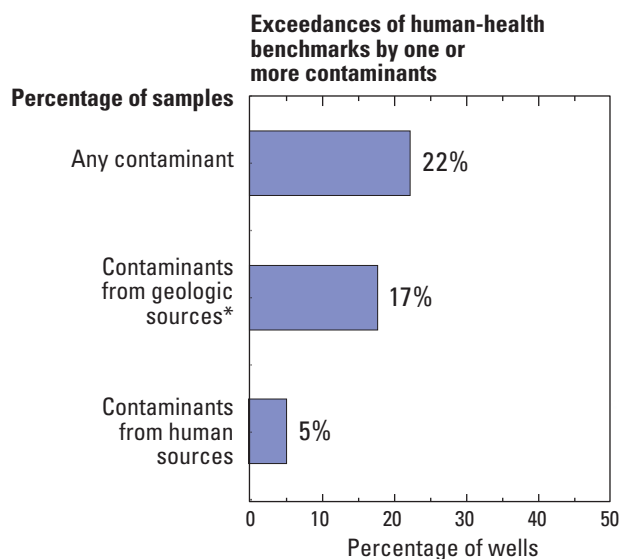


Figure 3–9. Groundwater is predominantly oxic in the volcanic-rock and unconsolidated sand and gravel aquifers, which are found mostly in the western United States. Anoxic conditions are more common in the glacial aquifer system and in aquifers of several other rock types that are found mostly in the North and East. These differences in redox conditions can affect the persistence of some contaminants, including nitrate and some pesticides and volatile organic compounds.

Chapter 4: *The Quality of Groundwater Resources For Drinking and Other Uses*

Is this water suitable for human consumption? This important and frequently asked question can be addressed by comparing the chemical constituents of the water to human-health benchmarks—guidelines and standards for concentrations in drinking water that are considered protective of human health (see sidebar, Human-health benchmarks and other guidelines used in this assessment, p. 38). Nationally, nearly 80 percent of the 3,700 wells sampled in drinking-water aquifers had concentrations of measured chemical constituents less than human-health benchmarks. About 20 percent of wells, however, had at least one contaminant present at a concentration greater than the human-health benchmark for that contaminant (fig. 4–1; see sidebar, What is a contaminant?, p. 38). Contaminants from geologic sources were responsible for 78 percent of the concentrations that exceeded a human-health benchmark (fig. 4–2).

This chapter identifies constituents that were detected at concentrations greater than human-health benchmarks and describes other aspects of water quality that can affect the use of the water.



* The higher of two proposed MCLs was used for radon.

Figure 4–1. Although most of the wells sampled in parts of aquifers used for drinking water had no constituent exceeding a human-health benchmark, 22 percent of wells had at least one contaminant whose concentration exceeded its benchmark. Contaminants from geologic sources accounted for most of these exceedances.

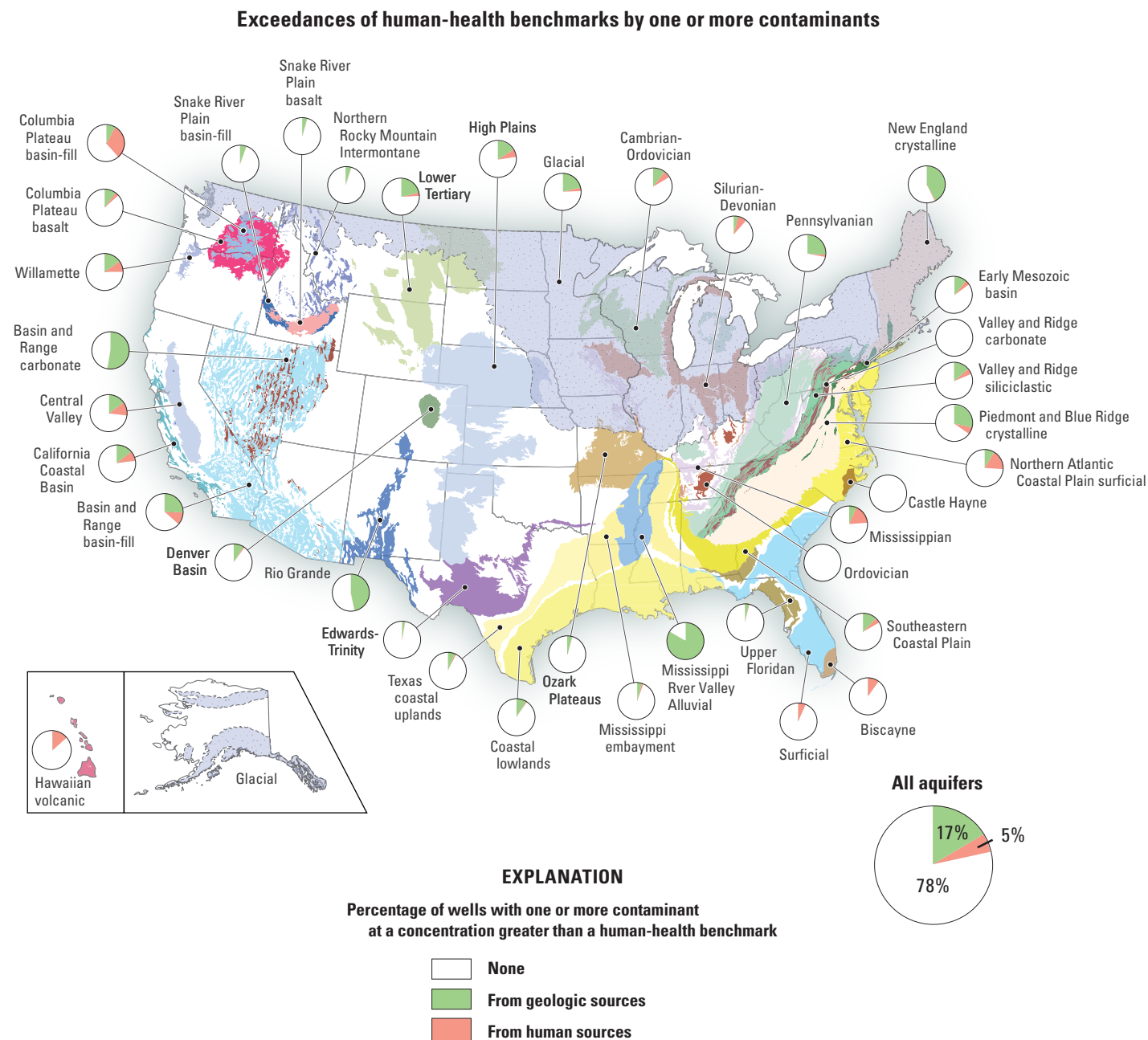


Figure 4-2. Contaminants from geologic sources exceeded human-health benchmarks more frequently than contaminants from manmade sources in most Principal Aquifers. In some aquifers, including the Ozark Plateaus, Snake River Plain, Edwards-Trinity, and Rio Grande aquifers or aquifer systems, the only contaminants greater than benchmarks were from geologic sources. Contaminants from manmade sources were responsible for larger proportions of benchmark exceedances than contaminants from natural sources in a few aquifers overlain by intensive agriculture and (or) urban development, such as the Hawaiian volcanic-rock aquifers, the Biscayne aquifer in Florida, and the Northern Atlantic Coastal Plain surficial aquifer system along the east coast. (Wells with exceedances of both geologic and manmade contaminants are counted in both categories and are proportionately reduced so that values add to 100.)

Sixteen contaminants—11 from geologic sources and 5 from human sources—accounted for nearly all (98 percent) of the instances in which concentrations were greater than human-health benchmarks in wells sampled in drinking-water aquifers (table 4–1). Another 16 constituents exceeded their benchmarks in samples from only 1 or 2 wells. Some of the potential health effects associated with elevated concentrations of these contaminants in drinking water include an increased risk of cancer; various neurological, developmental, and reproductive effects; liver problems; and blue-baby syndrome.^(16–18) Concentrations that are greater than human-health benchmarks are of particular concern in drinking water supplied by domestic wells because routine inspection or testing of these wells is not required.

Concentrations that are greater than human-health benchmarks are of particular concern in drinking water supplied by domestic wells because routine inspection or testing of these wells is not required.

Table 4–1. The constituents that most frequently exceeded human-health benchmarks are 11 contaminants from geologic sources and 5 from human sources. These 16 contaminants accounted for 98 percent of all concentrations greater than benchmarks measured in groundwater samples from the parts of aquifers used for drinking water.

[See appendix 2 for contaminants in individual Principal Aquifers. AMCL, Alternative Maximum Contaminant Level, proposed for radon;⁽¹⁹²⁾ MCL, U.S. Environmental Protection Agency Maximum Contaminant Level;⁽⁶⁰⁾ HBSL, U.S. Geological Survey Health-Based Screening Level, current as of April 2012;^(194, 195) pCi/L, picocurie per liter; µg/L, microgram per liter; mg/L, milligram per liter]

Contaminant	Human-health benchmark		Number of wells sampled	Percentage of samples with concentrations greater than the benchmark	Number of Principal Aquifers with one or more exceedances of the benchmark
	Value	Type			
Contaminants from geologic sources					
Manganese	300 µg/L	HBSL	3,662	6.9	25 of 41
Arsenic	10 µg/L	MCL	3,074	6.7	20 of 37
Radon	*4,000 pCi/L (300 pCi/L)	Proposed AMCL (Proposed MCL)	3,120	3.6 (62)	15 of 41
Strontium	4,000 µg/L	HBSL	1,956	1.7	10 of 29
Uranium	30 µg/L	MCL	3,258	1.6	12 of 37
Fluoride	4 mg/L	MCL	3,655	<1	8 of 41
Molybdenum	40 µg/L	HBSL	3,036	<1	8 of 37
Lead	15 µg/L	Action level	3,035	<1	3 of 37
Antimony	6 µg/L	MCL	3,026	<1	4 of 37
Selenium	50 µg/L	MCL	3,036	<1	4 of 37
Zinc	2,000 µg/L	HBSL	2,979	<1	3 of 37
Any	Various	Various	3,669	16	35 of 41
Contaminants from human sources					
Nitrate	10 mg/L as N	MCL	3,621	4.1	21 of 41
Dieldrin	†0.002 µg/L	HBSL	3,553	<1	14 of 41
Perchloroethene	5 µg/L	MCL	3,272	<1	5 of 41
Trichloroethene	5 µg/L	MCL	3,322	<1	5 of 41
1,2-Dibromo-3-chloropropane (DBCP)	0.2 µg/L	MCL	3,321	<1	2 of 41
Any	Various	Various	3,669	4.5	29 of 41

*The proposed Alternative Maximum Contaminant Level is the primary human-health benchmark used in this circular for radon.

† Low end of HBSL range corresponding to a 10⁻⁶ (one in a million) cancer risk. The HBSL range corresponds to a 10⁻⁶ to 10⁻⁴ cancer risk range.

Human-health benchmarks and other guidelines used in this assessment

Concentrations of constituents measured for this assessment were compared to human-health benchmarks to place study findings in the context of human health. The benchmarks are threshold concentrations in water above which the concentration of a contaminant in drinking water could adversely affect human health. Human-health benchmarks were available for about two-thirds of the 290 constituents and properties measured for the Principal Aquifer assessments. Two types of human-health benchmarks were used: U.S. Environmental Protection Agency (USEPA) Maximum Contaminant Levels (MCLs) (<http://water.epa.gov/drink/contaminants/index.cfm>) and U.S. Geological Survey (USGS) Health-Based Screening Levels (HBSLs). MCLs are legally enforceable drinking-water standards that specify the maximum permissible level of a constituent in water that is delivered to any user of a public water system.⁽²⁰³⁾ Although MCLs are used to regulate the quality of drinking water only from public-supply sources, they also are useful for evaluating the quality of water from domestic and monitoring wells. An MCL was available for 53 of the constituents measured. For some constituents for which an MCL has not been established, the USGS, in collaboration with the USEPA and others, developed non-enforceable HBSLs by using standard USEPA methods for establishing drinking-water guidelines and current toxicity information^(194, 195, 198) (values used in this report were current as of February 2012; see <http://water.usgs.gov/nawqa/HBSL>). An HBSL was available for 135 constituents measured. Radon has neither an MCL nor an HBSL, but two MCLs have been proposed.^(193, 196) Copper and lead have USEPA action levels rather than an MCL.

In addition to human-health benchmarks, non-health-based guidelines—Secondary Maximum Contaminant Levels (SMCLs)—were available for some of the constituents measured in this assessment. The SMCLs are non-enforceable guidelines for concentrations of “nuisance” constituents in drinking water that can cause unwanted cosmetic effects such as skin or tooth discoloration; aesthetic effects such as unpleasant taste, odor, or color; or technical effects such as corrosion or sedimentation of plumbing or reduced effectiveness of water treatment.⁽²⁰⁴⁾

Screening-level assessments, such as this one, provide perspective on the potential relevance of detected contaminants to human health and can help in planning future studies⁽¹⁹⁴⁾. They are not designed to evaluate specific effects of contaminants on human health and are not a substitute for comprehensive risk assessments. It is important to note that occurrence of a contaminant at a concentration greater than its benchmark does not mean that adverse effects are certain to occur, because the benchmarks are conservative (protective) and source-water samples were collected prior to any treatment or blending that could alter contaminant concentrations in finished drinking water. There are water-treatment options, such as charcoal filtration, that can be used to lower the concentration of the contaminant to below the benchmark before the water is consumed.

What is a contaminant?

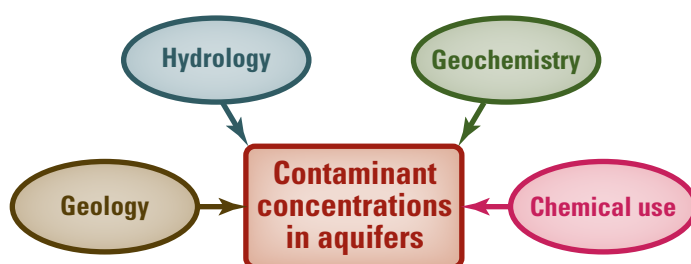
Contaminants have a wide range of sources, both manmade and geologic. Most organic chemicals in groundwater that are of concern for human health are manmade. In contrast, most inorganic constituents in groundwater have geologic or other natural sources, although their concentrations in groundwater may be altered by human activities, such as irrigation and groundwater pumping. Some contaminants have both manmade and natural sources. For example, nitrate in groundwater has many natural sources, but nitrate concentrations in groundwater underlying agricultural and urban areas commonly are higher than in other areas because of contributions from sources associated with human activities.

But what exactly is a contaminant? The word means different things to different people. For example, a contaminant is defined by the Safe Drinking Water Act (SDWA) as “any physical, chemical, biological, or radiological substance or matter in water” (<http://www.epw.senate.gov/sdwa.pdf>). This broad definition of contaminant includes every substance that may be found dissolved or suspended in water—everything but the water molecule itself. This is not a very practical definition because this would imply that all water is “contaminated.” Pure water that has nothing dissolved in it does not occur naturally—not even rainfall is pure water because it contains, at a minimum, some dissolved gases.

The U.S. Environmental Protection Agency defines a contaminant as “Any physical, chemical, biological, or radiological substance or matter that has an adverse effect on air, water, or soil.” (See <http://epa.gov/region04/superfund/qfinder/glossary.html>.) This definition is more practical and allows both manmade constituents and those with geologic sources in water to be defined as contaminants. However, it does not define what “adverse” means, and what may be adverse in one way might be beneficial in another. In this circular, a contaminant is defined as any physical, chemical, biological, or radiological substance or matter in groundwater that is manmade or that impairs the use of water for its intended purpose. Impairment is determined by comparing a measured concentration to benchmarks or guidelines. By this definition, all manmade compounds, such as pesticides and volatile organic compounds, are contaminants because they do not occur naturally in groundwater. If a constituent with a geologic source, such as arsenic, occurs in drinking water at a concentration above its human-health benchmark, it also is considered a contaminant.

Because of differences in geology, hydrology, geochemistry, and overlying chemical use among aquifers, contaminants can exceed human-health benchmarks much more—or less—frequently in individual aquifers than the national statistics indicate (fig. 4–3; appendix 2). For example, radon concentrations exceeded the higher of the two proposed USEPA MCLs for radon in 25 to 50 percent of samples from wells in the crystalline-rock aquifers, but in only 3.5 percent of wells sampled nationally. Concentrations of arsenic concentrations exceeded the MCL in more than 20 percent of wells sampled in two unconsolidated sand and gravel aquifers in the Southwest, which is nearly three times the national exceedance value of 6.7 percent for arsenic for all aquifers. In other aquifers, concentrations of arsenic, radon, and other contaminants from geologic sources did not exceed benchmarks in any of the sampled wells. Concentrations of dieldrin, an insecticide banned since 1987, exceeded its MCL in only 0.8 percent of wells nationally, but most of these occurrences were clustered in a few aquifers. Many of these differences and the reasons for them are investigated in the NAWQA Principal Aquifer assessments; findings, for those constituents that most frequently exceeded benchmarks, are summarized in chapters 5 and 6 of this circular.

Because of differences in geology, hydrology, geochemistry, and chemical use, contaminants can exceed human-health benchmarks much more—or less—frequently in individual aquifers than the national statistics indicate.



Exceedances of human-health benchmarks by selected contaminants in

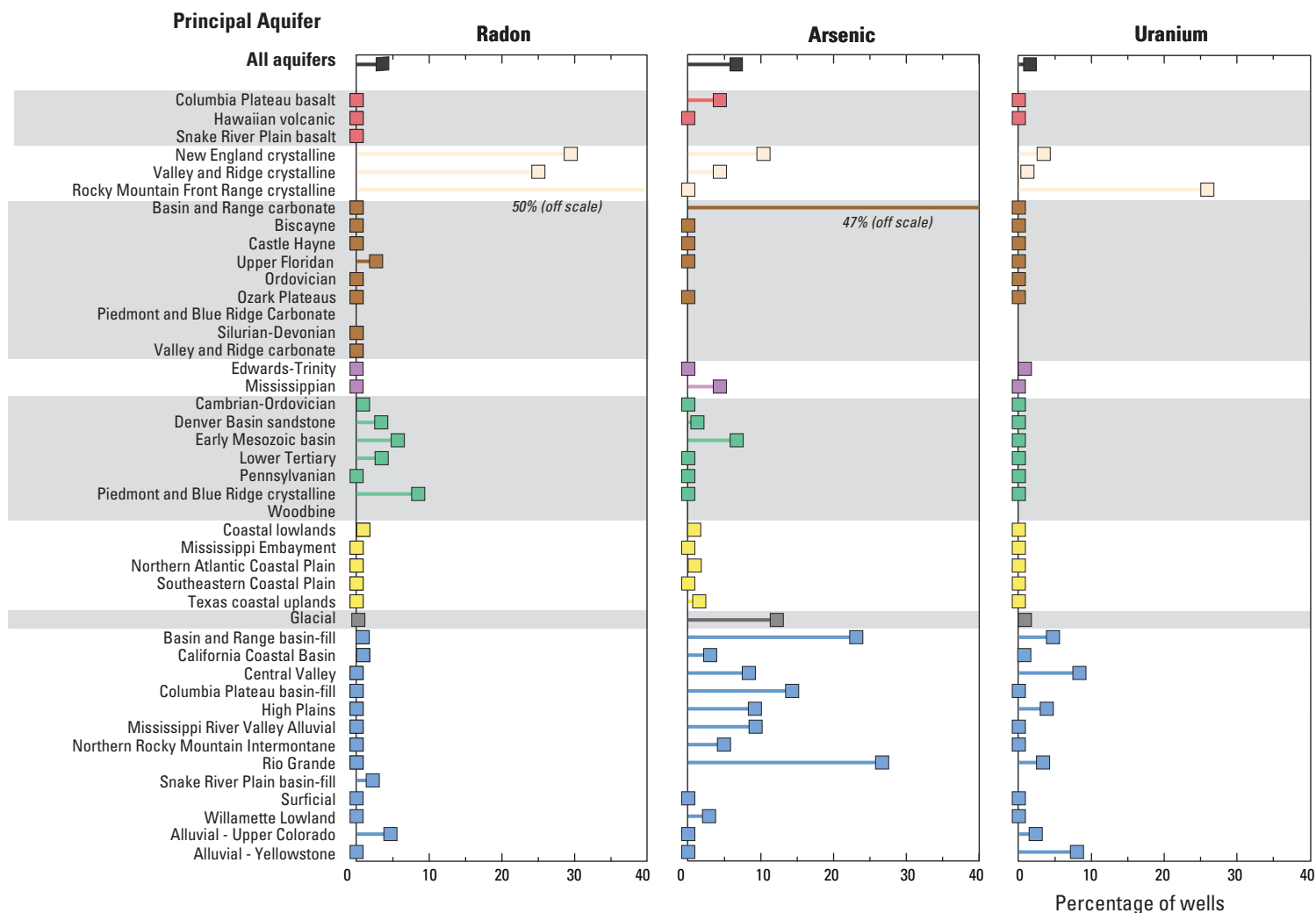
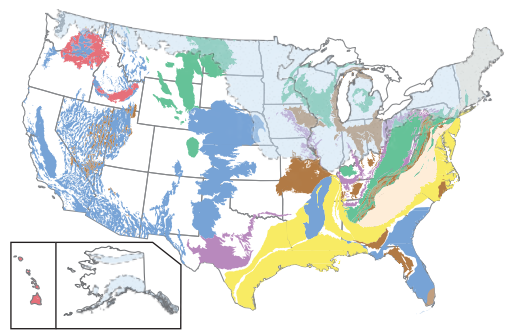
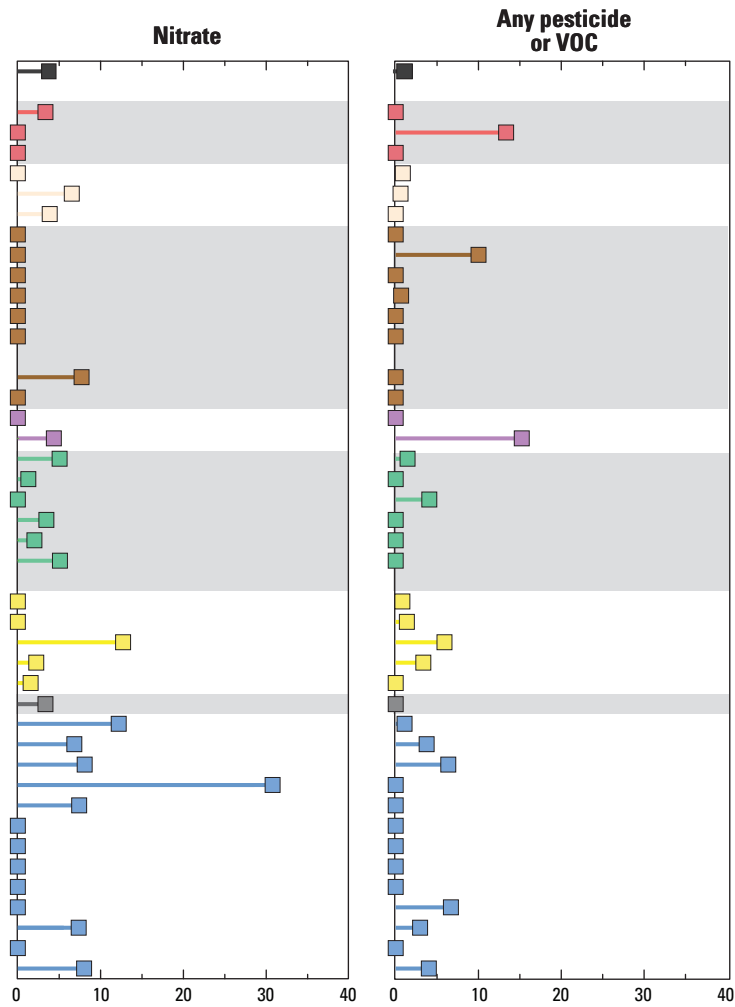


Figure 4–3. Contaminant concentrations higher than human-health benchmarks are unequally distributed among Principal Aquifers. For example, the national rate, but did not exceed this benchmark at all in most of the carbonate or semiconsolidated sand aquifers. Concentrations of arsenic or rate, but did not exceed their MCLs at all in most of the basaltic-rock, carbonate, or sandstone aquifers.

parts of aquifers used for drinking water



EXPLANATION

Principal Aquifer rock type

- | | |
|---------------------------------|--------------------------------|
| Basalt and other volcanic rocks | Sandstone |
| Crystalline | Semiconsolidated sand |
| Carbonate | Glacial |
| Sandstone and carbonate | Unconsolidated sand and gravel |

concentrations of radon exceeded the higher of two proposed MCLs 7 to 14 times more frequently in the crystalline-rock aquifers than uranium exceeded their MCLs two to five times more frequently in some unconsolidated sand and gravel aquifers than the national

Microbiological Contaminants

In addition to chemical constituents, groundwater can contain microbiological contaminants that can be of concern for human health. Microbiological contaminants were assessed by measuring *Escherichia coli* (*E. coli*) and other indicator organisms in a subset (about 1,400) of the wells sampled in NAWQA Principal Aquifer studies. *E. coli* is a type of bacteria that can signal the presence of fecal contamination and can be associated with pathogenic microorganisms. *E. coli* was detected in 8 percent of the wells, indicating the potential importance of microbiological contaminants in untreated groundwater. *E. coli* and other indicator organisms were detected more frequently in carbonate-rock and crystalline-rock aquifers (see sidebar, Bacteria in groundwater in the Piedmont, Blue Ridge, and Valley and Ridge aquifers, this page) than in aquifers of other rock types.⁽¹⁹⁾

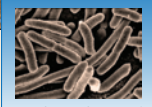
Bacteria in groundwater in the Piedmont, Blue Ridge, and Valley and Ridge aquifers

In the Piedmont, Blue Ridge, and Valley and Ridge aquifers, total coliform bacteria were detected in 100 percent of groundwater samples from springs and in 60 percent of samples from wells. The bacteria *E. coli* were detected in 91 percent of samples from springs and 17 percent of samples from wells. Although detections were frequent in all aquifers and settings in the region, the carbonate-rock aquifers had higher frequencies of detection for these bacteria than aquifers of other rock types, as did areas overlain by agricultural land use. Karst features such as sinkholes and large fractures make the carbonate-rock aquifers more vulnerable than aquifers of other rock types to bacterial contamination. Groundwater in agricultural areas is more vulnerable to bacterial contamination because of the relatively high density of livestock and manure application. In undeveloped areas or areas of residential land use, septic systems or wildlife could be sources of bacteria in groundwater. Characteristics of well construction also are important factors that affect whether bacteria, particularly *E. coli*, are present.⁽¹²⁷⁾

Human consumption of bacterial-laden water from domestic wells probably is common and is likely to cause a number of unreported illnesses.⁽¹²⁸⁾ Education focused on homeowner awareness of the benefits of maintaining well integrity, testing water regularly, and treating as needed could reduce exposure to bacteria from drinking water. Pathogenic viruses that cause illness—not just indicator organisms—are present in water drawn from wells tapping the Piedmont and Blue Ridge crystalline-rock aquifers and the Valley and Ridge carbonate-rock and siliciclastic aquifers.⁽¹²⁹⁾



Photograph from the Chesapeake Bay Program



Escherichia coli

Total coliform and *Escherichia coli* (*E. coli*) bacteria are found in the feces of warm-blooded animals; total coliform bacteria are also present in soils. Total coliform bacteria are typically not harmful but they can signal the presence of other microbial contaminants. *E. coli* is an indicator of direct fecal contamination. Some strains of *E. coli* can cause gastrointestinal illness and other, serious health effects.

Shallow Groundwater Beneath Agricultural and Urban Land—A Concern for the Future?

Nitrate or manmade organic chemicals (pesticides or VOCs) exceeded a human-health benchmark in 24 percent of the shallow wells beneath agricultural areas—four times more frequently than in wells in the deeper parts of aquifers used for drinking water, underlying mixed land uses (fig. 4–4). Eleven percent of shallow wells beneath urban areas had a concentration of nitrate or a manmade organic chemical greater than a human-health benchmark. Elevated concentrations of contaminants from human activities are more common in shallow groundwater in agricultural and urban areas because shallow groundwater is both younger and more heavily influenced by chemical use at the land surface than is deeper groundwater. Eventually, the shallow groundwater is likely to move downward into the aquifer, where it may threaten the quality of future water supplies. Whether the contaminants in shallow groundwater reach the parts of an aquifer used for drinking-water supply depends on the physical and chemical processes that affect the movement of the chemicals through an aquifer. Movement of contaminants into deeper aquifers also depends on whether there are alterations to the groundwater flow system, such as groundwater withdrawals for water supply, that accelerate the downward movement of shallow groundwater (see chapters 7 and 8).

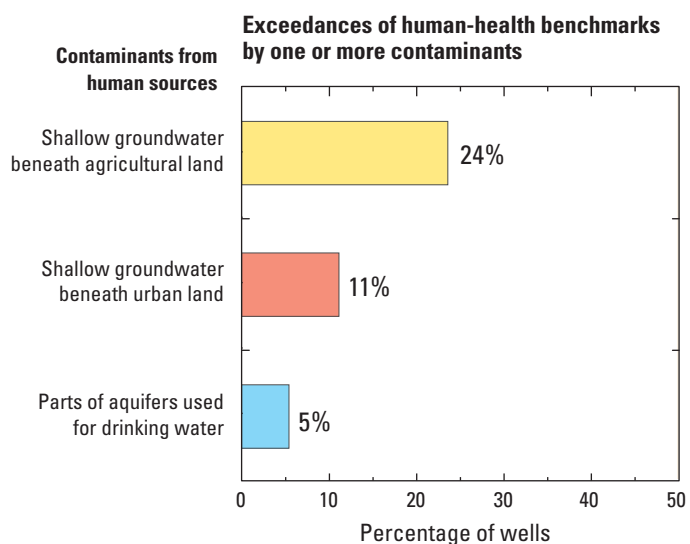


Figure 4–4. Contaminants from human sources—nitrate, pesticides, and VOCs—exceeded human-health benchmarks much more frequently in shallow groundwater beneath agricultural or urban land use than in groundwater from parts of aquifers used for drinking water, beneath mixed land uses.



Photograph by Dr. Rand Schaal, Ph.D., pilot, photographer, and geologist

Human activities, from agriculture (top left) to urban and residential development (bottom right), have greatly altered the land surface in many places. These activities commonly are accompanied by waste disposal and the use of manmade chemicals, and can affect the quality of the underlying groundwater.



Photograph by Lynn Betts, USDA, Natural Resources Conservation Service (NRCS)

Other Water-Quality Concerns

Nuisance Contaminants in Drinking Water

Health concerns are not the only criteria by which we judge the quality of our drinking water. In fact, often the most noticeable qualities that determine whether water is acceptable to consumers result from constituents that cause problems such as unpleasant taste or odor, staining, poor reaction with soap, or mineral buildup in pipes and plumbing. Iron, manganese, hardness, pH, total dissolved solids, and several major ions factor into these unwanted effects, which are a common reason why household water-treatment systems are used. The USEPA recommends limits, called Secondary Maximum Contaminant Levels (SMCLs), for these constituents in public water supplies. Overall, about half (55 percent) of the wells sampled in the parts of aquifers used for drinking water had levels of one or more unwanted constituents or properties outside of USEPA recommended values for drinking water (table 4–2; appendix 2).



Photograph courtesy of Culligan

Iron in groundwater is not a health concern, but it is a nuisance because it can cause rust-colored stains on sinks, bathtubs, and laundry.

Quality of Water for Irrigation

More groundwater is pumped from the Nation’s Principal Aquifers for irrigation than for any other use;⁽⁴⁾ (fig. 3–2). Quality requirements for irrigation water generally are less stringent than those for drinking water. However, elevated concentrations of dissolved solids—a measure of the salinity of the water—and several other constituents can reduce the yield of agricultural crops and damage soils. Concentrations of dissolved solids between 450 and 2,000 milligrams per liter (mg/L) in water can lead to slight to moderate restrictions on its use on crops, and concentrations greater than 2,000 mg/L can severely limit use.⁽²⁰⁾ Elevated concentrations of boron, sodium, and chloride also can lead to restrictions on the use of water for irrigation. Nationally, 21 percent of wells from drinking-water aquifers had concentrations of dissolved

Table 4–2. Iron, manganese, and a number of other constituents from geologic sources were outside of non-health-related U.S. Environmental Protection Agency Secondary Maximum Contaminant Levels.

[SMCL, U.S. Environmental Protection Agency Secondary Maximum Contaminant Level;⁽¹⁸⁾ µg/L, microgram per liter; mg/L, milligram per liter]

Constituent	SMCL	Number of wells sampled	Percentage of wells outside of the SMCL	Number of Principal Aquifers with values outside of the SMCL
Any	Various	3,662	56	41 of 41
Manganese	50 µg/L	3,662	23	38 of 41
Iron	300 µg/L	3,662	21	39 of 41
pH	>6.5 and <8.0	3,640	18	32 of 41
Total dissolved solids	500 mg/L	3,569	18	34 of 40
Aluminum	50 to 200 µg/L	2,896	0.5 to 2.2	(6 to 13) of 37
Sulfate	250 mg/L	3,658	5.1	16 of 41
Fluoride	2 mg/L	3,655	3.8	24 of 41
Chloride	250 mg/L	3,658	3.3	25 of 41

solids greater than 450 mg/L, and 1.7 percent had concentrations greater than 2,000 mg/L. In shallow groundwater beneath agricultural areas, 32 percent of wells had concentrations of dissolved solids greater than 450 mg/L, and 2.2 percent had concentrations greater than 2,000 mg/L. Most of the wells with concentrations greater than 2,000 mg/L, which would severely restrict the use of the water for irrigation, were from unconsolidated or sandstone aquifers in the western United States or from deep, confined aquifers. More information on the distribution of dissolved solids is given in chapters 5 and 7.

Quality of Groundwater Flowing to Streams and Coastal Waters

Groundwater in many aquifers ultimately flows into streams, lakes, or coastal waters. Consequently, groundwater quality can affect aquatic life or the beneficial uses—such as fisheries and recreation—that we derive from these waters. Nitrogen (primarily nitrate in groundwater) and phosphorus are of particular concern because they can cause excessive plant growth, noxious algal blooms, and depleted dissolved oxygen, which are among the top impairments that degrade our streams, lakes, and estuaries.⁽²¹⁾ Groundwater contributions to streams, lakes, and estuaries are not obvious and are hard to measure. Studies have shown, however, that groundwater discharge can provide as much as 50 percent of the flow and nitrogen load delivered to streams that drain to sensitive coastal waters, such as the Chesapeake Bay.^(22, 23) Under such conditions, groundwater quality is essential to consider when developing programs to reduce contaminant loads, such as Total Maximum Daily Loads (TMDLs), to coastal waters.⁽²⁴⁾ Groundwater and surface-water interactions and nitrogen in groundwater are detailed in the USGS circular, “Nitrogen in the Nation’s Streams and Groundwater, 1992–2004.”⁽²⁵⁾



Photograph by Chris Waldron, USGS

Excessive amounts of nutrients in streams and coastal embayments can lead to noxious algal blooms, such as those in an estuary along the Massachusetts coast. Nitrate from groundwater can be a major source of nitrogen in streams that flow to coastal embayments.

Cost of water treatment

Even when water is plentiful, it is not truly available for use unless the quality is acceptable for the intended use. Both water quality and availability are essential to maintaining water supply for municipal, domestic, agricultural, and recreational uses and for aquatic life. Where water quality is poor, there are options to reduce or remove harmful constituents, but they come with costs. Treatment costs and options for addressing groundwater contamination vary depending on the type of contaminant and the specifics of water-supply management, but treatment can cost thousands of dollars per household.

Some options available to domestic well users and public-supply providers include:

- installing and maintaining household treatment devices;
- buying drinking water, either in bottles or from another supplier;
- blending water (diluting a contaminated source with water from an uncontaminated source);
- locating and developing a new, uncontaminated source of drinking water; and
- building or upgrading and operating a treatment plant to remove contaminants.



Photograph by Bruce Lindsey, USGS

A variety of point-of-use household water treatments are available

"My home system consists of a filter, a water softener, and an ultraviolet (UV) light system. I also have a reverse osmosis (RO) system serving the kitchen area. The filter, UV light, and RO systems treat for nitrate and bacteria, and cost about \$1,600. The UV light and RO filters are changed annually for about \$200. The water softener is for extremely hard water, which was recently replaced for about \$1,500 and costs about \$100 a year for salt."

—Pennsylvania homeowner with domestic supply well

Chapter 5: *Understanding Where and Why Constituents From Geologic Sources Occur*

As groundwater flows, it reacts with the diverse minerals, rocks, and sediments that make up the aquifer and soil. Chemical constituents are released into the groundwater from these geologic sources. Some of these constituents can be a concern for human health, when present in drinking water, or may make the water less desirable for other uses. Differences in geology, recharge rates, groundwater residence times, and geochemical conditions contribute to differences in chemical concentrations among and within Principal Aquifers. Despite these complexities, regional patterns in the distribution of constituents from geologic sources can be recognized and, in many cases, understood.

This chapter describes the sources of arsenic, uranium, radon, manganese, and dissolved solids and factors that affect their concentrations in the Principal Aquifers.



Arsenic



Arsenic occurs in minerals such as arsenopyrite (top) and sorbed to iron oxide coatings (bottom) in a variety of rock types.

Arsenic occurs naturally as a trace component in many rocks and sediments. Whether the arsenic is released from these geologic sources into groundwater depends on the chemical form of the arsenic, the geochemical conditions in the aquifer, and the biogeochemical processes that occur. Arsenic also can be released into groundwater as a result of human activities, such as mining, and from its various uses in industry, in animal feed, as a wood preservative, and as a pesticide. In drinking-water supplies, arsenic poses a problem because it is toxic at low levels and is a known carcinogen.^(17, 26) In 2001, the USEPA lowered the MCL for arsenic in public-water supplies to 10 micrograms per liter ($\mu\text{g/L}$) from 50 $\mu\text{g/L}$.⁽²⁷⁾

Arsenic was detected in nearly half of the wells sampled in parts of aquifers used for drinking water (41 percent of wells, concentrations greater than 1 $\mu\text{g/L}$). Detections were more common and concentrations generally were higher in the western United States, especially in several unconsolidated sand and gravel aquifers and in a carbonate-rock aquifer, than in the East (figs. 5–1 and 5–2). Concentrations were greater than the MCL in 6.7 percent of all wells sampled in the parts of aquifers used for drinking water. In about half of the aquifers included in these assessments, at least one well sampled contained arsenic at a concentration that exceeded the MCL (fig. 5–2; table 4–1). Processes that cause arsenic to accumulate in groundwater are complex and differ among aquifers.

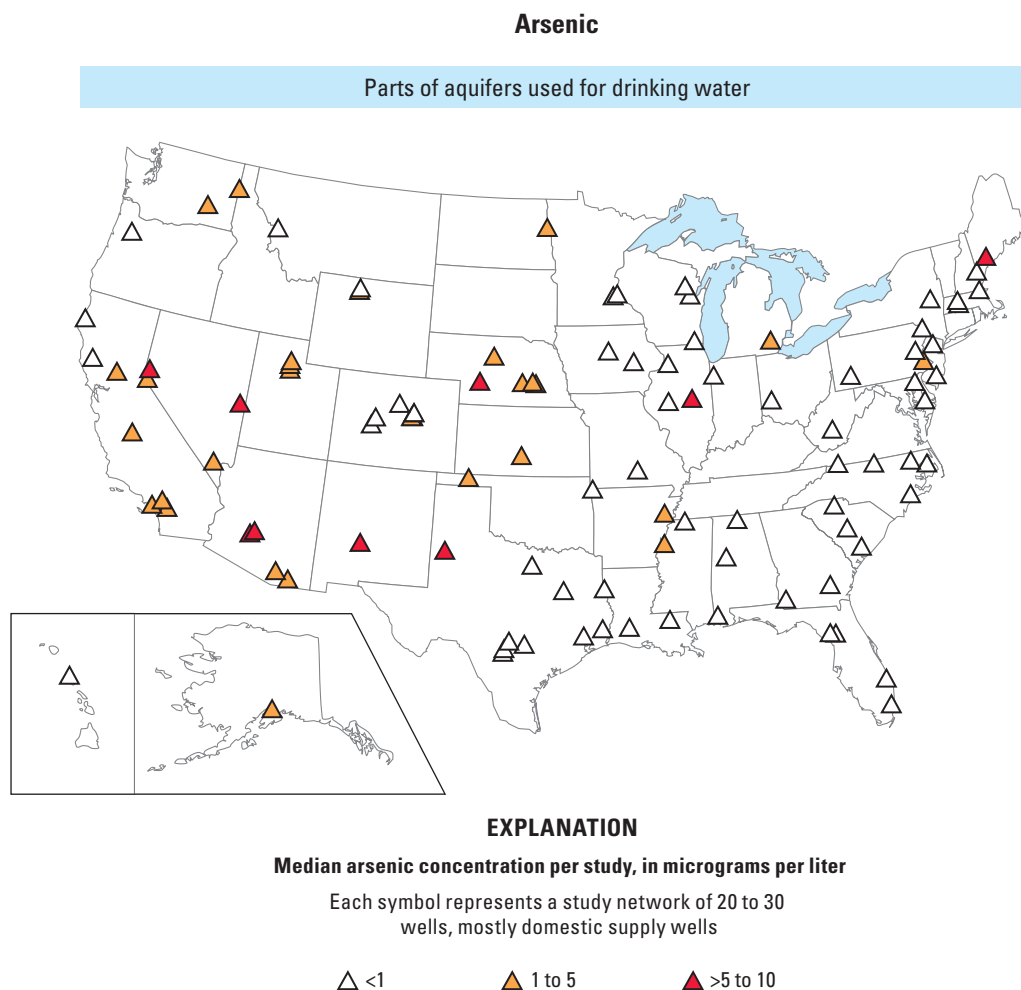


Figure 5–1. Arsenic was more frequently detected and concentrations were higher in groundwater in the western United States than in the East.

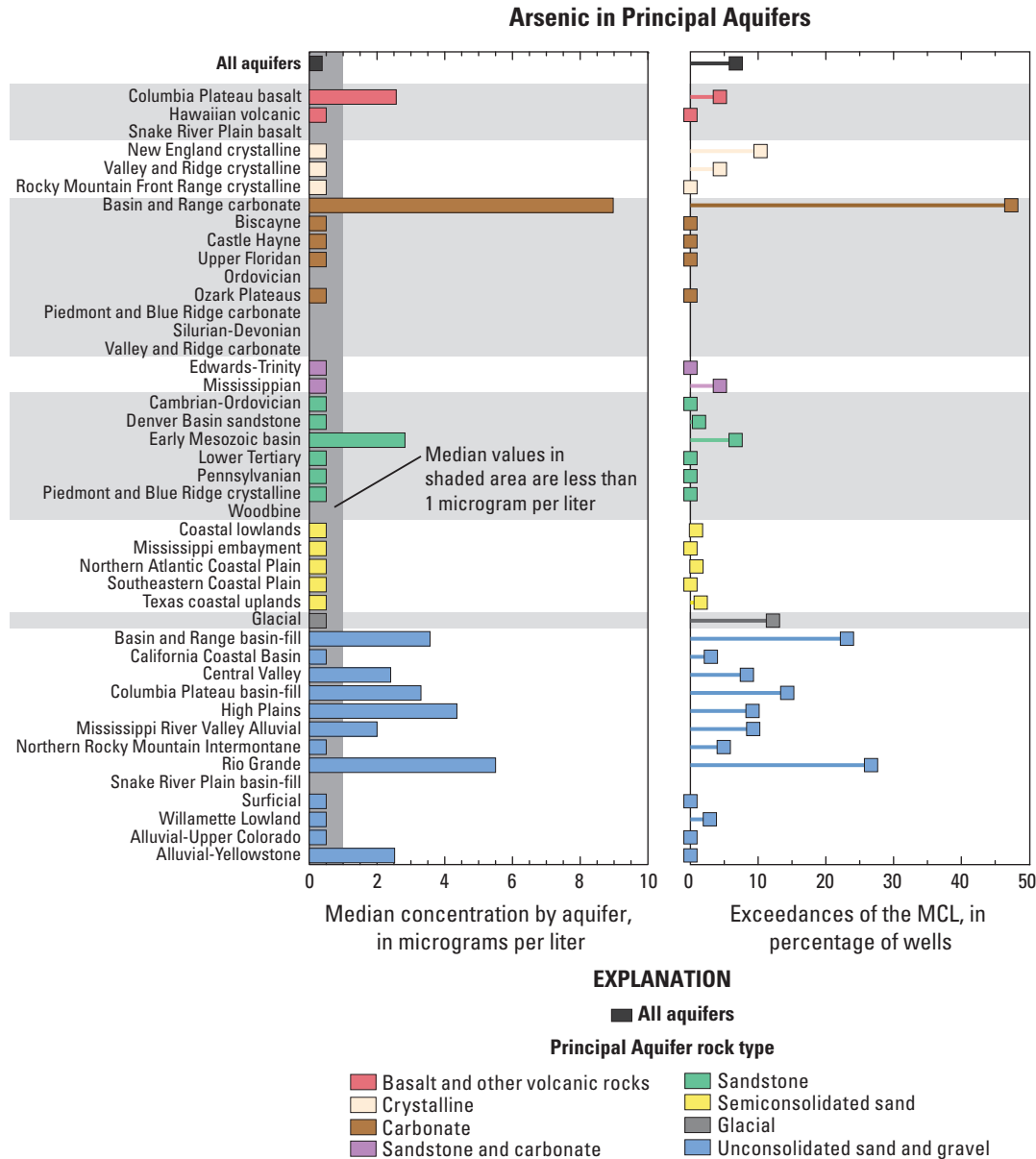
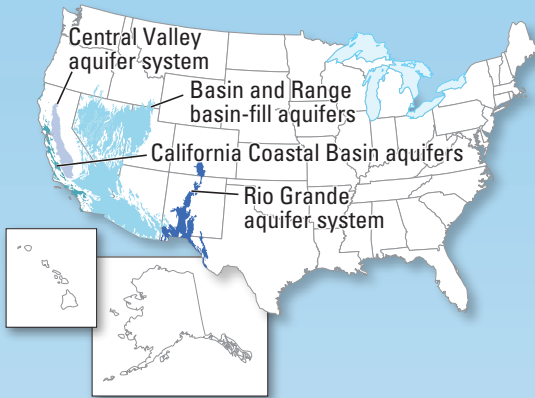


Figure 5-2. Principal Aquifers in the western United States that have relatively high arsenic concentrations include several unconsolidated sand and gravel aquifers, the Basin and Range carbonate aquifers, and the Columbia Plateau basalt aquifers. Concentrations greater than the MCL of 10 µg/L for arsenic also were measured in several aquifers in the East, including the early Mesozoic basin sandstone aquifers, glacial aquifer system, and the crystalline-rock aquifers.



Southwest Basin-Fill Aquifers—*Rock Type, Climate, and Long Groundwater Flow Paths Yield Elevated Concentrations of Arsenic*

Concentrations of arsenic in basin-fill aquifers of the Southwest were among the highest in the Nation, with concentrations greater than the MCL in 3 to 26 percent of wells (fig. 5–2). Geology, a dry climate, and long groundwater residence times are some of the reasons why arsenic concentrations are elevated in these aquifers.^(28, 29) The Southwest basin-fill aquifers—the Basin and Range, California Coastal Basin, Central Valley, and Rio Grande aquifers or aquifer systems—are made up of unconsolidated sand and gravel sediments that originated from weathering of the surrounding mountains. The type of rock in the surrounding mountains is an important control on arsenic concentrations: concentrations are higher in groundwater in basin-fill sediments that are derived from volcanic or crystalline rocks than in groundwater in sediments that are derived from carbonate or clastic sedimentary rocks. Geothermal water and sulfide minerals in aquifer rocks are other geologic sources of elevated arsenic in the groundwater of these aquifers.^(29, 30)



Residents of the Albuquerque area, New Mexico, depend on water from the Rio Grande and from the basin-fill aquifer system. Groundwater west and north of the city contains elevated concentrations of arsenic.

Groundwater flows from the mountainous basin margins, where the sand and gravel deposits are coarse grained and thick, towards the low-lying valley floors. There is little recharge through the basin-fill sediments, and under natural conditions, it can take more than 1,000 years for groundwater to reach the center of the valley. The long flow paths and slow groundwater flow rates result in long groundwater residence times. Thus, there is ample time for chemical reactions to occur that release arsenic from the sediments, and arsenic concentrations increase as groundwater moves from mountain fronts to the lowlands in the centers of basins (fig. 5–3). In basins where recharge rates are relatively high (greater than about 2 inches per year—still quite low compared with humid regions), less arsenic accumulates than in the more arid areas. In general, the more water that flows through the system, the lower the concentrations of constituents, such as arsenic, from geologic sources are likely to be. Basins that have no natural surface-water outflow—water leaves these closed basins only through evapotranspiration or deep groundwater underflow—are particularly vulnerable to the accumulation of arsenic and other constituents from geologic sources.^(15, 28, 30)

Arsenic concentrations increase as the groundwater interacts with the aquifer sediment along flow paths

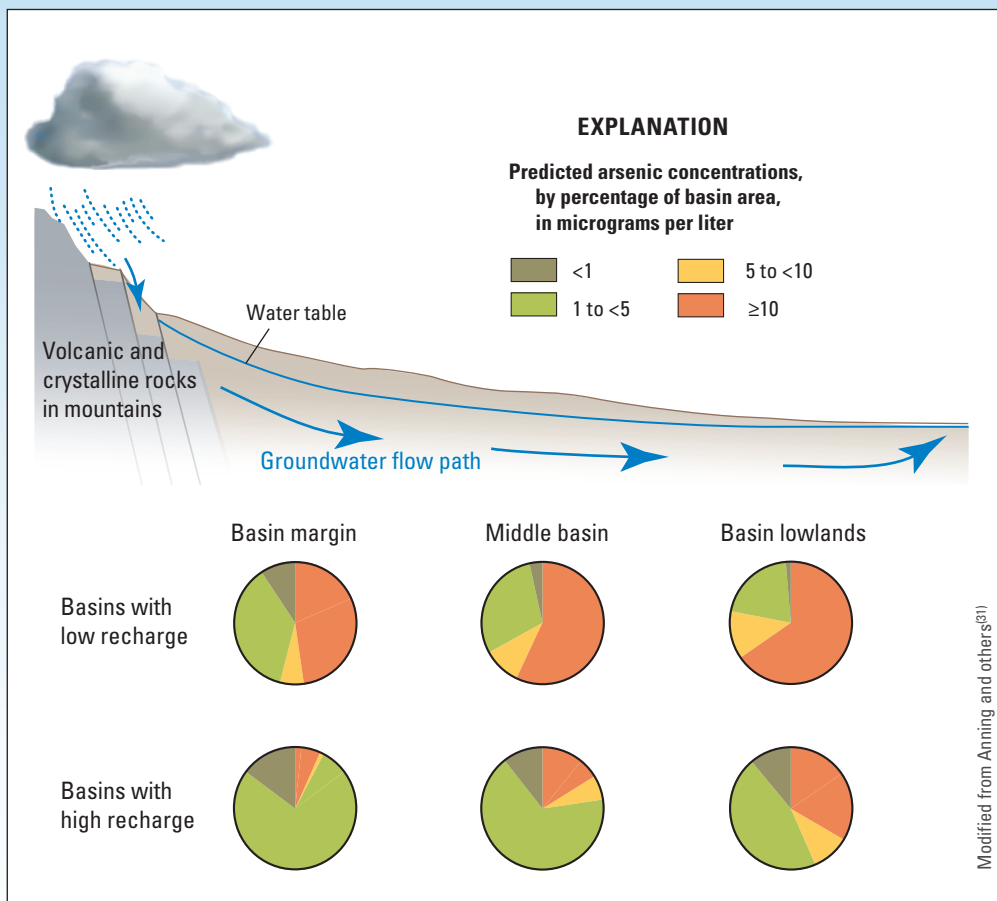


Figure 5–3. In the Southwest basin-fill aquifers, arsenic concentrations increase along flow paths from recharge areas at mountain fronts to low-lying areas in the valley center. Where recharge rates are higher and more water moves through the system, concentrations still increase along flow paths but are lower throughout the basin than in more arid areas.

A regional study predicted that arsenic concentrations would exceed the MCL in groundwater beneath about 43 percent of the areal extent of the four Southwest basin-fill aquifers⁽³¹⁾ (fig. 5–4). This percentage is higher than the percentage of measured concentrations from wells because the areal extent of the basin-fill aquifers includes large areas with arsenic-bearing rocks and constricted groundwater flow—many of these areas are sparsely populated, with little groundwater pumping and few wells. The predicted concentrations can be used to anticipate the water-quality conditions likely to be encountered in unsampled or undeveloped areas and to understand the limitations that water quality can impose on water-supply development—for example, by adding costs for water treatment (see sidebar, The cost of arsenic contamination, p. 53). Such predicted concentrations also can be used to represent concentrations of contaminants in water consumed in the past in areas where there are no monitoring data.

Predicted arsenic concentrations in the Southwest basin-fill aquifers

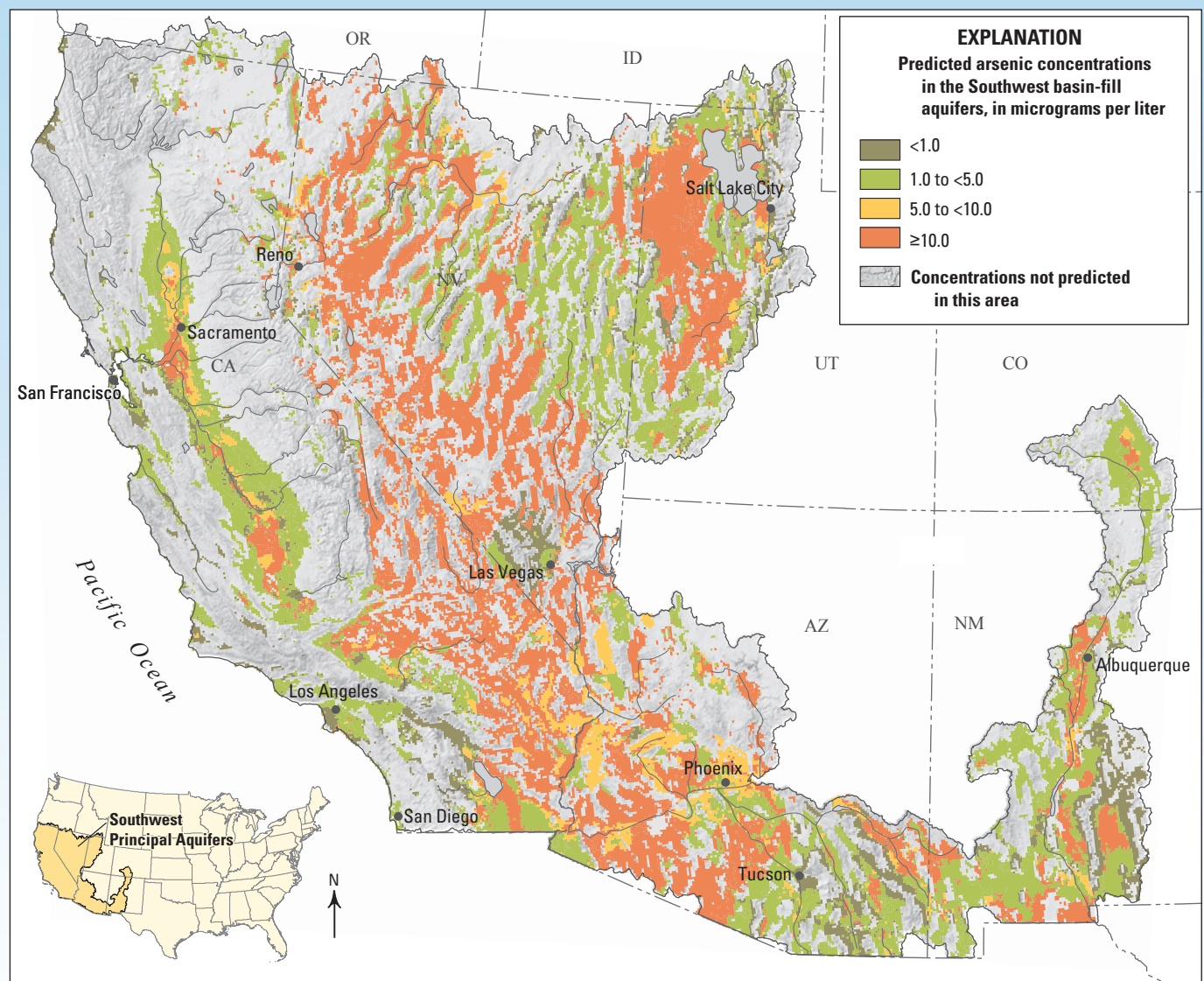


Figure 5–4. Predicted concentrations of arsenic in groundwater exceed the MCL of 10 µg/L in 43 percent of the areal extent of the four Southwest basin-fill aquifers. The Basin and Range basin-fill aquifers in Nevada, Utah, southern California, and western Arizona encompass the largest area where arsenic concentrations are predicted to exceed the MCL, largely due to the presence of volcanic rocks, the arid to semiarid climate, and many closed basins (basins with no surface-water outflow).

The cost of arsenic contamination

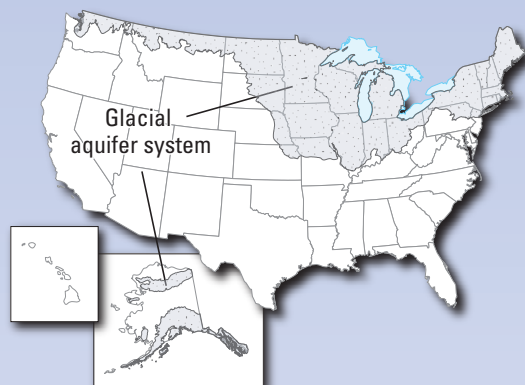
The USEPA estimated in 2001 that the annual cost to reduce arsenic concentrations to below the MCL would range from \$0.86 to \$32 per household for customers of large public water systems (more than 10,000 people) to \$165 to \$327 per household for very small systems (25–500 people).⁽²⁷⁾ Water supplies in the southwest are limited and often naturally contain arsenic concentrations high enough to require treatment. According to fiscal year 2010 statistics,⁽¹³⁰⁾ 274 public water systems in California, Nevada, Utah, Arizona, and New Mexico—mostly

small systems that lack a large customer base to pay for water treatment—had a water source containing arsenic concentrations that exceeded the MCL for arsenic. In Fallon, Nevada, groundwater supplying about 8,400 residents and a nearby naval air station regularly contains arsenic concentrations exceeding the MCL. In 2004, a treatment facility was installed for arsenic removal at a cost of \$19 million.⁽¹³¹⁾ Upgrades to water systems throughout Nevada to remove arsenic are estimated to cost tens of millions of dollars.⁽⁹⁷⁾



Photograph by Jeff Ross

The arsenic treatment system for Fallon, Nevada, adds dissolved iron to the water. The iron reacts with the dissolved arsenic to form particles that are then filtered out of the water.



Arsenic in the Glacial Aquifer System—*The Important Roles of Redox and pH*

Arsenic concentrations in the glacial aquifer system were higher in deeper aquifers, which are used for drinking water, than in shallow parts of the aquifer system: 12 percent of wells from the deeper aquifers used for drinking water had arsenic concentrations that exceeded the MCL, whereas only 4 percent of shallow wells had concentrations that exceeded the MCL. This difference is largely because groundwater in the deeper aquifers is more likely to be anoxic, and redox conditions, along with pH, are an important control on concentrations of arsenic in these aquifers.

Much of the arsenic in the glacial aquifer system is sorbed to iron and manganese oxides that coat the aquifer sediments.^(8, 32) In anoxic groundwater, arsenic occurs in its reduced redox state, arsenite (AsIII), which is not strongly attracted to iron oxides and largely remains dissolved in water. Moreover, iron oxides themselves can dissolve under anoxic conditions, eliminating that mechanism of retaining arsenic on aquifer solids. In contrast, under oxic conditions, arsenic occurs in its oxidized state of arsenate (AsV), which is strongly attracted to iron oxide minerals and will sorb onto these surfaces, leading to lower concentrations of arsenic in groundwater. Sorption of arsenate is pH dependent, however, and does not occur much in alkaline groundwater. Consequently, arsenic concentrations were higher in anoxic groundwater than in oxic groundwater and higher in alkaline groundwater than in acidic groundwater throughout the glacial aquifer system (fig. 5–5). Concentrations were highest in the central region of the glacial aquifer system, where strongly reducing conditions are present in deep groundwater in buried bedrock-valley aquifers (fig. 5–6).

Photograph by Kelly Warner, USGS



The sands, gravels, and fine-grained sediments of the glacial aquifer system extend across the northern United States in river valleys, buried bedrock valleys, and broad lenses. These aquifers are important water sources, providing more water for public supply than any other aquifer system in the United States.

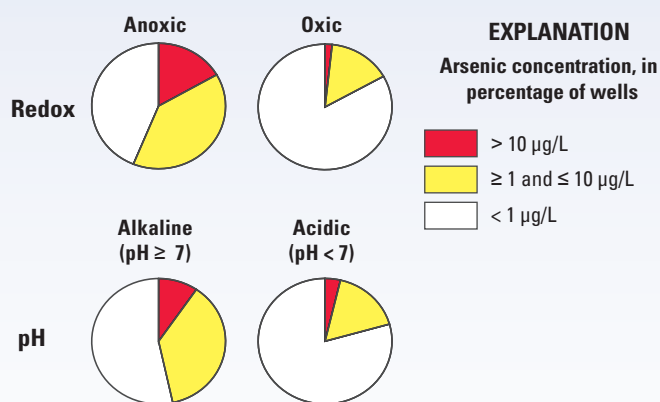


Figure 5–5. In the glacial aquifer system, arsenic concentrations were higher in anoxic groundwater and in alkaline groundwater than in oxic or acidic groundwater. Arsenic that is sorbed to iron and manganese oxides under oxic conditions is released into groundwater by desorption or by the dissolution of the oxide minerals under reducing conditions; pH also is important in this process.

Anoxic conditions are more common in the glacial aquifer system than in many other Principal Aquifers because of the presence of buried organic carbon and reduced minerals such as pyrite (iron sulfide) in the glacial sediments.⁽¹⁵⁾ However, redox and pH also are important controls on arsenic concentrations in a number of other Principal Aquifers. In the Mississippi River Valley alluvial aquifer, arsenic concentrations exceeded the MCL in 9 percent of wells (fig. 5–2). These elevated arsenic concentrations were present only when concentrations of dissolved iron also were high, suggesting that, as in the glacial aquifer system, dissolution of iron oxides was a likely cause of the high arsenic.⁽³³⁾ In the New England crystalline aquifers, the importance of pH-dependent desorption from iron oxides is indicated by the more frequent occurrence of elevated arsenic concentrations in alkaline groundwater than in acidic groundwater, although multiple sources and mechanisms for arsenic in groundwater are likely in these aquifers.^(34, 35)

Although anoxic conditions generally are more common in older, deeper groundwater than in young, shallow groundwater, redox conditions can be quite variable across short distances. Consequently, concentrations of arsenic in groundwater, when they are strongly influenced by redox conditions, are difficult to predict precisely. Water testing for arsenic is essential in this type of hydrogeologic setting to identify drinking-water supplies that contain concentrations of potential health concern.



Photographs by Denis Leblanc, USGS; Joseph Ayotte, USGS

Redox conditions in the glacial aquifer system can be apparent from the color of the sediments. Sand grains from parts of the aquifer that are anoxic (top) are grayish in color and lack the iron-oxide coatings that gives sand from oxic parts of the aquifer (bottom) its rusty reddish hue.

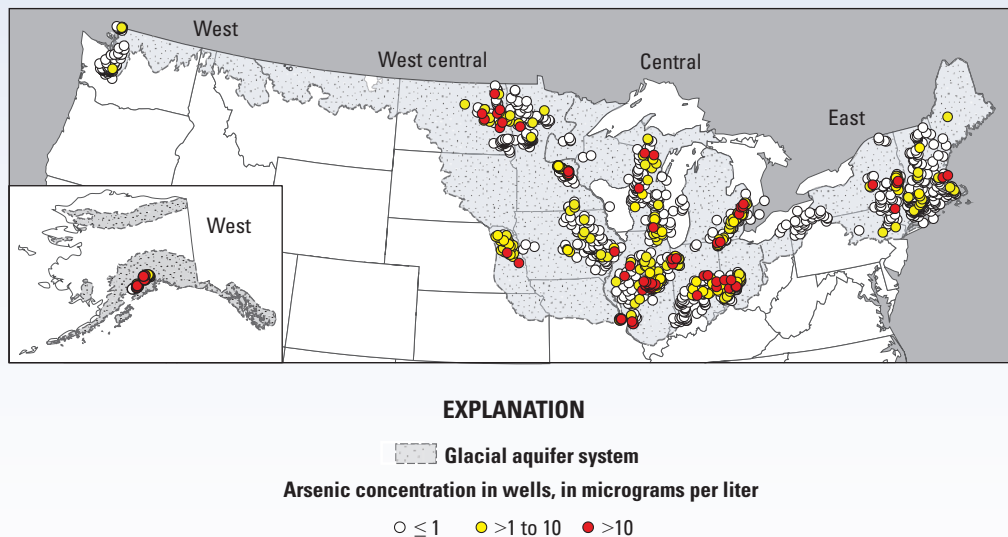
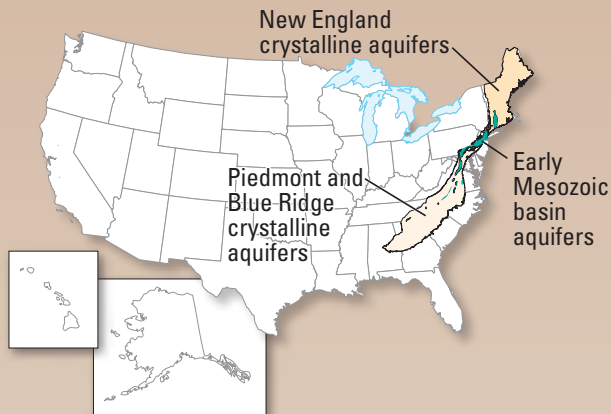


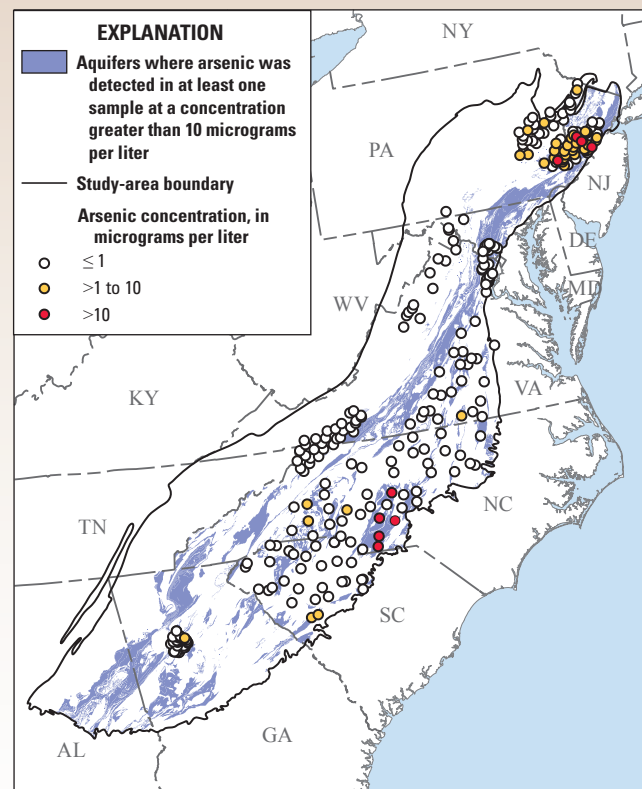
Figure 5–6. Arsenic concentrations were relatively high in the glacial aquifer system, especially in wells sampled in the deeper parts of the aquifer system used for drinking water. Wells in deeper parts of the aquifer in the western and central regions of the glacial aquifer system more frequently contained arsenic at concentrations that exceeded the MCL of 10 µg/L than did wells in the west-central and eastern regions.



Arsenic in the Piedmont and Blue Ridge Crystalline, New England Crystalline, and Early Mesozoic Basin Aquifers—Local Patterns of Occurrence

Geology plays a key role in determining where arsenic occurs in groundwater, and in some aquifers, elevated concentrations are found only in specific rock types. The Piedmont and Blue Ridge crystalline, New England crystalline, and early Mesozoic basin aquifers each contain several different types of fractured igneous, metamorphic, and sedimentary rocks. These aquifers are used for public supply in some areas, but they are especially important sources of domestic supply in rural areas, where they can be the only source of water supply. In the Piedmont and Blue Ridge crystalline aquifers, concentrations of arsenic greater than the MCL were measured only in wells from one type of rock, metamorphosed sedimentary clastic rocks (fig. 5–7)⁽³⁶⁾. Similarly, in the early Mesozoic basin aquifers, only wells in the sedimentary rock composed of ancient lake sediments had concentrations of arsenic greater than the MCL. Within each of these rock types, 9 percent of wells had concentrations greater than the arsenic MCL. Patterns of occurrence among rock types also were apparent in parts of the New England crystalline-rock aquifers. Arsenic concentrations were greater than the MCL in 11 to 25 percent of wells sampled in areas of certain calcareous metasedimentary rocks and granites, whereas concentrations exceeded the MCL in only 3 to 5 percent of wells in another type of granite and in several other metamorphic rock types.^(35, 37, 38) Local patterns such as these can be used to evaluate how likely it is that supply wells in unsampled areas have elevated concentrations of arsenic and to guide testing regulations for domestic wells in rural areas of domestic supply.

Figure 5–7. Only two rock types in the Piedmont and Blue Ridge crystalline-rock aquifers and the early Mesozoic basin aquifers had concentrations of arsenic greater than the MCL of 10 µg/L. Nine percent of samples from wells screened in either of these rock types had arsenic concentrations greater than the MCL, but no concentrations greater than the MCL were measured in samples from wells in the other rock types in these aquifers or in the adjacent Valley and Ridge aquifers.



Modified from Lindsey and others⁽³⁶⁾

Radionuclides

Many people might be surprised to learn that drinking-water sources can contain radioactive elements (radionuclides). Radionuclides in groundwater are primarily from geologic sources and include isotopes of uranium, radon, radium, polonium, and lead (see sidebar, What are radionuclides and which ones are important in groundwater?, p. 63). Rock type, groundwater geochemistry, and, in some cases, human modifications to flow systems influence the distribution of radionuclides in groundwater. The radioactive decay process itself adds complexity because radionuclides transform into different elements. Radionuclides in drinking-water sources can be a concern for human health because several are toxic or carcinogenic.

Uranium and Radon

Uranium is a common trace element in many rock types, but it is particularly enriched in crystalline rocks, such as granites, and in sediments derived from crystalline rocks. Because uranium is highly soluble in its oxidized forms but only slightly soluble in its reduced forms, its mobility in groundwater depends on redox conditions. Uranium sorption is pH dependent, and uranium can form bonds with other ions that keep it in solution over a wider range of conditions than otherwise possible. Although weakly carcinogenic, uranium is chemically toxic, and



Photograph by Steve Krull, copyright istockphoto.com

Granite rocks, such as those shown on Pikes Peak in the Rocky Mountains of Colorado, are a source of uranium to groundwater.



Photograph from alptan, copyright istockphoto.com

is a concern for human health because it causes kidney damage at elevated concentrations when consumed in drinking water.⁽³⁹⁾

Uranium was detected (concentrations greater than 1 µg/L) in 35 percent of wells sampled in the parts of aquifers used for drinking water but exceeded the USEPA MCL of 30 µg/L in only 1.6 percent of samples nationally. Concentrations in groundwater were higher in the western United States than in the East (fig. 5–9). Low recharge rates, oxic groundwater, long flow paths, and high concentrations of naturally occurring uranium in rocks and soils contribute to the accumulation of uranium in the unconsolidated sand and gravel aquifers of the West. Crystalline-rock aquifers in the Rocky Mountains and in the northeastern United States also had relatively high concentrations of uranium, as did several sandstone aquifers in the mid-Atlantic region and in Colorado (fig. 5–8). In these aquifers, the MCL was exceeded in 3 to 26 percent of wells.

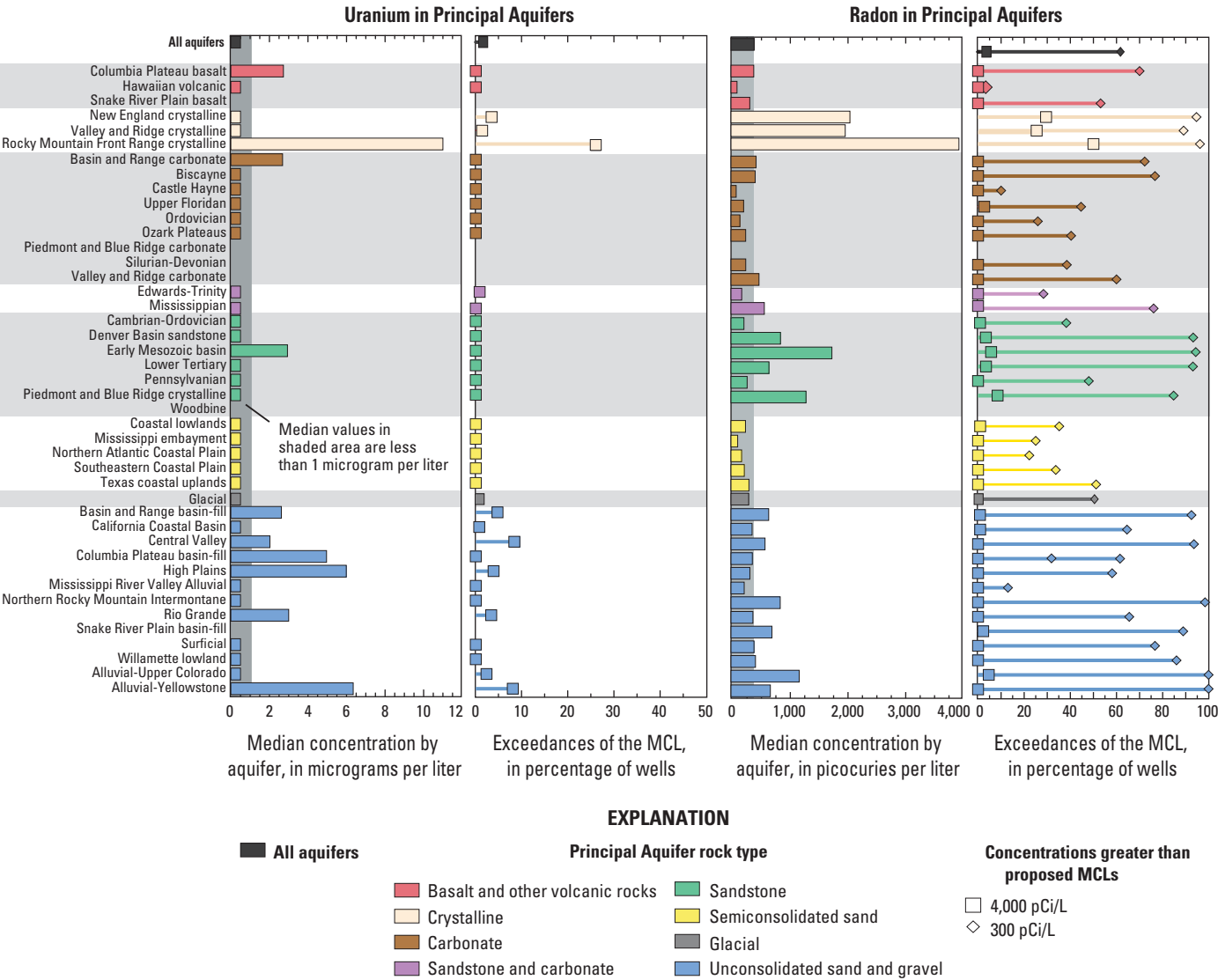
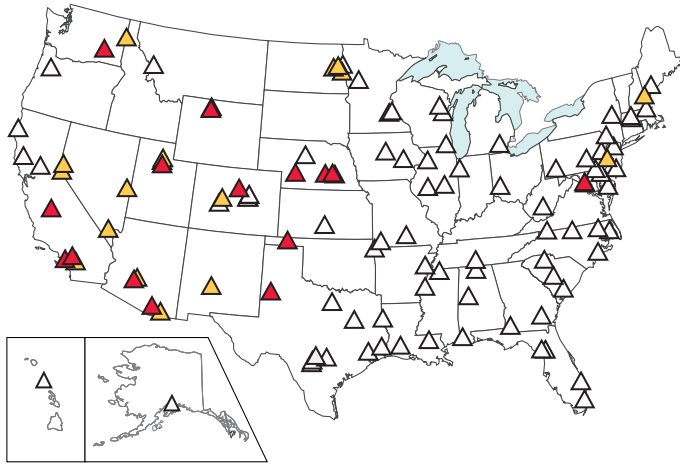


Figure 5–8. Unconsolidated sand and gravel aquifers and one crystalline-rock aquifer, all in the West, had the highest concentrations of uranium among Principal Aquifers. Nearly all the exceedances of the MCL for uranium of 30 µg/L were in these aquifers. Concentrations of radon, on the other hand, were higher in the three crystalline-rock aquifers than in any other aquifer. The higher of two proposed MCLs for radon (4,000 pCi/L) was exceeded most frequently in groundwater samples from the crystalline-rock aquifers.

Uranium in groundwater

Parts of aquifers used for drinking water

**EXPLANATION**

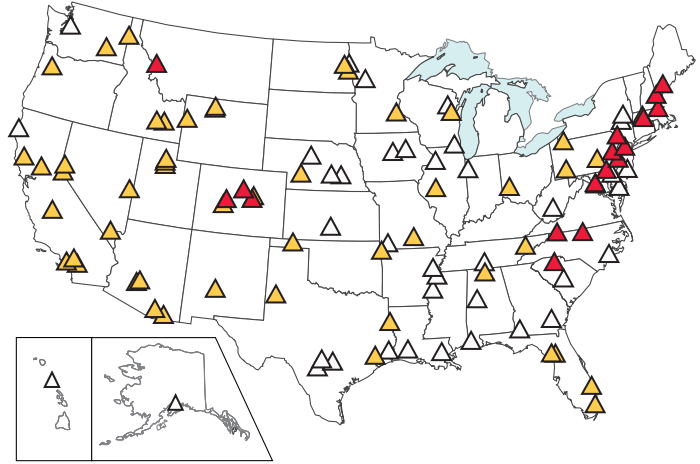
Median uranium concentration per study, in micrograms per liter

△ <1 △ 1 to 3 △ >3 to 11

Each symbol represents a study network of 20 to 30 wells, mostly domestic supply wells

Radon

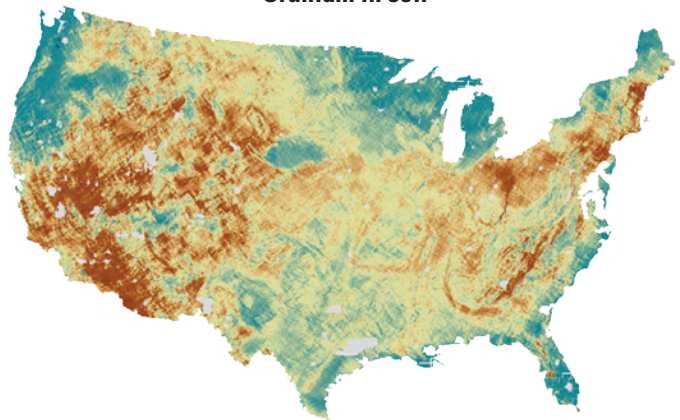
Parts of aquifers used for drinking water

**EXPLANATION**

Median radon concentration per study, in picocuries per liter

△ <300 △ 300 to 1,000 △ >1,000 to 2,150

Each symbol represents a study network of 20 to 30 wells, mostly domestic supply wells

Uranium in soilData from Phillips and others⁽²⁰²⁾**EXPLANATION**Uranium (²³⁸-U) in soil, from aerial gamma-ray surveys, in parts per million equivalent uranium (ppm eU)

High 5.4

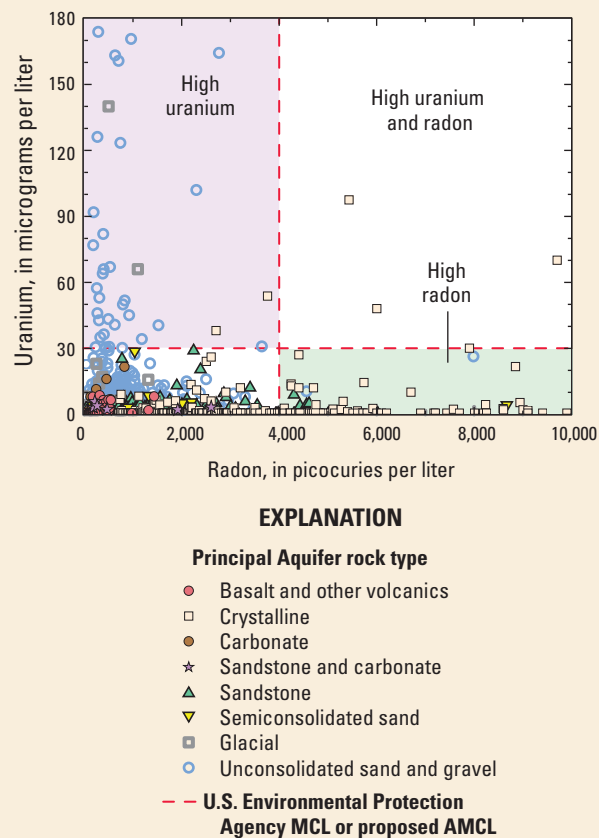


Low -0.44

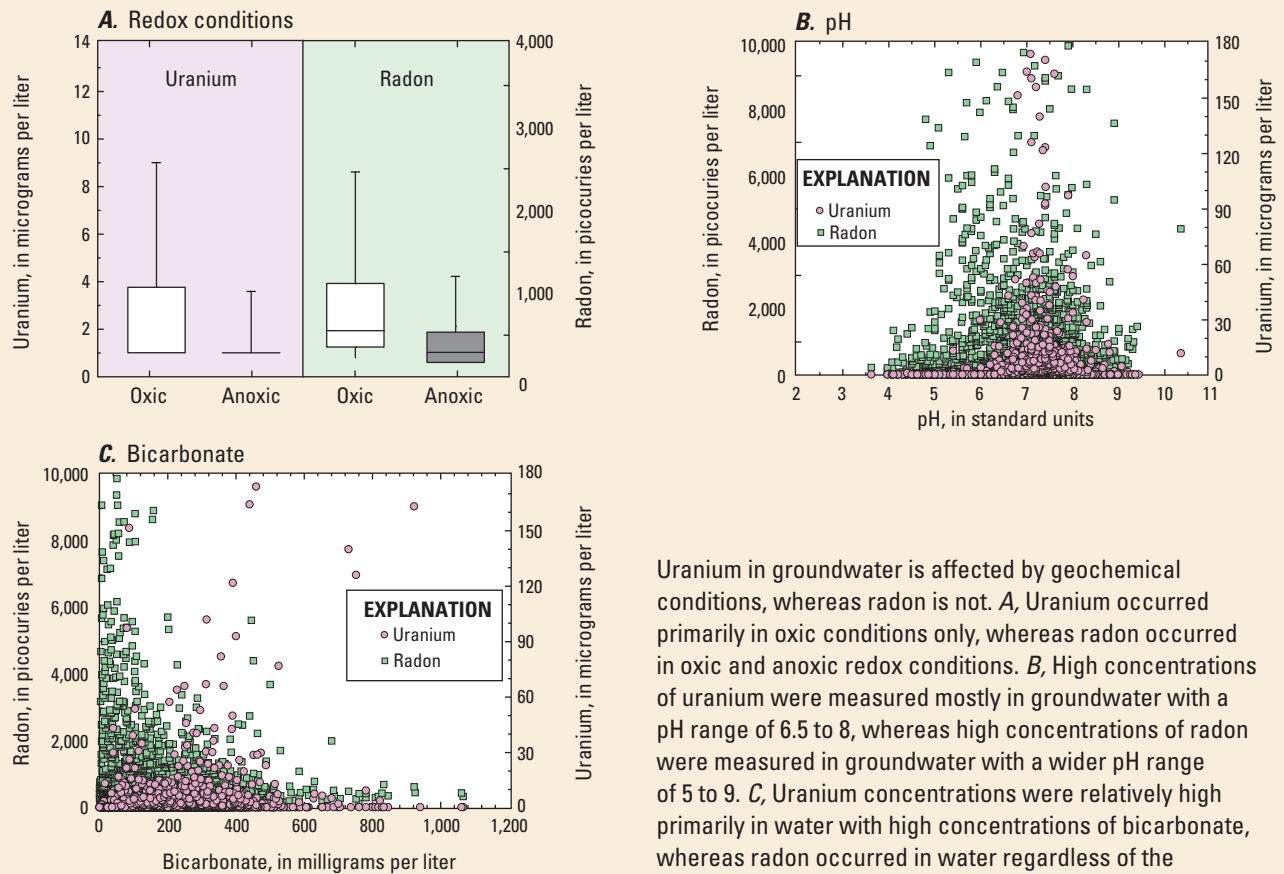
Figure 5–9. Concentrations of uranium in groundwater (top left) generally were higher in the West and Northeast than in other parts of the United States. The concentration of uranium in aquifer rocks, which is reflected in concentrations in soils (bottom left), is one factor that influences groundwater concentrations. High concentrations of radon in groundwater, in contrast, (top right) occurred primarily in the Northeast.

Uranium and Radon—Why don't they occur together in groundwater?

Uranium-238 and radon-222 have the same geologic source because radon-222 is a daughter isotope in the uranium-238 decay series. Why, then, don't high concentrations of uranium and radon occur together in groundwater? The answer lies in the geochemical and radiological differences between the two elements. Uranium is more likely to stay dissolved when groundwater is oxic, pH is slightly alkaline, and there are high concentrations of bicarbonate or sulfate. Radon, on the other hand, is less affected by groundwater geochemistry and is dissolved in groundwater over a wide range of pH and redox conditions. When uranium is present in aquifer materials but geochemical conditions do not favor its mobility, concentrations of radon in groundwater can be high when concentrations of uranium are not. The difference in their radioactive decay rates is another factor. Uranium-238 has a half-life in the billions of years, whereas radon-222 has a half-life of less than 4 days. This difference in half-life means that uranium-238 can travel long distances from its source in aquifer rocks or sediments before it decays. Radon-222, on the other hand, can travel only a short distance from its source before it decays to its daughter products. Finally, radon-222, a dissolved gas, can escape from the water, whereas uranium, a dissolved ion, cannot.



High concentrations of uranium and radon don't often co-occur.



Uranium in groundwater is affected by geochemical conditions, whereas radon is not. *A*, Uranium occurred primarily in oxic conditions only, whereas radon occurred in oxic and anoxic redox conditions. *B*, High concentrations of uranium were measured mostly in groundwater with a pH range of 6.5 to 8, whereas high concentrations of radon were measured in groundwater with a wider pH range of 5 to 9. *C*, Uranium concentrations were relatively high primarily in water with high concentrations of bicarbonate, whereas radon occurred in water regardless of the concentration of bicarbonate.

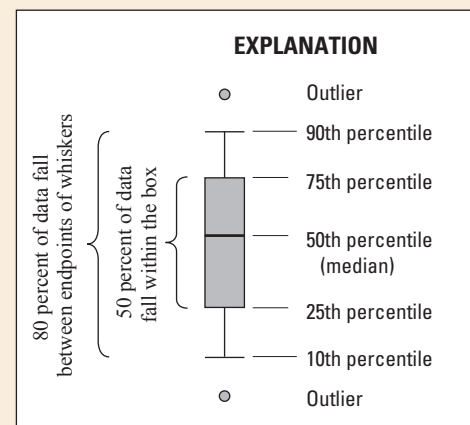
Boxplots

Boxplots are used to illustrate how results are distributed within a group. The “box” ranges from the 25th to the 75th percentile and represents 50 percent of the data. The horizontal line in the middle of the box is the median value—one-half of the values in the group are greater than the median and one-half are less.

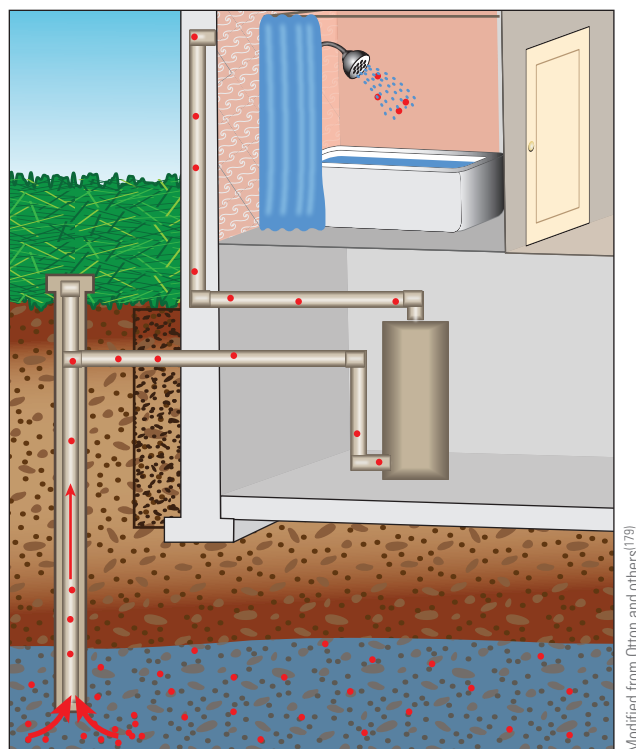
Percentiles describe the percentage of values in a group that are less than the given value: 25 percent of the values in a group are less than the 25th percentile; 75 percent of the values in a group are less than the 75th percentile. The median is also the 50th percentile.

If, for example, the 75th percentile for the measured concentration of a contaminant in a group of wells is equal to the human-health benchmark for that contaminant, then 75 percent, or three-fourths, of the wells have a concentration of that contaminant less than the benchmark, and 25 percent, or one-fourth, have a concentration greater than the benchmark.

The “whiskers” (vertical lines) in these figures extend to the 10th and 90th percentiles; box and whiskers together represent 80 percent of the data. Values greater than the 90th or less than the 10th percentile are shown as individual points (outliers). Outliers are not shown on all graphs.



Radon (radon-222) is present in most groundwater in the United States and was detected in 94 percent of wells sampled in the parts of aquifers used for drinking water. Radon in water is a dissolved gas that does not react with other chemicals. When water that contains radon is used in a home, most of the radon is released from the water into the air and can be inhaled (fig. 5–10). Inhalation of radon poses a risk of lung cancer.⁽⁴⁰⁾ The USEPA has proposed an MCL of 300 pCi/L and an Alternative MCL (AMCL) of 4,000 pCi/L for radon in public water systems.^(40–42) The lower proposed MCL for radon would apply to States and public water systems that do not develop programs to address health risks from radon in indoor air; the higher proposed AMCL would apply to States and public water systems that have established such programs. Concentrations exceeded the lower proposed MCL in 64 percent of wells, including at least one well from every Principal Aquifer in this study. The proposed AMCL was exceeded in only 3.6 percent of wells. Most of the concentrations greater than 4,000 pCi/L were measured in crystalline-rock aquifers in the Northeast, the mid-Atlantic region, and Colorado (figs. 5–8 and 5–9).



Modified from Orton and others⁽¹⁷⁹⁾

Figure 5–10. Radon gas (red dots) that is dissolved in groundwater can be pumped from a well and travel through a household water distribution system. Once the water is aerated through a faucet, the radon is released into the air and can be inhaled when people are close to showerheads or drinking directly from faucets.

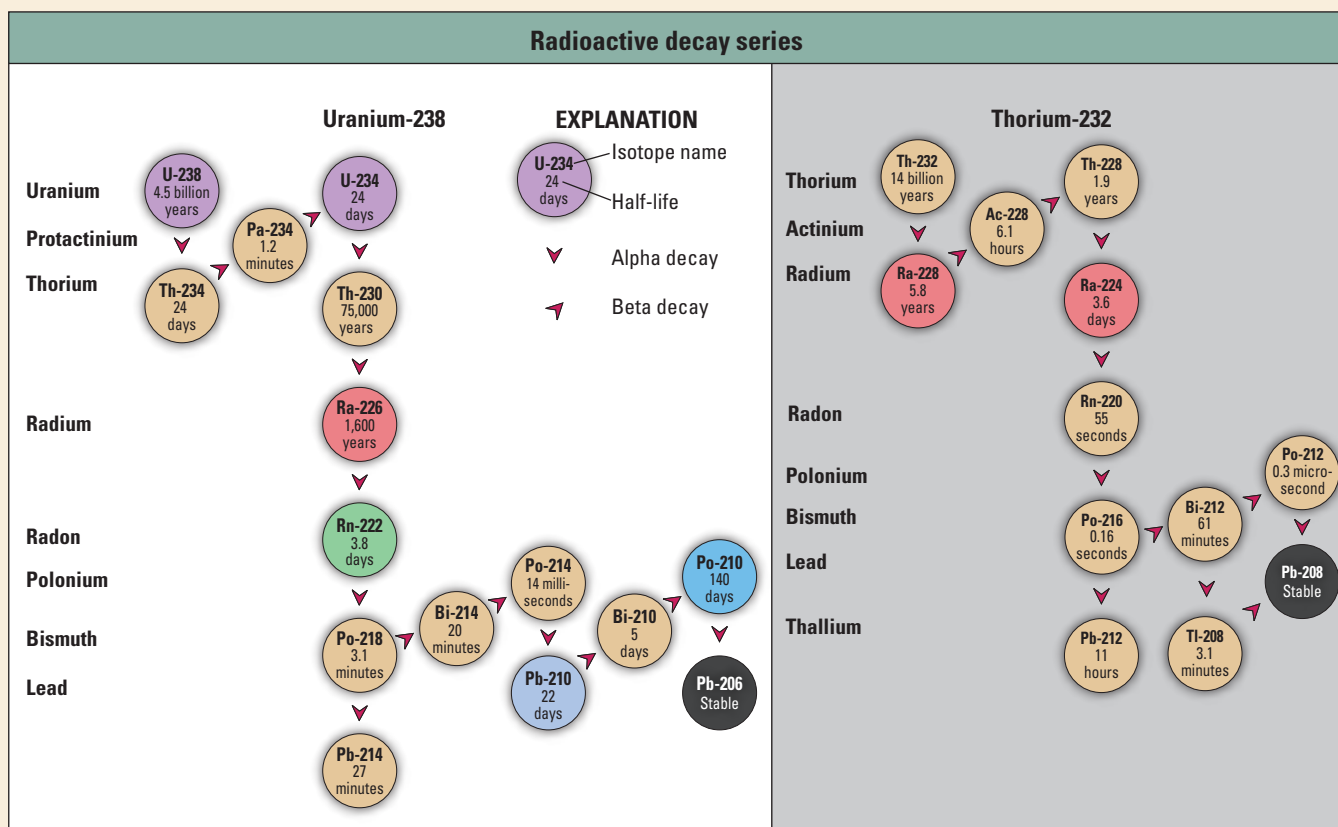
What are radionuclides and which ones are important in groundwater?

A radionuclide is an atom (element) with an unstable nucleus (core). The nucleus of the atom has excess energy that is released by different types of radioactive decay. Radionuclides in rocks and soils are produced naturally by the decay of radioactive parent elements such as uranium and thorium.

When an atom undergoes radioactive decay, it can become a different element, or it can become a different isotope of the same element. Isotopes are atoms of an element that contain the same number of protons (the same atomic number) but a different number of neutrons. For example, uranium-234, uranium-235, and uranium-238 each have 92 protons—which defines them as uranium—but the number of neutrons differs; the number after the element name refers to the number of protons plus neutrons in the atom. The most common mechanisms for radioactive decay are emission of alpha particles (loss of two protons and two neutrons) and emission of beta particles (loss of an electron). Through radioactive decay, parent isotopes produce intermediate radioactive daughter isotopes with predictable half-lives—the

time needed for half of the initial amount of a radionuclide to decay. The half-lives of isotopes vary from fractions of a second to billions of years.

Radioactive isotopes in water typically are measured by the amount of radioactive energy that is released from their decay, called activity. There are several different units used for measuring the activities of isotopes; picocuries per liter of water is the most commonly used unit in the United States. Uranium is an exception; it commonly is measured in water by its mass using micrograms per liter, which is a concentration rather than an activity. Nearly all the natural uranium in water is uranium-238, and activity and concentration units are consistently comparable for uranium. In this study, radon and radium were measured as activities and uranium was measured as a concentration, which is consistent with common practice and with the MCLs or other human-health benchmarks available for these constituents. For simplicity, however, both units of measurements are referred to as concentrations in this report.



Modified from Zapecza and Szabo⁽¹³²⁾

Natural radioactive decay series for parent elements uranium-238 and thorium-232. The radionuclides produced in these decay series include those that occur in groundwater and can pose health concerns in drinking-water sources (purple, red, and green circles). Polonium-210 (dark blue) and lead-210 (light blue) can also occur in groundwater under certain conditions and be health concerns, but few data are available on their concentrations in groundwater. Lead-206 and lead-208 (dark grey) are stable elements at the end of the decay series.

Radium

Radium can enter groundwater by dissolution of aquifer materials, by desorption from rock or sediment surfaces, and by release from minerals during radioactive decay. Radium-226 and radium-228 are the two most common isotopes of radium, and both are carcinogenic. Radium dissolved in drinking water is a human-health concern because it accumulates in bone and other tissues, thereby increasing lifetime cancer risks. The USEPA MCL for radium is 5 pCi/L for the combined concentration of radium-226 and radium-228.

Nationally, 3.2 percent of 1,270 wells for which samples were analyzed for radium-228 and (or) radium-226 had concentrations greater than the MCL for combined radium.^(43, 44) Elevated concentrations were more common in groundwater in the eastern and central United States than in other regions (fig. 5–11).

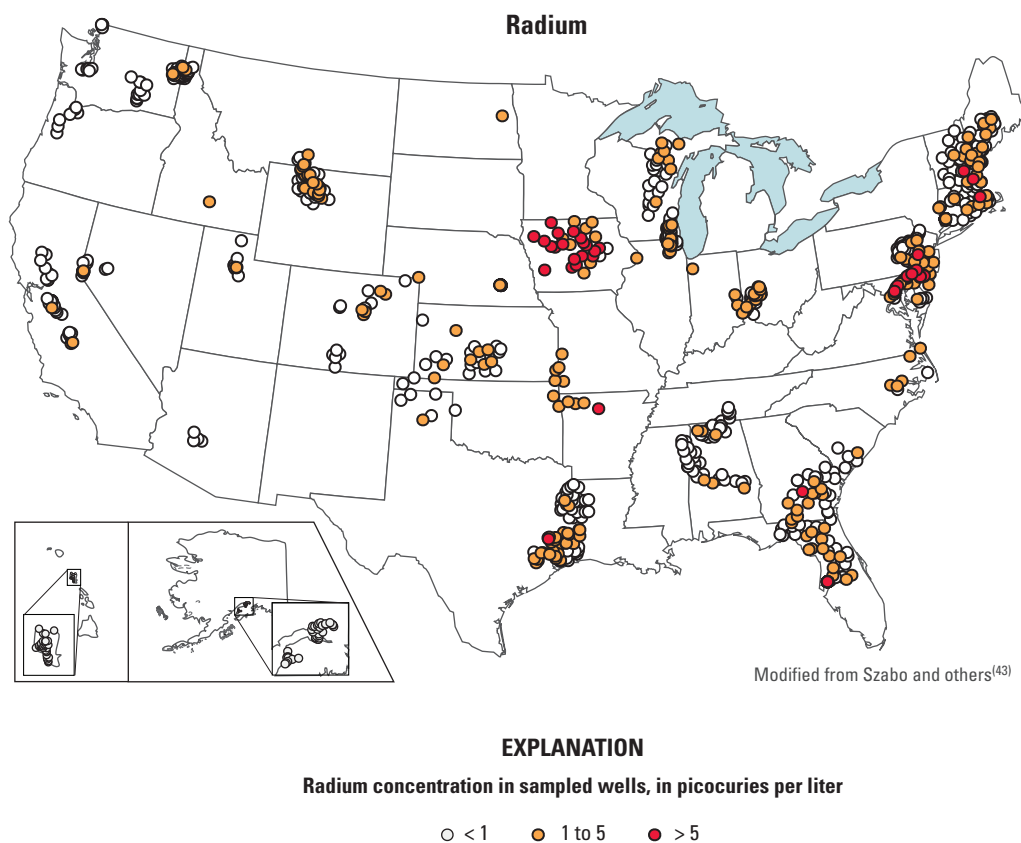


Figure 5–11. Nationally, about 3 percent of sampled wells had concentrations of radium greater than the MCL of 5 pCi/L. Nearly all these elevated concentrations were in the eastern and central United States. Radium data are shown here for individual wells, rather than grouped by groundwater study.

Aquifers with the highest combined radium concentrations were the Cambrian-Ordovician aquifers and Ozark Plateau aquifers (Iowa, Kansas, Missouri, Oklahoma, and Arkansas) and the Northern Atlantic Coastal Plain aquifer system (New Jersey, Delaware, Maryland, Virginia, and North Carolina). More than 20 percent of groundwater samples from these aquifers had concentrations of radium greater than the MCL (fig. 5–12). Concentrations of radium are high in these aquifers because geochemical conditions favor radium mobility rather than because the aquifer materials are enriched in uranium or thorium. Anoxic conditions, low pH, and high concentrations of dissolved solids (especially cations such as calcium, barium, and magnesium) hinder the sorption of radium onto aquifer sediments and thus favor the release of radium into the surrounding groundwater. The factors that enhance radium mobility also are quite different from those that favor the mobility of uranium. Although one of the common isotopes of radium (radium-226) is derived from uranium, high concentrations of uranium and radium rarely coincided in the Principal Aquifers studied.

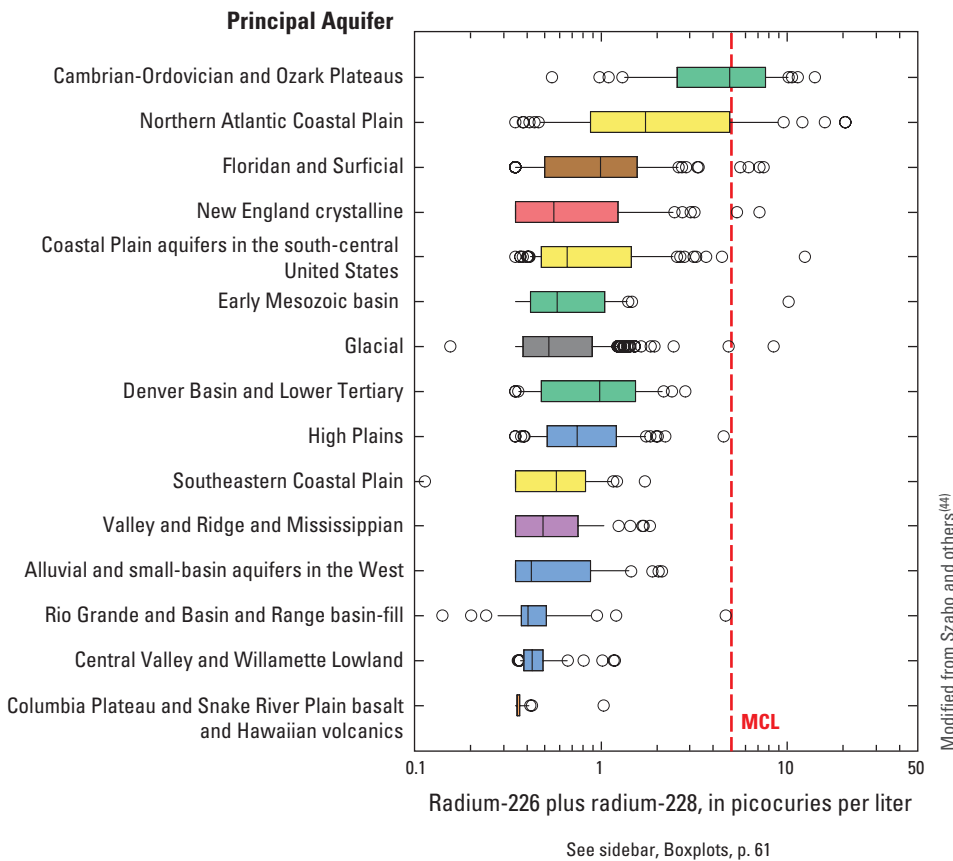


Figure 5–12. Concentrations of radium were higher than the MCL of 5 pCi/L in some wells in a number of aquifers, including the Cambrian-Ordovician and Ozark Plateau aquifers and the Northern Atlantic Coastal Plain aquifer system. Geochemical conditions rather than abundance of the parent elements uranium and thorium in aquifer materials were primarily responsible for these elevated concentrations.



Denver Basin Aquifer System—Redox Conditions and Uranium Concentrations Vary With Depth and May Be Changed by Human Activities

Layered sandstones make up the Denver Basin aquifer system, east of the Rocky Mountains in Colorado. Concentrations of uranium in drinking-water wells from deep parts of the aquifer system are low. However, 19 percent of samples of shallow groundwater from the shallow Dawson sandstone and overlying alluvial aquifer had concentrations of uranium greater than the MCL (fig. 5–13). This difference is because there is more dissolved oxygen in groundwater at shallow depths than deep in the aquifer system. Uranium, a trace component of the layered sandstones and sediments, is more soluble in oxygenated groundwater than in groundwater in which dissolved oxygen has been depleted. The decrease in dissolved oxygen with depth is natural; oxygen from the atmosphere is depleted by reactions with organic matter and reduced minerals as groundwater recharge moves further and deeper into the aquifer. Groundwater recharge from precipitation is very low, generally less than 1 inch per year. Irrigation and pumping for water supply, however, have increased the flow of oxygenated water into the aquifer and increased the rate at which groundwater moves downward.⁽⁷⁾ These changes have the potential to flush uranium and other constituents from the shallow aquifers into the deeper layers used for drinking water. More information and examples of how changes like these can alter groundwater quality are provided in chapter 7.

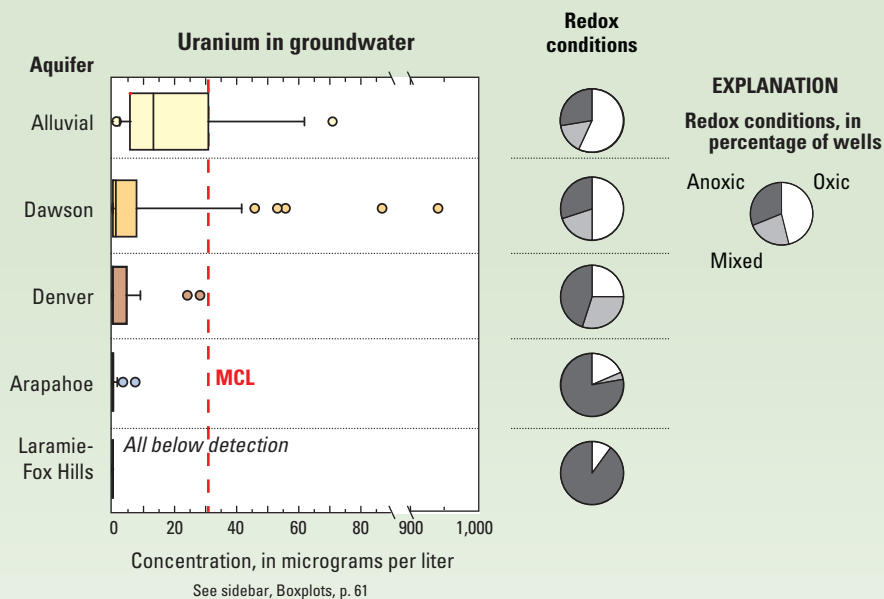
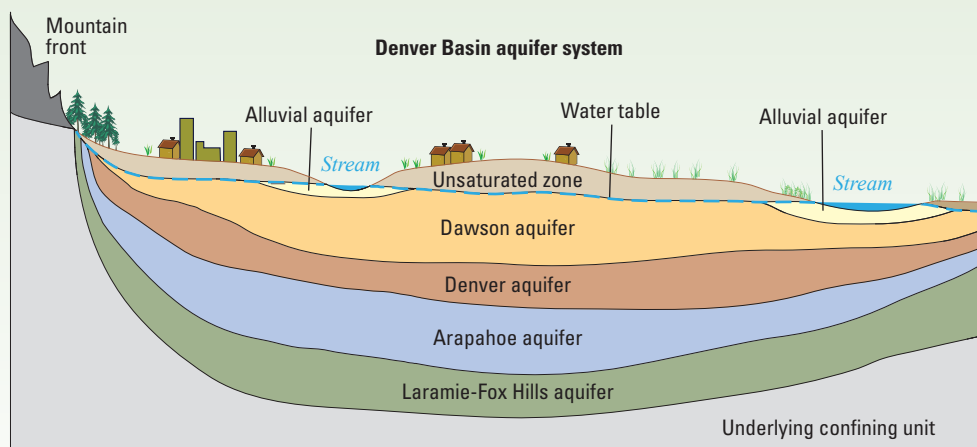


Figure 5–13. Uranium concentrations are much higher in shallow layers of the Denver Basin aquifer system than in deeper layers because oxic groundwater (water with dissolved oxygen) at shallow depths keeps the uranium dissolved. Nineteen percent of groundwater samples from the shallow alluvial and Dawson sandstone aquifers had uranium concentrations greater than the MCL of 30 µg/L, whereas no concentrations greater than the MCL were measured in samples from the deeper sandstone aquifers.

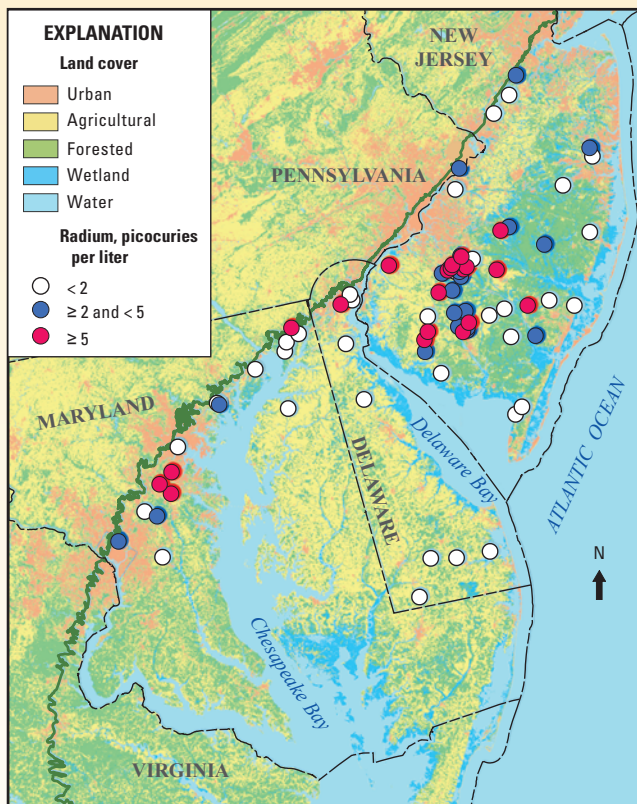
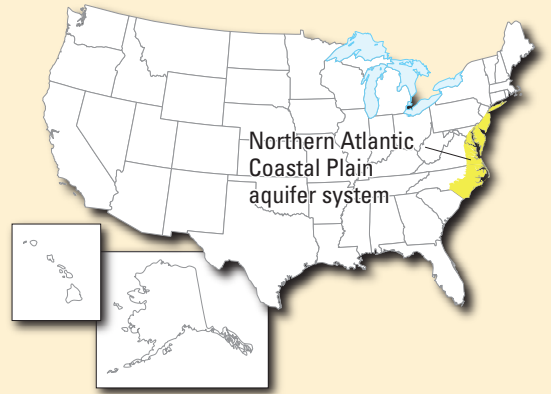


Northern Atlantic Coastal Plain Surficial Aquifer System— Naturally Acidic Waters and Elevated Radium

Weathered, quartz-rich sediments in the Northern Atlantic Coastal Plain surficial aquifer system have little capacity to buffer the pH of naturally acidic rainfall and soil water. Consequently, groundwater in this aquifer system typically is acidic; the median pH of groundwater from wells in aquifer studies was about 5. These conditions are optimal for dissolving or desorbing radium from aquifer sediments and contribute to the elevated concentrations of radium^(43–45) in parts of the aquifer system (fig. 5–14).

Groundwater concentrations of radium also were greater in agricultural areas than in nonagricultural areas^(45, 46) in parts of the Northern Atlantic Coastal Plain aquifer system (see chapter 7). The influx of nitrogen from fertilizer and septic-system effluent can enhance the natural acidity of groundwater in the aquifer because geochemical reactions that transform organic nitrogen and ammonia to nitrate (including nitrification; see chapter 3) also generate hydrogen ions (acidity). Lime commonly is applied where nitrogen fertilizers are used, and resulting ion-exchange reactions involving ions in the lime also can stimulate the release of radium from aquifer sediments into the groundwater. Radium concentrations decrease with depth in these areas as acidic groundwater is slowly neutralized (the pH is increased) by geochemical reactions with aquifer sediments.

The presence of radium at concentrations greater than the MCL has led to new guidelines for the testing of domestic wells in parts of Maryland and New Jersey.^(47, 48) Because radium generates most of the gross alpha radiation (see sidebar, What are radionuclides and which ones are important in groundwater?, p. 63) in acidic groundwater of the Northern Atlantic Coastal Plain aquifer system, testing for gross alpha radiation, which is relatively quick and inexpensive, is used to identify groundwater that is likely to contain elevated concentrations of radium.⁽⁴⁹⁾ Radium can be remediated (lowered or removed) in drinking water with a well-maintained water softener (cation-exchange) system^(44, 50) or by many other options.



Modified from Denver and others⁽⁴⁵⁾

Figure 5–14. Concentrations of radium exceeded the MCL of 5 pCi/L in the Northern Atlantic Coastal Plain aquifer system in areas with well-weathered quartz-rich sediments and naturally acidic groundwater and in areas of agricultural and urban land use. In agricultural and urban areas, the groundwater can become more acidic as the result of biogeochemical reactions involving applied nitrogen compounds.⁽⁴⁹⁾

Manganese

Manganese is a nuisance in water supplies because it stains plumbing and laundry, but it can be a health concern as well because it can cause neurological effects at elevated concentrations.^(51, 154) Manganese is a metallic element that is present in igneous, metamorphic, and sedimentary rocks. Though common in aquifer rocks and sediments, manganese occurs in groundwater only when concentrations of dissolved oxygen are low.

Nationwide, concentrations of manganese were greater than the human-health benchmark of 300 µg/L in about 7 percent of the wells sampled in the parts of aquifers used for drinking water (table 4–1). Redox conditions were clearly important—manganese concentrations were much greater in anoxic groundwater (concentrations of dissolved oxygen less than 0.5 mg/L) than in oxic groundwater, and no concentrations greater than the benchmark were measured in oxic groundwater (fig. 5–15). Concentrations generally were higher in the eastern United States than in the West (fig. 5–16), reflecting broad regional patterns in redox conditions (fig. 3–9). Anoxic conditions are more common in the glacial, semiconsolidated sand, sandstone, and carbonate-rock aquifers—largely, aquifers in the eastern United States—than in the unconsolidated sand and gravel and basaltic-rock aquifers of the western United States. However, redox conditions can be quite variable within most aquifers, and manganese concentrations greater than the human-health benchmark were measured across the Nation and in at least one well in more than half the aquifers included in this study (fig. 5–17).

Manganese in anoxic and oxic groundwater

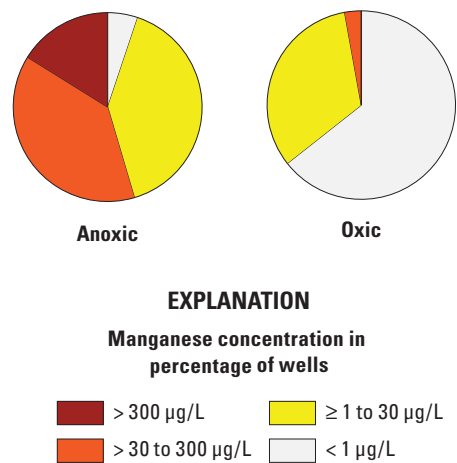


Figure 5–15. Manganese concentrations were much higher in anoxic groundwater than in oxic groundwater.

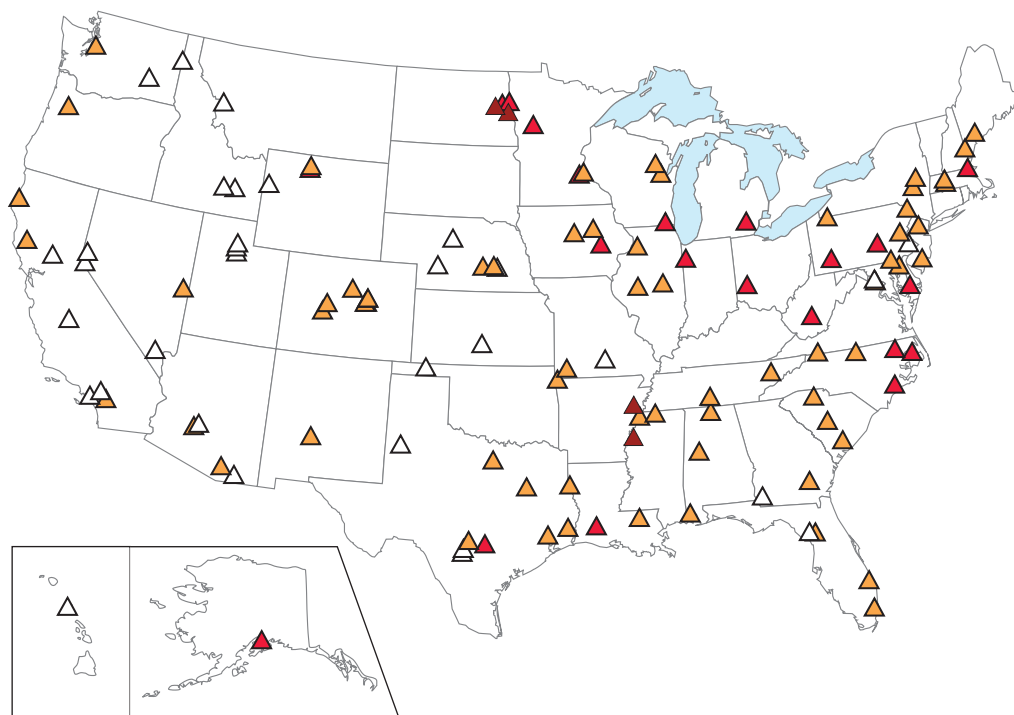


Photograph By D.R. Leblanc, USGS

Manganese dissolved in anoxic, sewage-contaminated groundwater flows to the shore of this pond on Cape Cod, Massachusetts. When the manganese comes into contact with the oxygen in the atmosphere, it oxidizes and precipitates, forming the dark colored manganese oxide coatings on cobbles along the shoreline.

Manganese

Parts of aquifers used for drinking water



EXPLANATION

Median manganese concentration per study, in micrograms per liter

Each symbol represents a study network of 20 to 30 wells,
mostly domestic supply wells

△ <1 ▲ 1 to 30 ▲ >30 to 300 ▲ >300

Figure 5–16. Manganese concentrations generally were higher in the eastern United States than in the West. Oxygenated groundwater, which limits manganese solubility, is common in the unconfined, unconsolidated sand and gravel and basaltic-rock aquifers of the western United States.

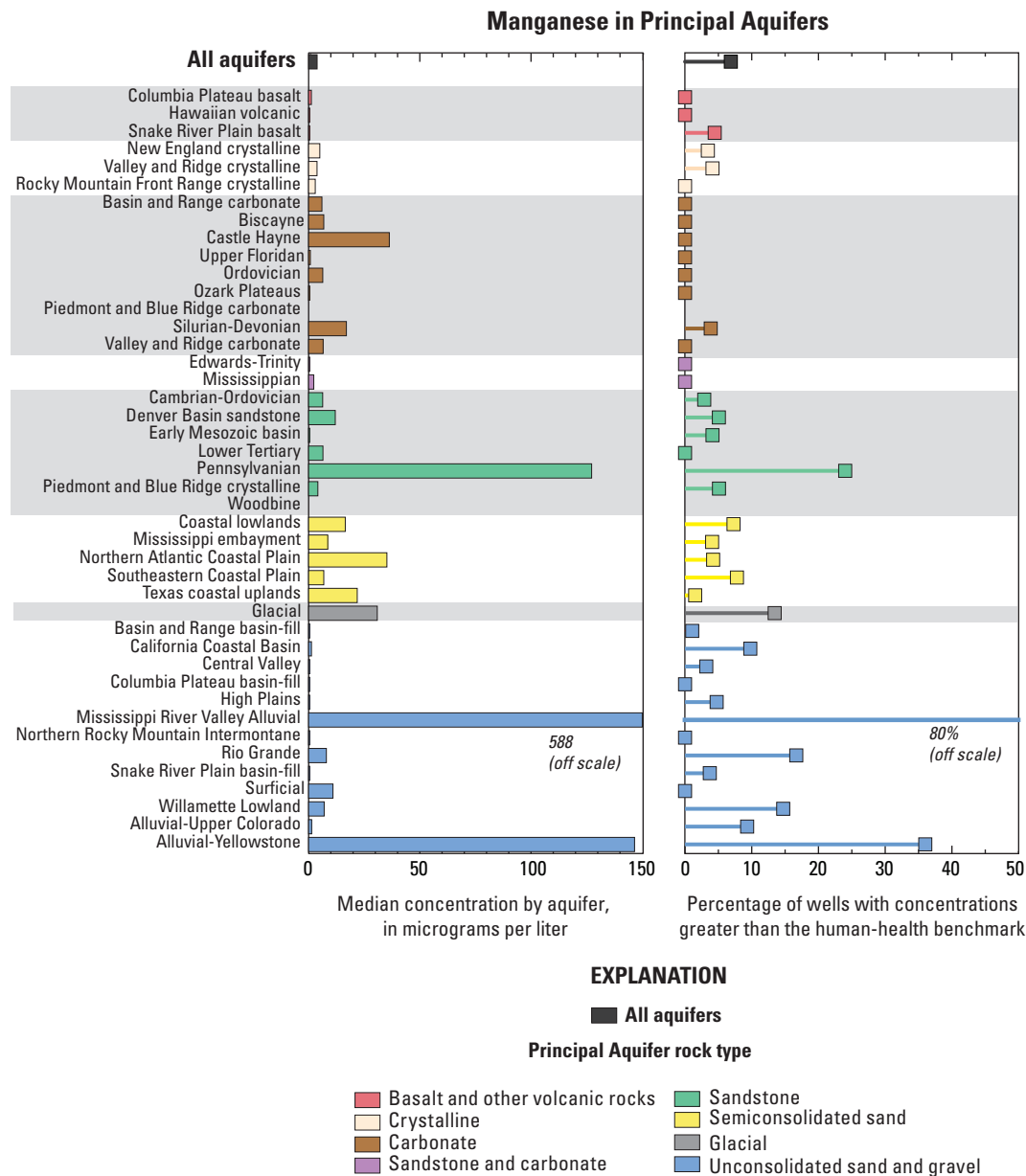
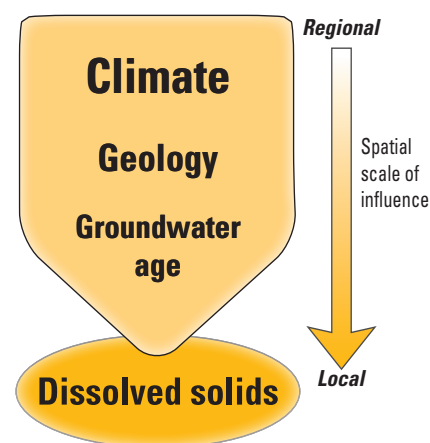


Figure 5–17. Concentrations of manganese greater than the human-health benchmark of 300 µg/L were measured in at least one well in more than half the aquifers included in this study and in aquifers all rock types.

Dissolved Solids

Is the water freshwater or salt water? This question is answered by the water's concentration of dissolved solids, which is a basic characteristic of all natural waters. Freshwater generally has dissolved solids concentrations less than 1,000 mg/L.⁽¹⁷⁾ Even in freshwater, however, dissolved solids in water can cause problems that impair water use. These problems include unpleasant taste, higher water-treatment costs, accumulation of minerals in plumbing, staining, corrosion, reduced equipment lifespan, and restricted use for irrigation. Concentrations less than 500 mg/L are recommended by the USEPA for public water supplies to avoid these problems in drinking water. When used for irrigation, water with high dissolved solids can reduce crop yield because the dissolved salts make it more difficult for plants to extract water from the soil. Dissolved solids in irrigation water can cause salts to build up in soils and aquifers (salinization) and can eventually make the land unsuitable for agriculture (see chapter 7 for more information).

Climate, geology, and groundwater age influence concentrations of dissolved solids in groundwater. Climatic differences extend across the widest spatial scales and result in broad regional patterns in concentrations. Geology and groundwater age vary at spatial scales from regional (such as differences in rock type among regionally extensive Principal Aquifers) to local (such as differences in geology or groundwater age with depth in an aquifer). Human activities can also influence concentrations of dissolved solids at a variety of scales, across large irrigated areas or at the sites of individual septic systems or pumping wells.



What are dissolved solids?

The sum of all the substances, organic and inorganic, dissolved in water is measured by the total concentration of dissolved solids in the water. Calcium, magnesium, sodium, potassium, bicarbonate, sulfate, chloride, nitrate, and silica typically make up most of the dissolved solids in water. Combinations of these ions—sodium and chloride, for example—form salts, and salinity is another term that commonly is used to describe the dissolved solids content of water. All natural waters contain some dissolved solids from contact with soils, rocks, and other natural materials.

Groundwater typically is considered freshwater, but saline groundwater is present in some aquifers near the coast, in arid climates, or at great depths. Slightly saline water (dissolved solids between about 1,000 and 3,000 mg/L) is used for domestic supply in areas where no other water source is available, but moderately saline water (dissolved solids between about 3,000 and 10,000 mg/L) generally is too salty to drink.⁽¹³³⁾

Saline groundwater lies beneath fresh groundwater across much of United States.^(133, 134) In some cases, the deep saline groundwater comes from seawater that was buried with the sediments when they were deposited in ancient oceans and bays. In other cases, saline water is the result of interaction

Natural waters can have a wide range of concentrations of dissolved solids.

Term	Dissolved solids concentration, in milligrams per liter
Fresh	Less than 1,000
Saline	1,000 to 35,000
Ocean water	About 35,000
Brine	Greater than 35,000

with deeply buried salt deposits or with other types of rocks and sediments over tens of thousands of years.^(135–137) Deep saline groundwater can mix with the overlying fresh groundwater when it travels upwards naturally along geologic faults or at the ends of long, regional flow paths. Saline water also underlies fresh groundwater along the coasts in a mixing zone where groundwater meets ocean water. Pumping wells can draw saline water inland and upwards into freshwater aquifers; this problem, called saltwater intrusion, is common in coastal settings (see chapter 7 for more information).

Climate affects dissolved solids because of differences in precipitation, evapotranspiration, and recharge rates; geology affects dissolved solids because some types of rocks are more resistant than others to weathering.

Climate affects concentrations of dissolved solids in groundwater through precipitation, evapotranspiration, and groundwater recharge. Where precipitation is low and evaporation rates are high, there is less water to dilute the products of rock weathering than in humid regions where precipitation and groundwater recharge are abundant. Consequently, dissolved solids are relatively high in the warm, dry parts of the western United States (fig. 5–18). Evaporation of shallow groundwater, where the water table is near the land surface, is another process that concentrates dissolved solids in groundwater in arid regions.

Geology affects dissolved solids concentrations because some types of rocks are more resistant to weathering than others. Some sedimentary rocks, such as shales, carbonate rocks, and evaporites, are more soluble and easily weathered than quartz-rich sandstones or crystalline rocks such as granites. Such easily weathered rocks in the mountains and basin-fill sediments of the Southwest contribute to the relatively high dissolved solids in unconsolidated sand and gravel aquifers in this region (figs. 5–18 and 5–19). In the East, concentrations of dissolved solids are relatively low in aquifers composed of materials that are resistant to weathering, such as the semiconsolidated sand aquifers of the Atlantic and Gulf of Mexico coastal plains and the crystalline-rock aquifers in the Northeast and mid-Atlantic region (fig. 5–19). Some of the highest concentrations of dissolved solids were measured in wells in the Lower Tertiary sandstone aquifer and the alluvial aquifer of the Yellowstone River Basin in Wyoming and Montana (fig. 5–19), which are in areas with abundant geothermal features. Geothermal water, another geologic source, typically is high in concentrations of dissolved solids and is found locally throughout the western States.⁽⁵²⁾

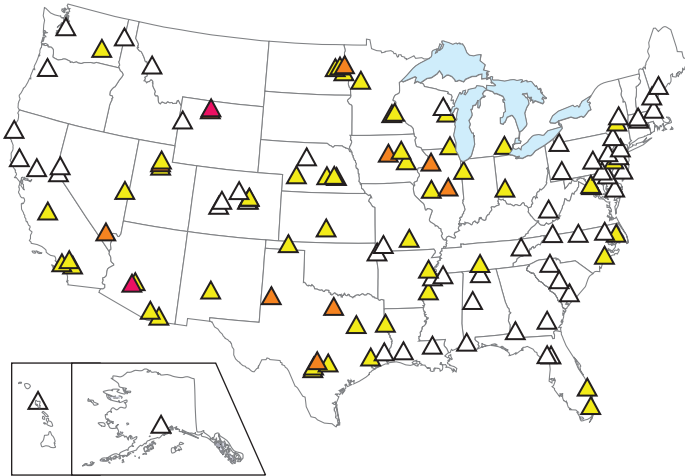


Photographs by Michael Rosen, USGS

Where the climate is very dry (top), salt deposits build up on the land surface from the evaporation of soil water and shallow groundwater. The groundwater left behind can have very high concentrations of dissolved solids as a result. Geothermal water—water that has been heated by magma or hot rocks in the subsurface (bottom)—contains high concentrations of dissolved solids, partly because most rock-water reactions are more intense at high temperatures. Mixing with geothermal water is another source of high dissolved solids in groundwater. Both photographs are from the Dixie Valley in central Nevada.

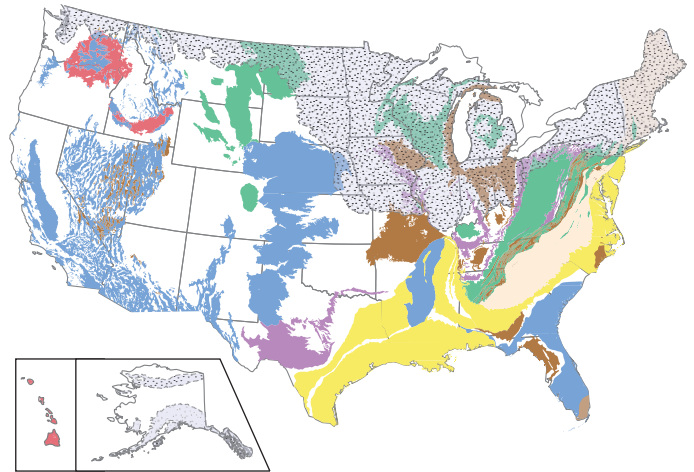
Dissolved solids

Parts of aquifers used for drinking water

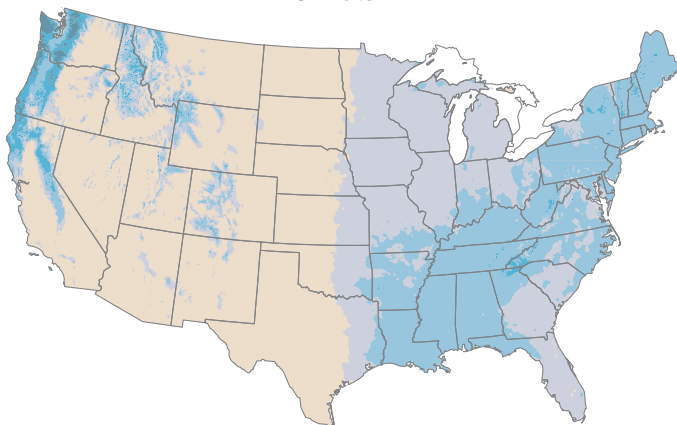
**EXPLANATION****Median dissolved solids concentration per study, in milligrams per liter**

Each symbol represents a study network of 20 to 30 wells, mostly domestic supply wells

△ <250 △ 250 to 500 △ >500 to 1,000 △ >1,000

Principal Aquifer rock type**EXPLANATION**

- | | |
|---------------------------------|--------------------------------|
| Basalt and other volcanic rocks | Sandstone |
| Crystalline | Semiconsolidated sand |
| Carbonate | Glacial |
| Sandstone and carbonate | Unconsolidated sand and gravel |

ClimateModified from Healy and others⁽¹⁸⁰⁾**EXPLANATION****Precipitation minus potential evapotranspiration, in inches per year**

- | | |
|-------------|-----------|
| < -63 to 0 | 34 to 72 |
| > 0 to 12.5 | 72 to 267 |
| 12.5 to 34 | |

Figure 5-18. Dissolved solids were generally higher in the southwestern and central United States and lower in the East and Northwest. Climate and aquifer rock type influence dissolved solids concentrations at national and regional scales.

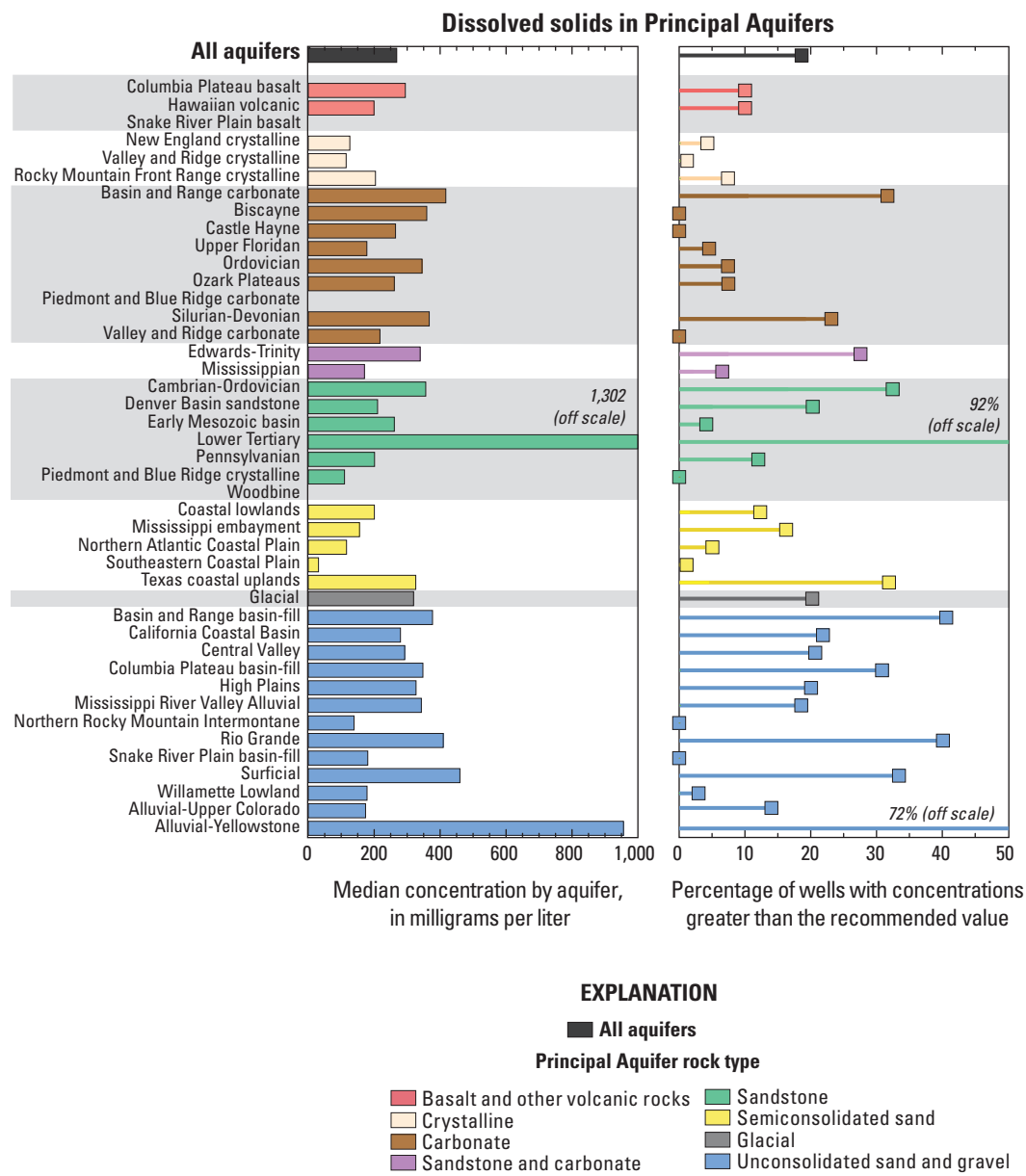


Figure 5–19. Median concentrations of dissolved solids were between 100 and 400 mg/L in most aquifers, but concentrations greater than 500 mg/L—the upper limit recommended by the U.S. Environmental Protection Agency for public water supplies—were measured in some wells in nearly all aquifers. Nationally, 18 percent of wells had concentrations greater than the recommended value. Dissolved solids at these concentrations can restrict the use of water for irrigation as well as for drinking.

Groundwater that has been in an aquifer for a long time has had more time to react with aquifer materials than has groundwater that has been recharged recently. Consequently, dissolved solids concentrations tend to be higher in aquifers with long flow paths and old groundwater than in shallow aquifers with relatively short travel times between recharge and discharge areas. For example, dissolved solids concentrations are high in deep, confined aquifers with long groundwater residence times in the glacial and Cambrian-Ordovician aquifer systems in the upper Midwest (figs. 5–18 and 5–19). Within an aquifer, concentrations of dissolved solids generally increase with depth in the aquifer and with distance along flow paths.

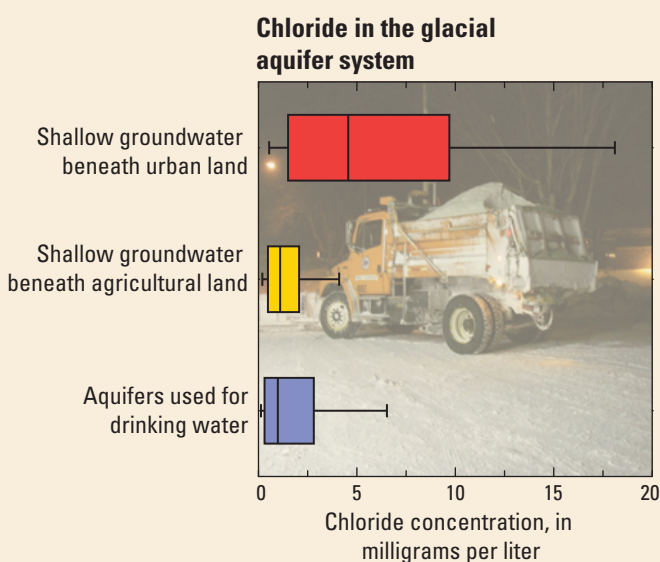
Human activities can add dissolved solids to recharging groundwater. Detergents, water softeners, fertilizers, road salt, urban runoff, and animal and human waste are some of the human sources that are delivered to groundwater by wastewater disposal, septic systems, or direct application to land surface. Irrigation can cause dissolved solids in groundwater to increase in arid and semiarid regions (see chapter 7). As a result, dissolved solids concentrations may be higher in shallow, recently recharged groundwater near the water table beneath urban, suburban, or agricultural areas than in shallow groundwater beneath undeveloped areas or in deeper groundwater.

Dissolved solids typically are higher in aquifers with long flow paths and old groundwater than in aquifers with short travel times.

Urbanization and chloride—A concern for streams

Chloride is a major component of dissolved solids, and is a good indicator of human influence on groundwater quality because it is present in wastewater and does not react with aquifer materials or other dissolved chemicals in dilute water. The application of road salt—sodium chloride, the same chemical as table salt—for deicing is also a major manmade source of chloride to groundwater in the northern United States. The use of road salt in the United States has more than doubled since 1980, while other uses of salt have remained stable or decreased.^(138, 139)

In the glacial aquifer system, which extends across the northern United States, chloride concentrations were highest in shallow groundwater beneath urban areas, reflecting the use of deicing salt and the many other manmade sources of chloride in urban and suburban areas.⁽¹¹⁶⁾ Shallow groundwater in the glacial aquifer system typically discharges to streams, providing the base flow that makes up most of the water in streams during periods of low flow. Elevated concentrations of chloride in groundwater discharging to streams are an ecological concern because chloride is toxic to aquatic organisms. Moreover, chloride concentrations in groundwater are increasing across the Nation (see chapter 8). Because of concerns about environmental effects and to reduce costs, many cities are taking measures to reduce salt applications or are introducing alternative deicing chemicals.⁽¹⁴⁰⁾





Dissolved Solids in the High Plains Aquifer—*Climate Effects and Vertical Gradients*

The High Plains aquifer extends across a broad region of the central United States, from South Dakota to Texas. Concentrations of dissolved solids increase from northern parts of the aquifer to southern parts, reflecting differences in climate and recharge rates (fig. 5–20). Warm air temperatures in the south increase evapotranspiration and decrease recharge, leading to the accumulation of dissolved solids in the unsaturated zone and underlying groundwater.⁽⁵³⁾

Concentrations of dissolved solids in the High Plains aquifer also vary with depth as a result of natural processes and human influences.

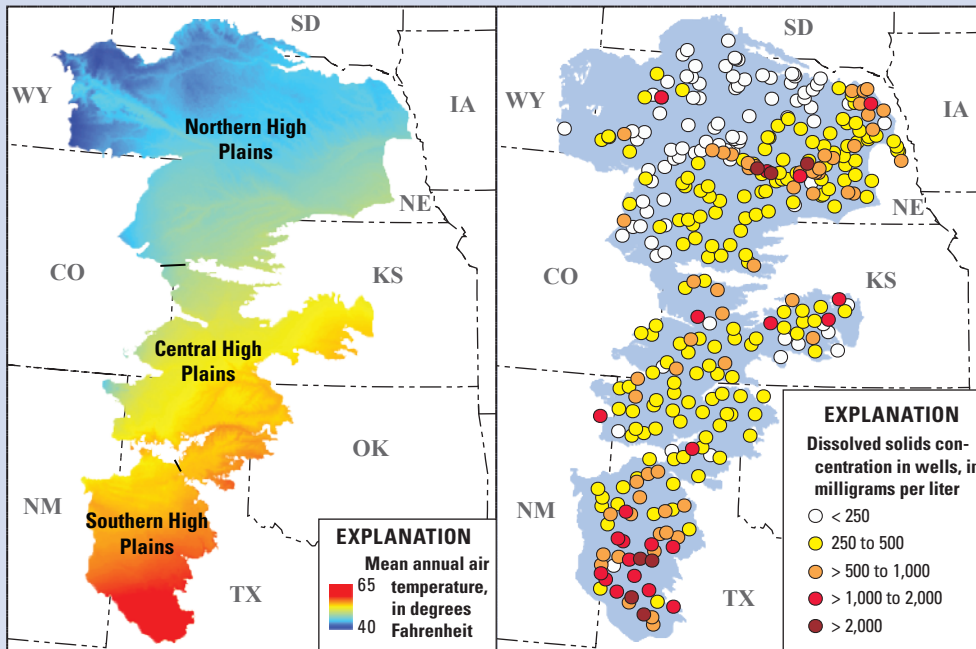
Deep groundwater in the High Plains aquifer is thousands of years old, whereas groundwater near the water table is much younger.^(53–56) Where the natural flow system in the High Plains aquifer is undisturbed and manmade sources are absent, concentrations of dissolved solids increase gradually with depth because the older, deep groundwater has had more time to react with aquifer sediments than the younger, shallow groundwater (fig. 5–21A). Parts of the High Plains aquifer are in contact with underlying geologic formations that contain deep saline groundwater.⁽⁵⁷⁾ In these parts of the aquifer, concentrations of dissolved solids can be very high. For example, concentrations near the bottom of the High Plains aquifer, at a site in the central High Plains, were more than 10 times greater than the concentrations of recently recharged groundwater at the water table (fig. 5–21B). The natural upwelling of saline water at this location is likely augmented by pumping deep wells for water supply, which draws water toward the wells from all directions. Conversely, where human activities, such as irrigated agriculture, are widespread, concentrations of dissolved solids at the top of the aquifer, near the water table, are likely to be higher than concentrations deeper in the aquifer (fig. 5–21C).



Photograph by Bill Johnson, The University of Kansas, courtesy of the Kansas Geological Survey

The High Plains aquifer is a sequence of layered sediments beneath the central United States. It is the Nation's largest aquifer, providing 20 percent of all groundwater pumped nationally, and is the sole source of drinking water for most of the region's population. This photograph shows an outcrop of the Ogallala Formation, which is the primary hydrogeologic unit of the High Plains aquifer.

Climate and dissolved solids concentrations in the High Plains aquifer

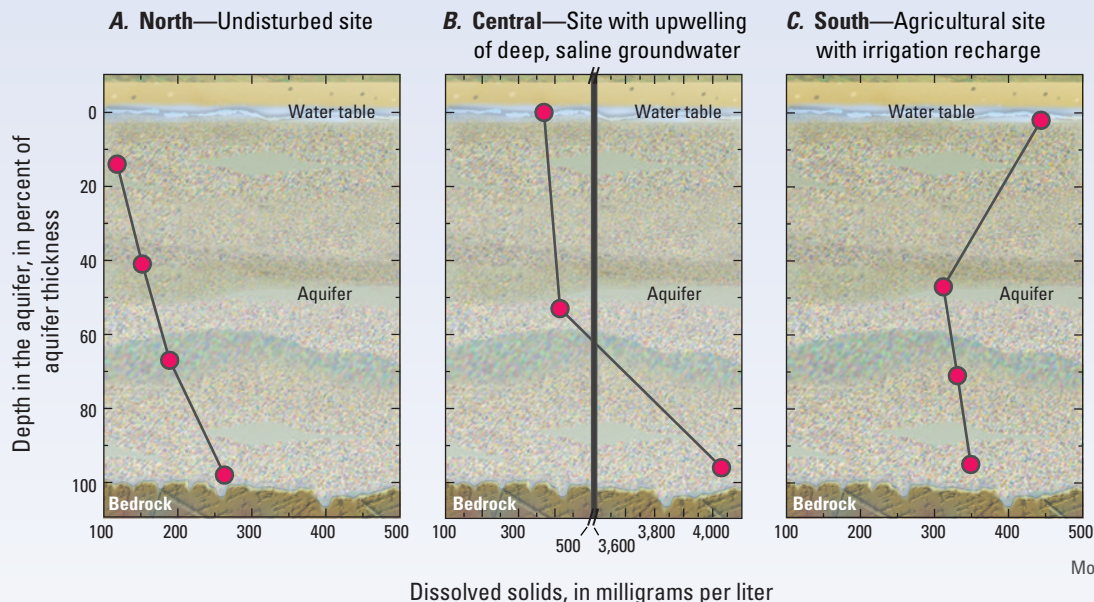


Base from U.S. Geological Survey digital data, 1:100,000
Albers equal-area projection
Standard parallels N 29°30' and 45°30', central meridian W -96°

Modified from McMahon and others⁽⁵⁶⁾

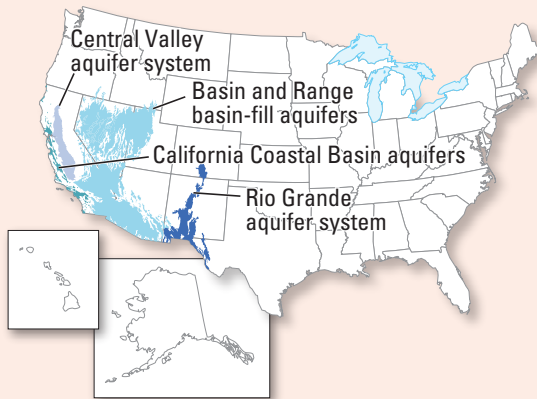
Figure 5-20. Dissolved solids concentrations in the High Plains aquifer increase from north to south, following broad regional patterns in climate. Data are from domestic wells in the Ogallala aquifer, the primary hydrogeologic unit in the aquifer system.

Vertical gradients in dissolved solids in the High Plains aquifer



Modified from McMahon and others⁽⁵⁶⁾

Figure 5-21. Dissolved solids concentrations typically increase with depth in the High Plains aquifer, but human activities can reverse the natural vertical gradient. *A*, Concentrations increase gradually with depth at a site in the northern High Plains in Lincoln, Nebraska, where the natural flow system is undisturbed and manmade sources are absent. *B*, Concentrations increase sharply near the bottom of the aquifer at a site near in the central High Plains in Cimarron, Kansas, where brackish water from underlying geologic layers has moved up into the aquifer because of regional groundwater flow and pumping of deep wells. *C*, In an agricultural area in the southern High Plains near Castro, Texas, irrigation recharge with higher concentrations of dissolved solids than would occur with natural recharge has increased concentrations in shallow groundwater, reversing the natural increase with depth.



Dissolved Solids in the Southwest Basin-Fill Aquifers—*Climate, Geology, Hydrology, and Human Activities All at Work*

In the unconsolidated sand and gravel basin-fill aquifers of the southwestern United States, all the factors that can result in elevated dissolved concentrations are at work (chapter 7)—a dry climate, easily weathered rocks, long groundwater flow paths, and human sources that include irrigation, wastewater, and urban runoff.^(28, 29) The hot, dry climate of the Southwest means that evapotranspiration rates are high; evapotranspiration concentrates the dissolved solids in precipitation, in artificial recharge, and in shallow groundwater in discharge areas. Sedimentary rocks that include carbonate and evaporite units are easily weathered and contribute to high concentrations of dissolved solids in parts of the basin-fill aquifers. Long

flow paths mean that interactions between water and aquifer rocks or sediments can occur over long periods of time for all rock types. Irrigation and the infiltration of wastewater or urban runoff are intense in some heavily developed basins.

Concentrations of dissolved solids can become so high in parts of the Southwest basin-fill aquifers that the groundwater is unsuitable for drinking, irrigation, or other uses.⁽²⁹⁾ Concentrations of dissolved solids greater than the recommended (SMCL) value for drinking water of 500 mg/L were measured in 20 to 40 percent of wells sampled in the parts of the four basin-fill aquifers used for drinking water (Basin and Range basin-fill, California Coastal Basin, Central Valley, and Rio Grande aquifers or aquifer systems, figure 5–19). Concentrations of dissolved solids greater than the SMCL were measured in 40 to 60 percent of shallow wells beneath agricultural or urban land in the four Southwest basin-fill aquifers. Concentrations greater than 10,000 mg/L are present in topographically low areas of closed basins, such as the Great Salt Lake Desert in western Utah and the Salton Sea in southern California (fig. 5–22).

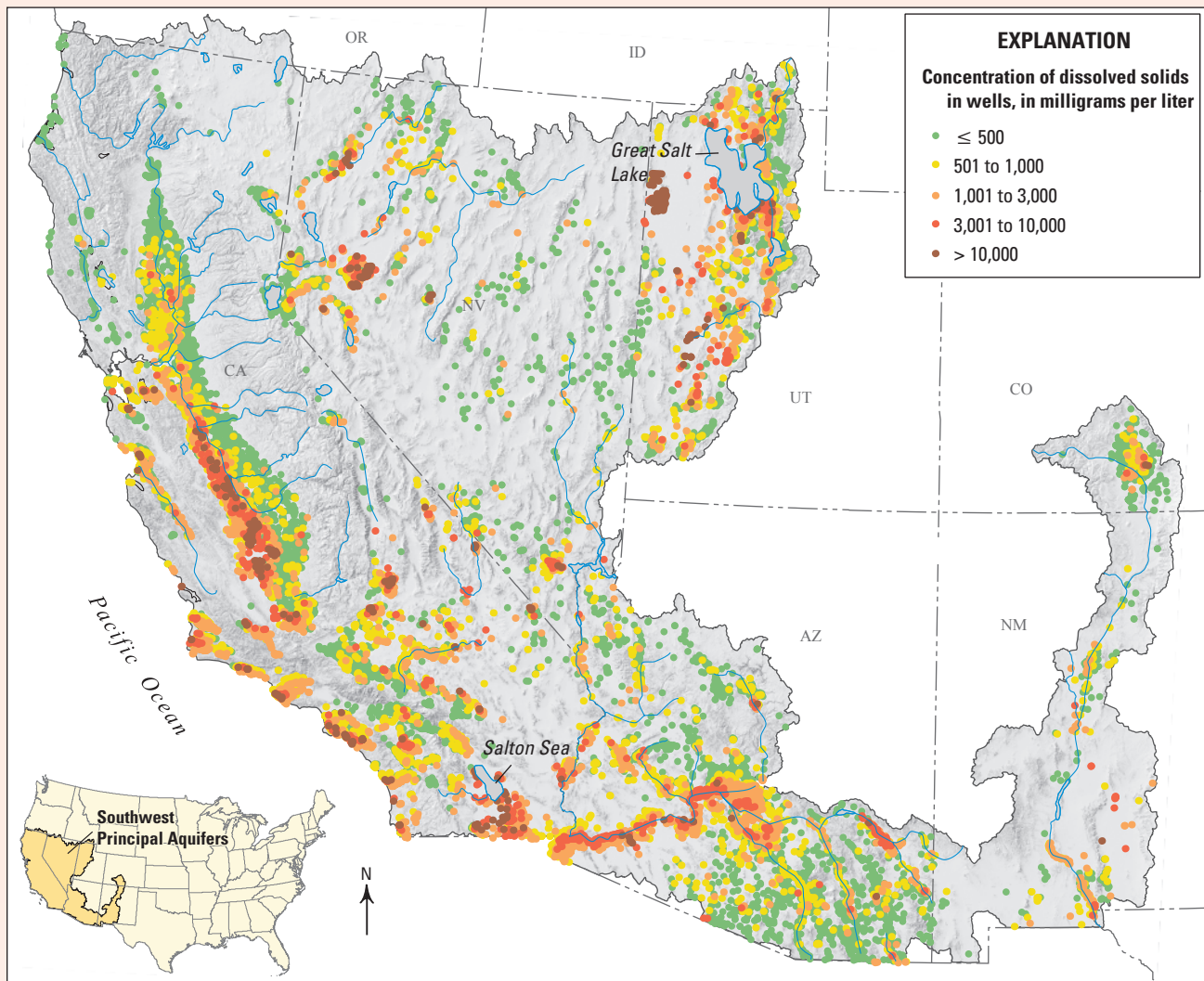
Dissolved solids in the Southwest basin-fill aquifers

Figure 5–22. High concentrations of dissolved solids are common in the Southwest basin-fill aquifers. Dissolved solids concentrations shown on this map were measured in water from more than 21,000 wells, primarily water-supply wells, sampled for numerous U.S. Geological Survey studies in the region. More than half of the wells had concentrations greater than the recommended upper limit of 500 mg/L.

Hardness—A common problem for water supplies from groundwater sources

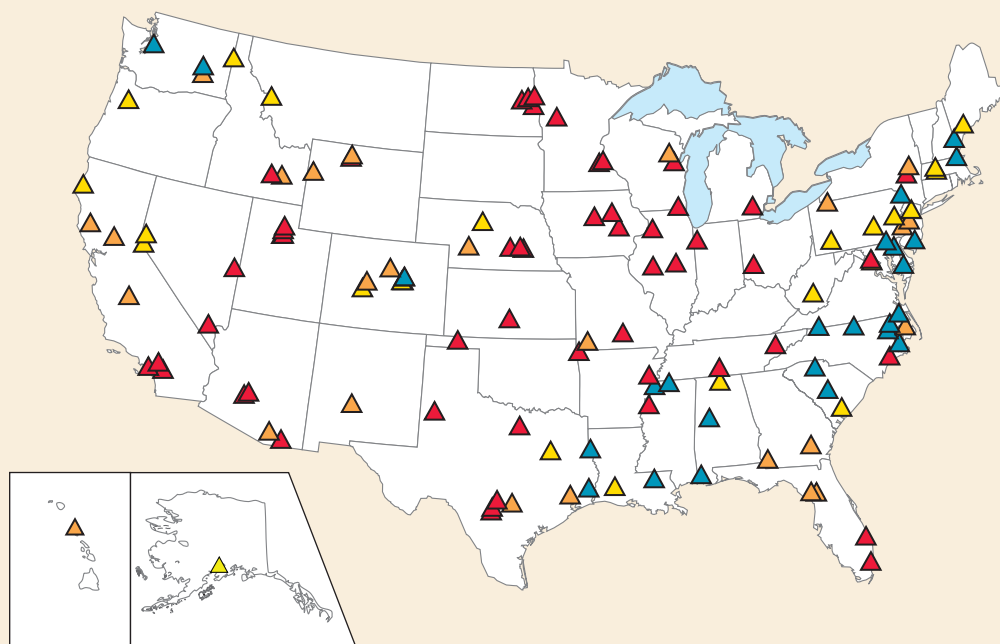
Hardness refers to a property of water that makes it react poorly with soap—forming scum rather than suds—and sometimes leave scale deposits in pipes and water heaters. Hardness is mostly caused by dissolved calcium and magnesium. Nationally, about 60 percent of groundwater samples from parts of aquifers used for drinking water had hard or very hard water, and about 20 percent had naturally soft water. Areas with hard groundwater usually also have high concentrations of dissolved solids because calcium and magnesium are two of the major components of dissolved solids in groundwater. Groundwater in carbonate-rock aquifers typically is hard because calcium and magnesium are released into groundwater when carbonate rocks dissolve. Hard water can be treated with water softeners, which replace the dissolved calcium and magnesium with sodium or potassium. Costs of household water softeners typically average from about \$500 to \$2,000 for installation, with additional costs for maintenance.⁽¹⁴¹⁾



Photograph copyright istockphoto.com

Hardness

Parts of aquifers used for drinking water



EXPLANATION

Median hardness, in milligrams per liter as calcium carbonate

Each symbol represents a study network of 20 to 30 wells, mostly domestic supply wells

- | | |
|-------------------------------|-------------------|
| Soft (< 60) | Hard (120 to 180) |
| Moderately hard (60 to < 120) | Very hard (> 180) |

Aquifers of several rock types in the western and central United States and carbonate and some sandstone aquifers in the East had hard or very hard water. These are many of the same aquifers and regions that have high concentrations of dissolved solids.

Chapter 6: *Understanding Where and Why Contaminants From Human Activities Occur*

Activities associated with agriculture, industry, and urbanization all can contribute contaminants to groundwater. Many of these contaminants, such as industrial solvents and pesticides, are manmade chemicals that have no natural sources. Others, such as nitrate and chloride, have geologic sources, but human activities greatly increase their concentrations in groundwater relative to natural levels. Where, when, and how chemicals are used influence the occurrence of these contaminants in groundwater. Chemical characteristics influence how contaminants are transported through soils and in groundwater; geochemical processes and biodegradation can alter contaminant concentrations as they move along flow paths.

This chapter describes the sources of and factors that affect nitrate, pesticides, and VOCs in the Principal Aquifers.

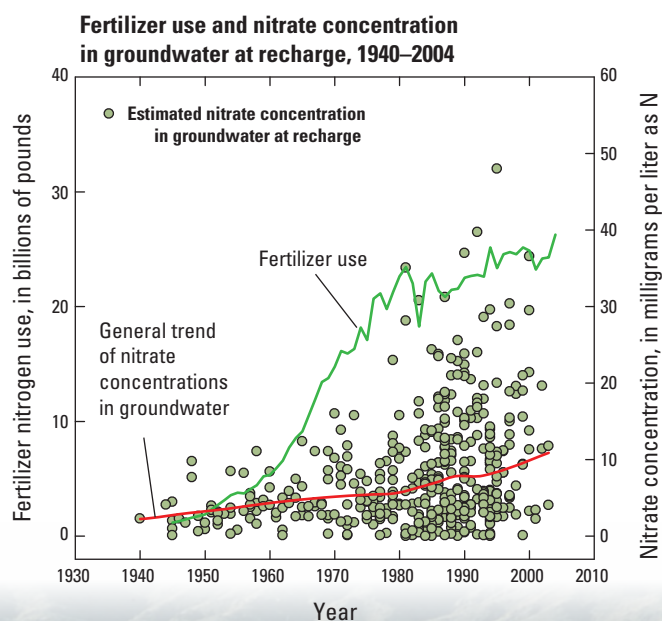


Nitrate

Nitrogen is an essential nutrient for all living things. It is abundant, as gaseous nitrogen (N_2), in the air we breathe. Bacteria convert N_2 to biologically available forms—organic nitrogen, ammonium, and nitrate. Most of the nitrogen in groundwater is in the form of nitrate.

Synthetic fertilizer use, waste disposal, and fossil-fuel combustion have greatly increased the amount of biologically available nitrogen in the environment.^(58, 59) As a result, concentrations of nitrate, the primary form of nitrogen in groundwater, have increased (fig. 6–1). Nitrate in groundwater used for drinking water is a health concern, and the USEPA has set an MCL for nitrate of 10 mg/L as nitrogen (N) to protect against methemoglobinemia, or blue baby syndrome.⁽¹⁹⁹⁾ Nitrate-rich groundwater can also cause problems when it is discharged into lakes, rivers, or the ocean because nitrogen stimulates algal and plant growth and can lead to anoxia and eutrophication. In most instances, concentrations of nitrate in groundwater that are high enough to pose human-health or ecological risks result from human activities.

Figure 6–1. Fertilizer use in the United States has increased greatly since the 1940s, and nitrate concentrations in groundwater recharge in agricultural areas have generally followed this trend.



Nitrate concentrations were greater than the MCL of 10 mg/L as N in about 4 percent of wells sampled in drinking-water aquifers (fig. 6–2), placing nitrate among the top four contaminants in terms of how frequently concentrations exceeded human-health benchmarks. More than one-third of wells sampled in the parts of aquifers used for drinking water had nitrate concentrations greater than 1 mg/L as N, a level that indicates the likely influence of human activities in most parts of the Nation (see sidebar, Background nitrate concentrations, p. 84). Concentrations were considerably higher in shallow groundwater beneath agricultural land than in shallow groundwater beneath urban areas or in deeper groundwater used for drinking-water supplies: 22 percent of wells in agricultural settings had concentrations greater than the MCL, and nearly two-thirds had concentrations greater than 1 mg/L as N. Elevated concentrations of nitrate in shallow groundwater are a concern because shallow groundwater in some agricultural areas is used for domestic water supply. Further, shallow groundwater beneath agricultural or urban land can move downward into deeper parts of the aquifer that are used for drinking water or may contribute to excess nitrogen in streams and coastal waters.

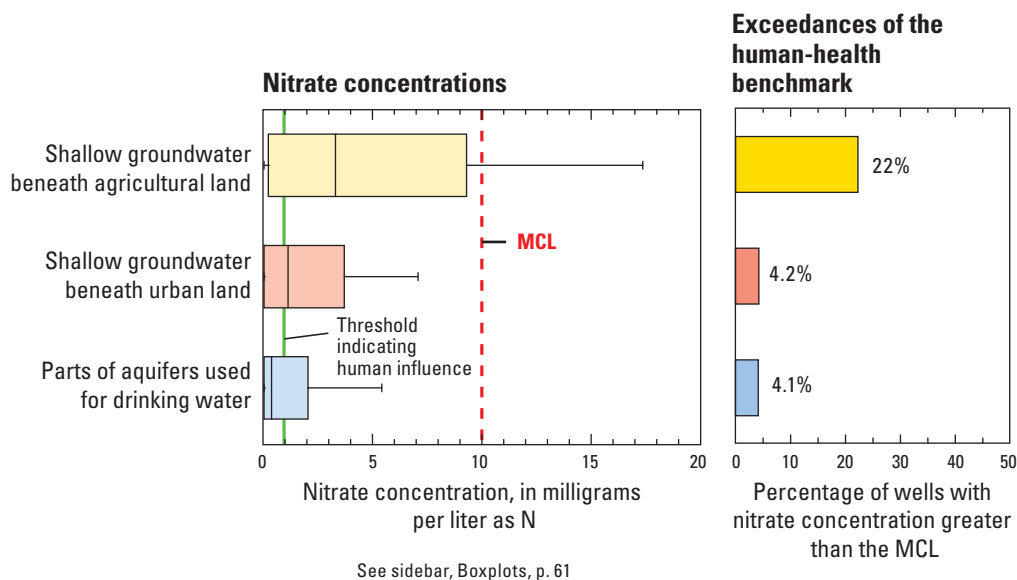
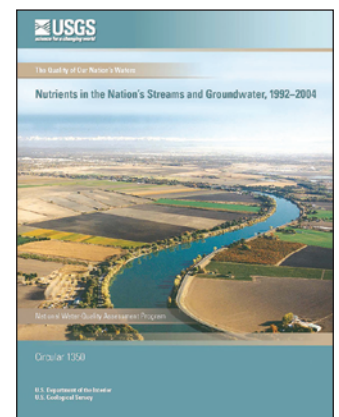
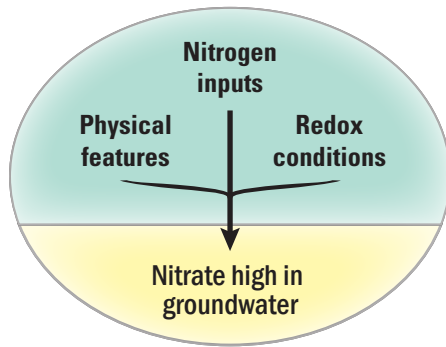


Figure 6–2. Nitrate concentrations were higher in shallow groundwater beneath agricultural areas than in shallow groundwater beneath urban areas or in deeper groundwater used for drinking water.



For more information on nitrate in the Nation's groundwater, see Dubrovsky and others (25)



Where and Why Are Nitrate Concentrations High?

Nitrogen use and release (nitrogen inputs) across the landscape, physical features that control how fast water flows through soils and aquifers, and redox conditions are the three main factors that influence nitrate concentrations in groundwater. Nitrogen inputs are widespread and include fertilizers applied to crops, lawns, and turf; septic systems; and precipitation and dry deposition. As a result, high concentrations of nitrate were distributed broadly across the Nation, especially in shallow groundwater beneath agricultural land (fig. 6–3). Nitrogen inputs from farm fertilizer are the largest source of nitrogen nationally.⁽⁶¹⁾

Physical features that enhance the permeability of sediment and rock, such as large amounts of sand and gravel, fractures, or karst features (see sidebar, Karst features and tile drains—Physical features that affect water infiltration can increase or decrease the susceptibility of aquifers to nitrate contamination, p. 87), allow water and any nitrate it contains to move relatively quickly from the land surface to the water table or from the water table to greater depths in the aquifer. High concentrations of nitrate in the Piedmont and Blue Ridge and the Valley and Ridge carbonate-rock aquifers (fig. 6–4), for example, reflect the rapid movement of nitrate from agricultural sources through karst features into the underlying aquifer. In contrast, soils that contain large amounts of clay and silt restrict the infiltration of water and nitrate to the water table. In the glacial aquifer system,⁽⁸⁾ concentrations of nitrate are surprisingly low under agricultural lands in parts of Illinois, Indiana, and Ohio, despite large inputs of nitrogen fertilizer at the land surface (fig. 6–3), because of clay-rich soils and artificial drainage (fig. 6–2). Confining layers—low-permeability geologic layers—below the water table can protect underlying deep, confined aquifers from the downward movement of nitrate.

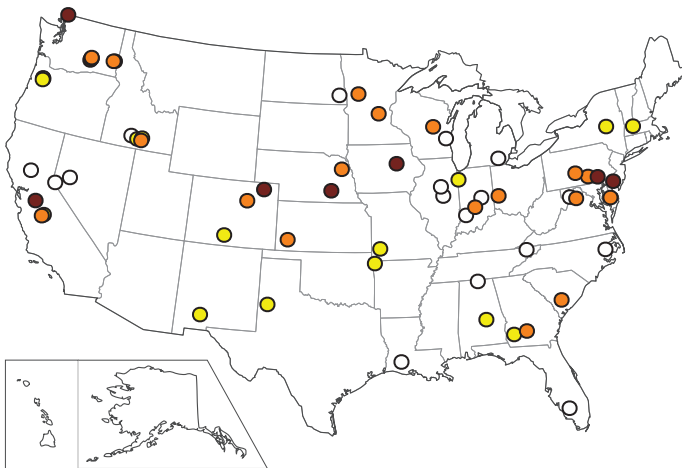
Background nitrate concentrations

What would be the concentrations of nitrate in groundwater without contributions from human activities? For many parts of the Nation, this is a difficult question to answer because the effects of human activities are pervasive and groundwater in undeveloped areas is not widely monitored. Nationally, groundwater nitrate concentrations in areas with minimal contributions from human activities are mostly less than 1 mg/L as N, based on samples from 419 wells in undeveloped areas.⁽²⁵⁾ Background nitrate concentrations in groundwater vary regionally, however, because of differences in geology,

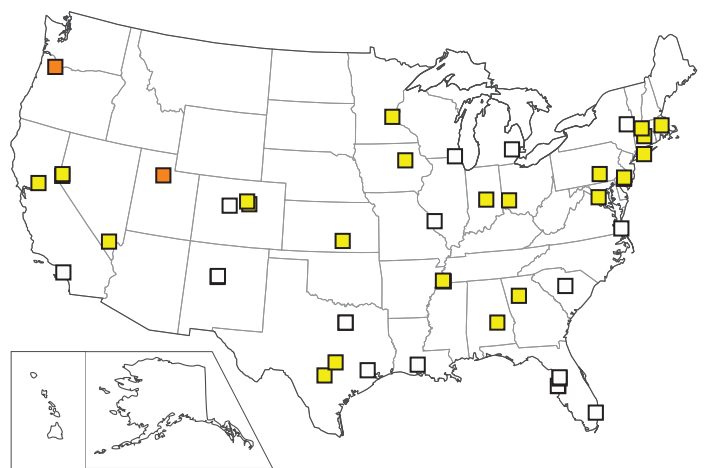
climate, precipitation chemistry, and biological processes. For example, nitrate concentrations as high as 3.2 mg/L as N have been measured in undeveloped areas of the High Plains aquifer,^(54, 55, 142) and concentrations of 5 mg/L as N or higher have been measured in groundwater beneath nitrogen-fixing plants in the Sonoran Desert in the southwest.⁽²⁹⁾ In contrast, throughout the Upper Floridan and overlying surficial aquifers, nitrate concentrations are typically less than 0.2 mg/L as N or below detection in groundwater that has not been affected by human activities.^(70, 143, 144)

Nitrate

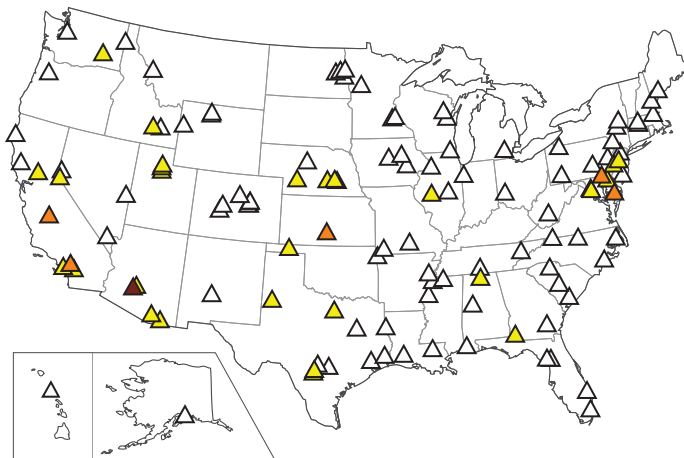
Shallow groundwater beneath agricultural land use



Shallow groundwater beneath urban land use



Parts of aquifers used for drinking water



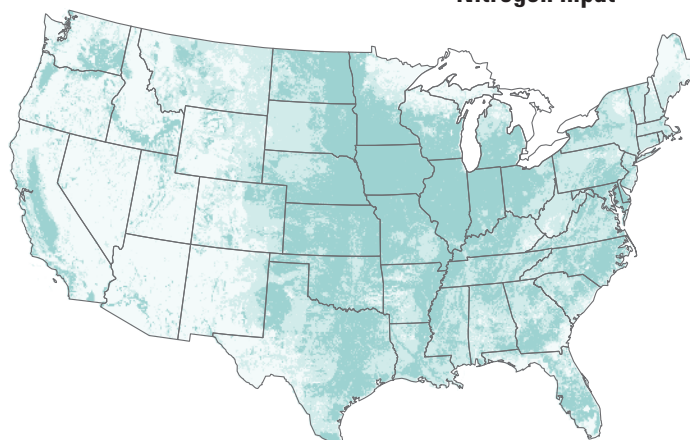
EXPLANATION

Median nitrate concentration per study, in milligrams per liter as N

Each symbol represents a study network of 20 to 30 wells, mostly domestic supply wells

△	○	□	< 1
▲	●	■	1 to 5
△	○	□	> 5 to 10
▲	●	■	> 10

Nitrogen input



EXPLANATION

Nitrogen input from fertilizer, manure, and atmosphere—
Estimated for 1997, in pounds per square mile

	< 2,900
	2,900 to 15,000
	> 15,000

Modified from Dubrovsky and others⁽²⁵⁾

Figure 6-3. High concentrations of nitrate were broadly distributed across the United States. Concentrations were especially high beneath agricultural land in the mid-Atlantic region, the Midwest, the Northwest, and in California. These areas have high nitrogen inputs and conditions favorable to nitrogen transport in groundwater. In shallow groundwater beneath urban land, concentrations of nitrate were elevated but with no clear regional patterns. Nitrate concentrations in the deeper parts of aquifers used for drinking water were high more frequently in the West than in the East (except for relatively high concentrations in the mid-Atlantic region, which reflect conditions in the shallow aquifers used for drinking water in this region).

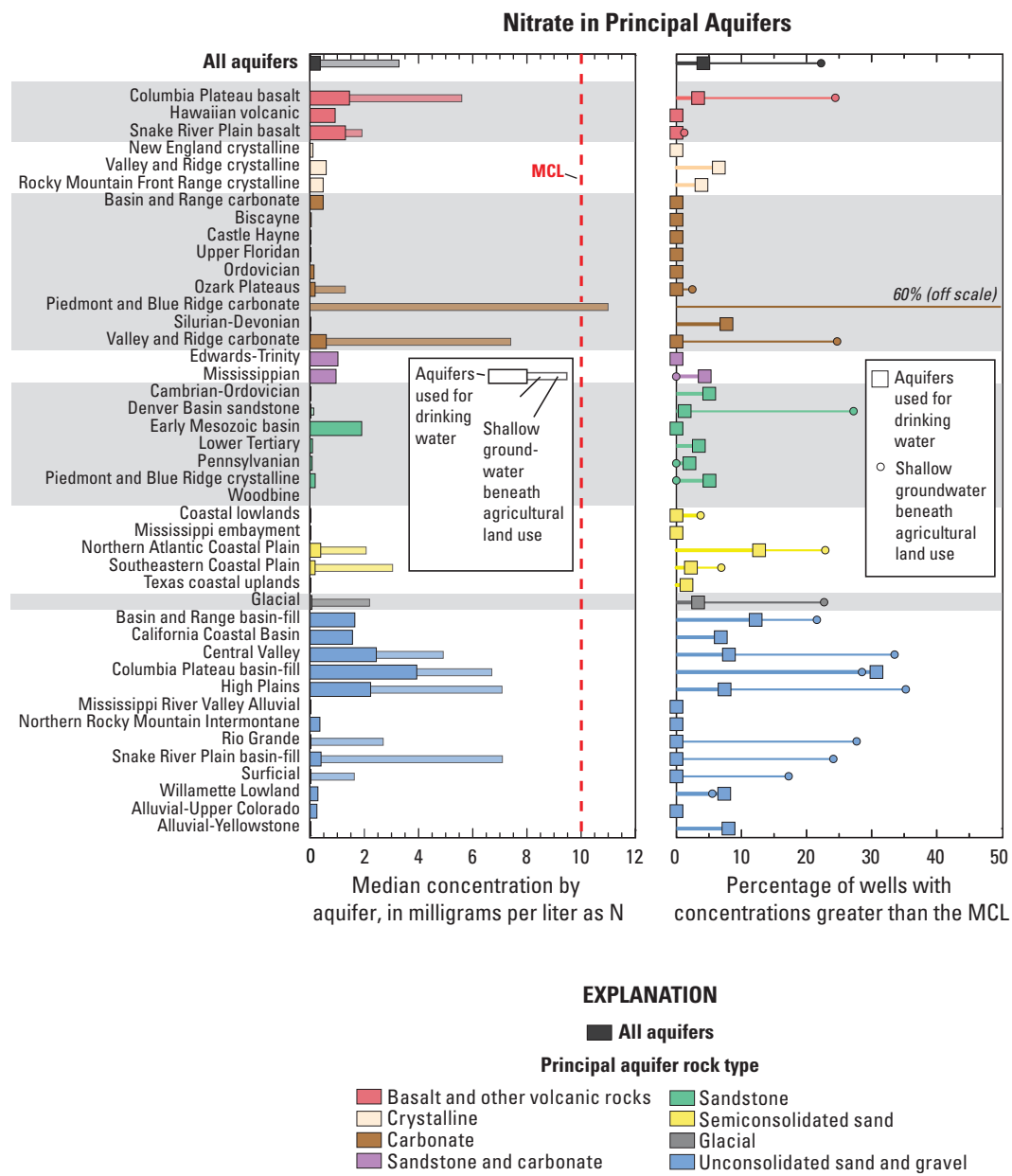
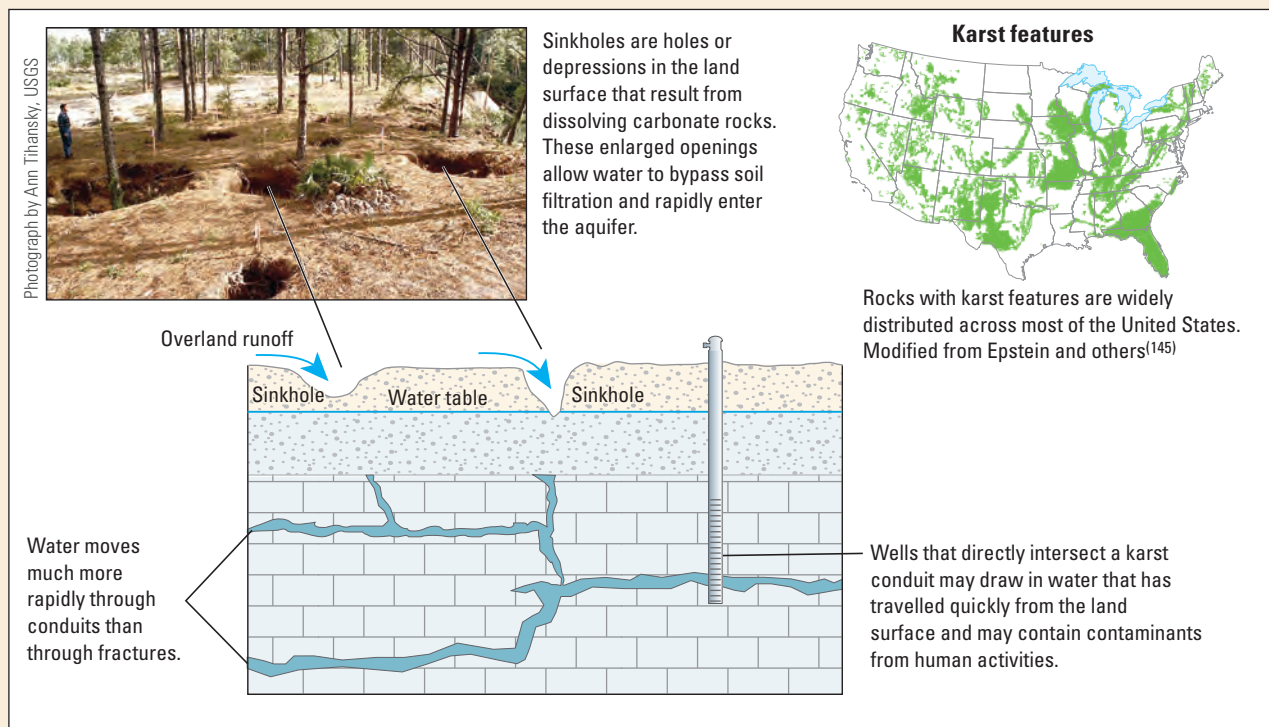


Figure 6-4. Nitrate concentrations were relatively high in several unconsolidated sand and gravel aquifers in the western United States and in agricultural areas of the Piedmont and Blue Ridge and the Valley and Ridge carbonate-rock aquifers in the mid-Atlantic region. These aquifers generally have high permeability, which promotes rapid infiltration of nitrogen-rich recharge, and generally have oxic groundwater, which favors the persistence of nitrate in the aquifer. In nearly all aquifers in which shallow groundwater in agricultural areas was sampled, that groundwater had higher concentrations of nitrate than did deeper groundwater used for drinking-water supply.

Karst features and tile drains—Physical features that affect water infiltration can increase or decrease the susceptibility of aquifers to nitrate contamination

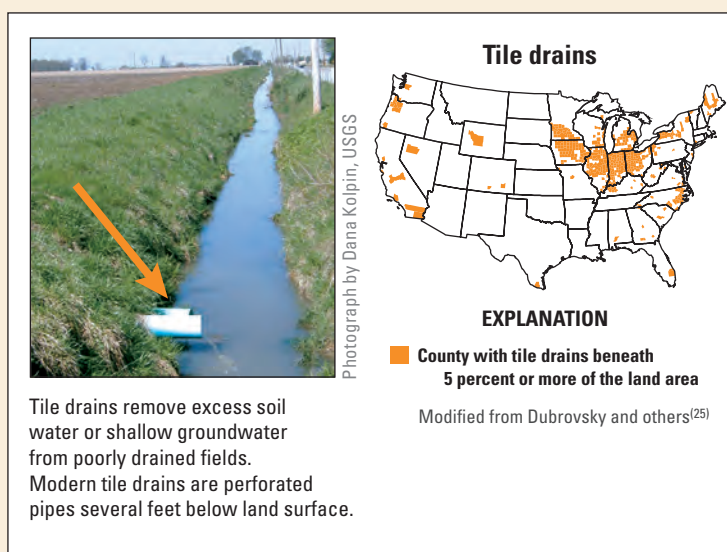
Karst

Some carbonate-rock aquifers have unique features called karst that make them very permeable. Carbonate rocks, mainly limestone and dolomite, are much more soluble than other rock types. As carbonate rocks dissolve, fractures and other open spaces in the rocks become enlarged, forming conduits, caverns, and sinkholes. Water from the land surface can enter aquifers directly through sinkholes and travel rapidly through conduits. These karst features make carbonate-rock aquifers highly susceptible to contamination from chemicals, such as nitrate, applied at the land surface.



Tile drains

Some aquifers lie beneath low-permeability, clay-rich soils that restrict water infiltration from the land surface. These soils are fertile, but their poor drainage properties make them unsuitable for agriculture. Low-permeability soils extend across much of the Corn Belt in the upper Midwest. When this land was developed for agriculture more than 150 years ago, drainage was improved by installing drainage pipes below the surface, which are called tile drains because they were originally made out of clay. The tile drains collect water (and any chemicals it contains) from saturated soils and, where the water table is near the land surface, from shallow groundwater. The drains reroute the water to surface ditches and streams. Aquifers beneath such artificially drained soils are less susceptible to contamination by chemicals applied at the land surface than they would be without the drains. On the other hand, the rivers and streams receiving the tile drainage are more likely to contain higher concentrations of these chemicals than they would without the altered drainage.



Nitrate can be removed in anoxic groundwater by denitrification, in which bacteria convert the nitrate to nitrogen gas.

Redox conditions influence nitrate concentrations because, although nitrate reacts little with aquifer materials, denitrification, a redox process, can remove nitrate in anoxic groundwater. Through denitrification, bacteria convert nitrate to N_2 gas. This process can happen only after the dissolved oxygen in the groundwater has been consumed and where organic carbon or other reduced chemicals are present to fuel the denitrification reaction (see sidebar, How do redox reactions work?, p. 33). Nitrate concentrations were lower in anoxic groundwater than in oxic groundwater in both shallow groundwater and in the deeper parts of aquifer used for drinking water (fig. 6–5), indicating that denitrification may play an important role in reducing nitrate concentrations in groundwater. Anoxic groundwater typically is older than oxic groundwater, however, and may be isolated from land surface by a confining layer; thus, anoxic groundwater may contain low concentrations of nitrate because the groundwater has not been affected by recent nitrogen inputs at land surface.

Detailed geochemical analyses can verify that denitrification has occurred in an aquifer. These analyses measure the gaseous products of denitrification in groundwater and the isotopic composition of the nitrate, which is changed by denitrification.^(62, 63) In the glacial aquifer system in central Minnesota, for example, denitrification has substantially reduced nitrate concentrations that were originally 5 to 10 mg/L as N or even higher when the groundwater was recharged. Many parts of the glacial aquifer system are relatively enriched in organic carbon and are anoxic. Denitrification is more likely to occur in the glacial aquifer system than in other aquifers (fig. 6–6), such as the unconsolidated sand and gravel aquifers, where anoxic groundwater is much less common.^(62, 63)

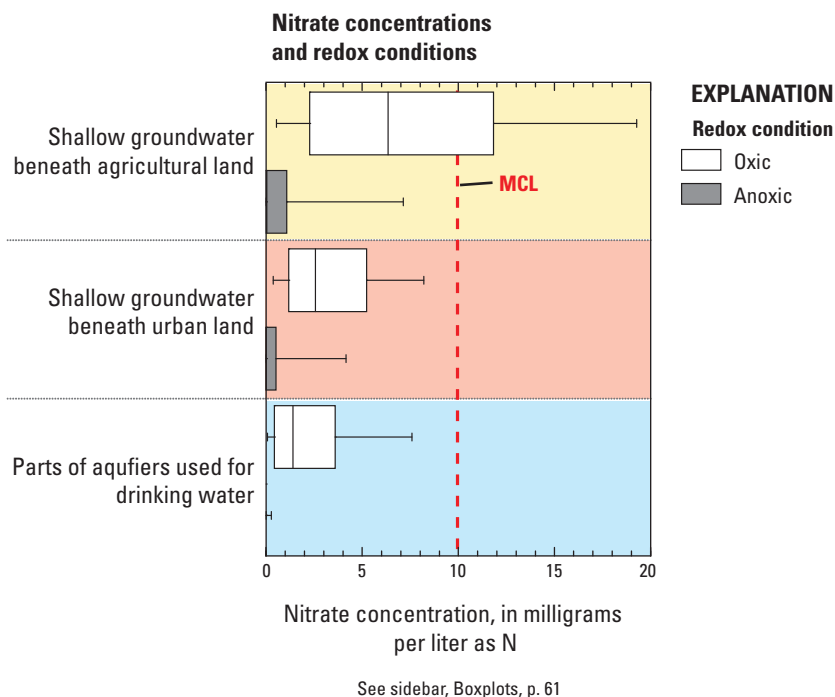


Figure 6–5. Nitrate concentrations were higher in oxic groundwater than in anoxic groundwater both in shallow groundwater underlying agricultural and urban land and in deeper groundwater used for drinking water. Anoxic conditions promote the removal of nitrate from groundwater through denitrification.

Removal of nitrate by denitrification in the glacial aquifer system, central Minnesota

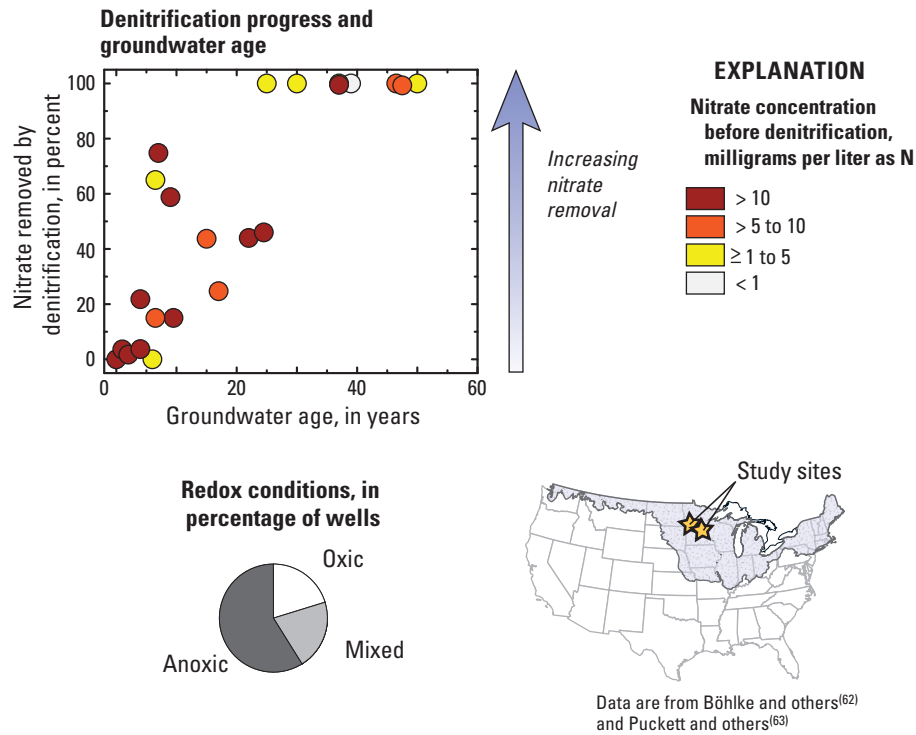


Figure 6-6. At two sites in the glacial aquifer system in central Minnesota, denitrification has substantially decreased nitrate concentrations within decades of the groundwater entering the aquifer. Denitrification can occur at these sites because of anoxic conditions and the presence of organic carbon in the aquifer sediments.

The cost of nitrate contamination in rural Pennsylvania

Where groundwater used for public supply is contaminated with nitrate, treatment can decrease nitrate concentrations but is costly, particularly for small communities. An example is Martinsburg, a borough in rural Pennsylvania, where groundwater is the principal source of municipal water supply. The water supply for Martinsburg, which has a population of about 2,000 people, regularly has nitrate concentrations that exceed the MCL of 10 mg/L as N (Randy Stoltz, Martinsburg Municipal Authority, written commun., 2012). Because there are no other water sources available, Martinsburg opened a water treatment facility in 2011 to remove nitrate. The ion-exchange facility, the first of its type in Pennsylvania, cost \$4.1 million, or more than \$2,000 per person.



The nitrate removal plant in Martinsburg, Pennsylvania.

Photograph from the Morrisons Cove Herald, used with permission

Measured nitrate concentrations, nitrogen sources, and factors associated with water transport and denitrification potential can be used to predict nitrate concentrations in groundwater across the United States (fig. 6–7).⁽⁶⁴⁾ These results can be used to identify areas that might warrant additional monitoring or are especially vulnerable to nitrate contamination. Nitrate concentrations in shallow, recently recharged groundwater are predicted to be greater than 5 mg/L as N (half the MCL) in groundwater beneath nearly 8 percent of the land area of the conterminous United States but predicted concentrations are lower in deeper groundwater, in the parts of aquifers used for drinking water (fig. 6–7). Nitrate concentrations also have been predicted at regional scales for the basin-fill aquifers of the southwestern United States,⁽³¹⁾ the High Plains aquifer,⁽⁶⁵⁾ and the glacial aquifer system.⁽⁶⁶⁾

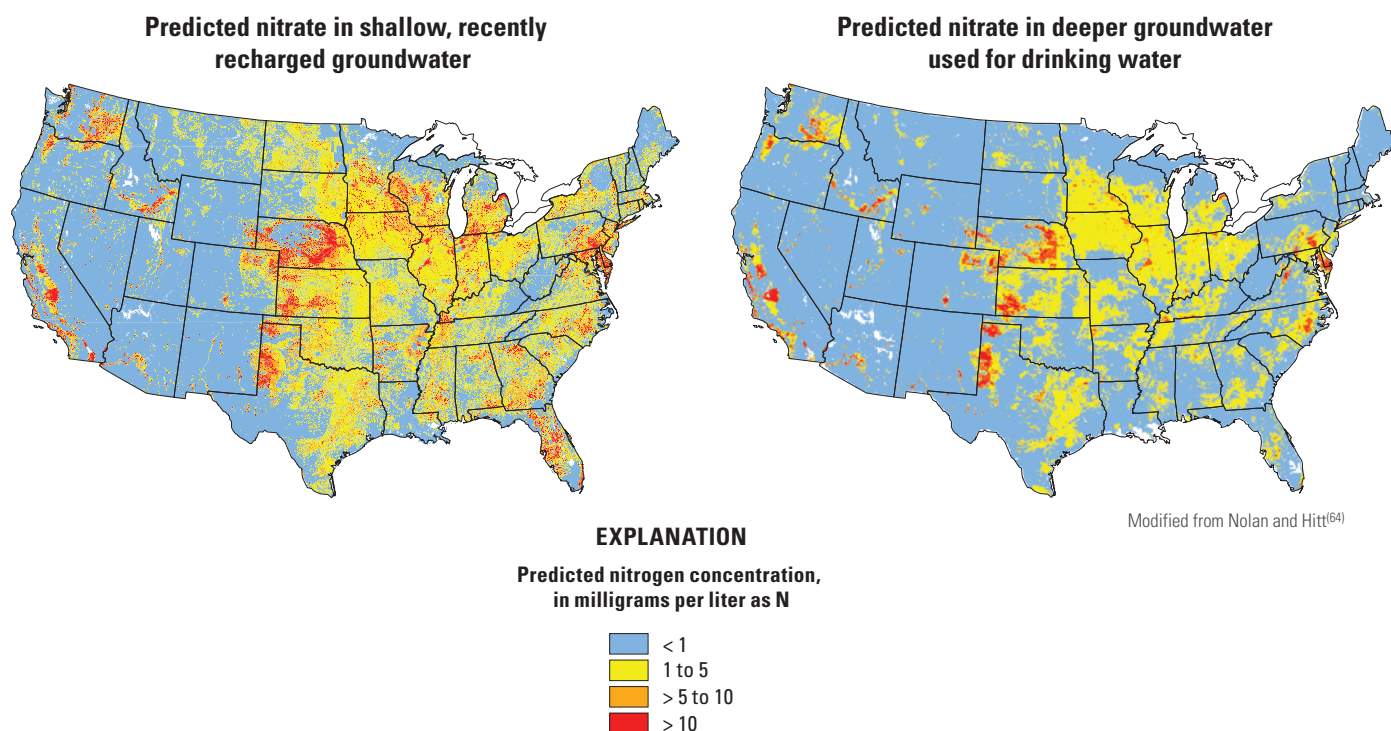
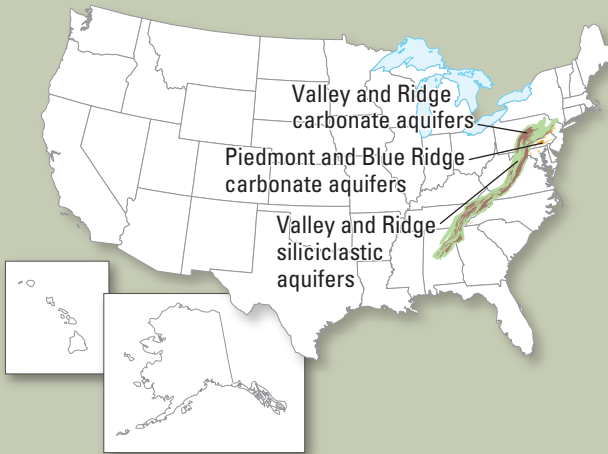


Figure 6–7. Nitrate concentrations greater than the MCL of 10 mg/L as N are predicted to occur primarily in the High Plains, northern Midwest, and areas of intense agriculture in the eastern and western United States. In shallow, recently recharged groundwater (left), concentrations are predicted to exceed the MCL of 10 mg/L as N beneath 2 percent of the land area of the conterminous United States and to be greater than half the MCL beneath nearly 8 percent of the land area. Concentrations are predicted to be lower in deeper groundwater from the parts of aquifers used for drinking water (right) than in shallow, recently recharged groundwater.



Piedmont, Blue Ridge, and Valley and Ridge Carbonate-Rock Aquifers—Large Nitrogen Inputs, High Permeability, and Oxic Groundwater Result in Nitrate Concentrations at Levels of Concern for Human Health

Some of the highest nitrate concentrations in the Nation were measured in shallow groundwater in agricultural areas of the Piedmont and Blue Ridge and the Valley and Ridge carbonate-rock aquifers. Concentrations were greater than the MCL in 60 percent of wells sampled in Piedmont and Blue Ridge carbonate-rock aquifers and in 25 percent of wells sampled in the Valley and Ridge carbonate-rock aquifers (figs. 6–4 and 6–8). Although they are small in area, these carbonate-rock aquifers are among the most heavily used for domestic water supply in the United States.⁽⁶⁾ Thus, high

nitrate concentrations in these aquifers are a concern to human health. In contrast, groundwater in the adjacent Valley and Ridge siliciclastic-rock aquifers (aquifers composed of sandstone, siltstone, and shale) had some of the lowest concentrations of nitrate measured nationally, and no nitrate concentrations exceeded the MCL (fig. 6–8). In the carbonate-rock and siliciclastic aquifers, recharge is abundant, groundwater flow paths are relatively short, and groundwater is typically less than 60 years old—common characteristics that make all three of these aquifers susceptible to contamination from recent human activities. Why are concentrations of nitrate in the carbonate-rock aquifers so much higher than those in the siliciclastic aquifers?

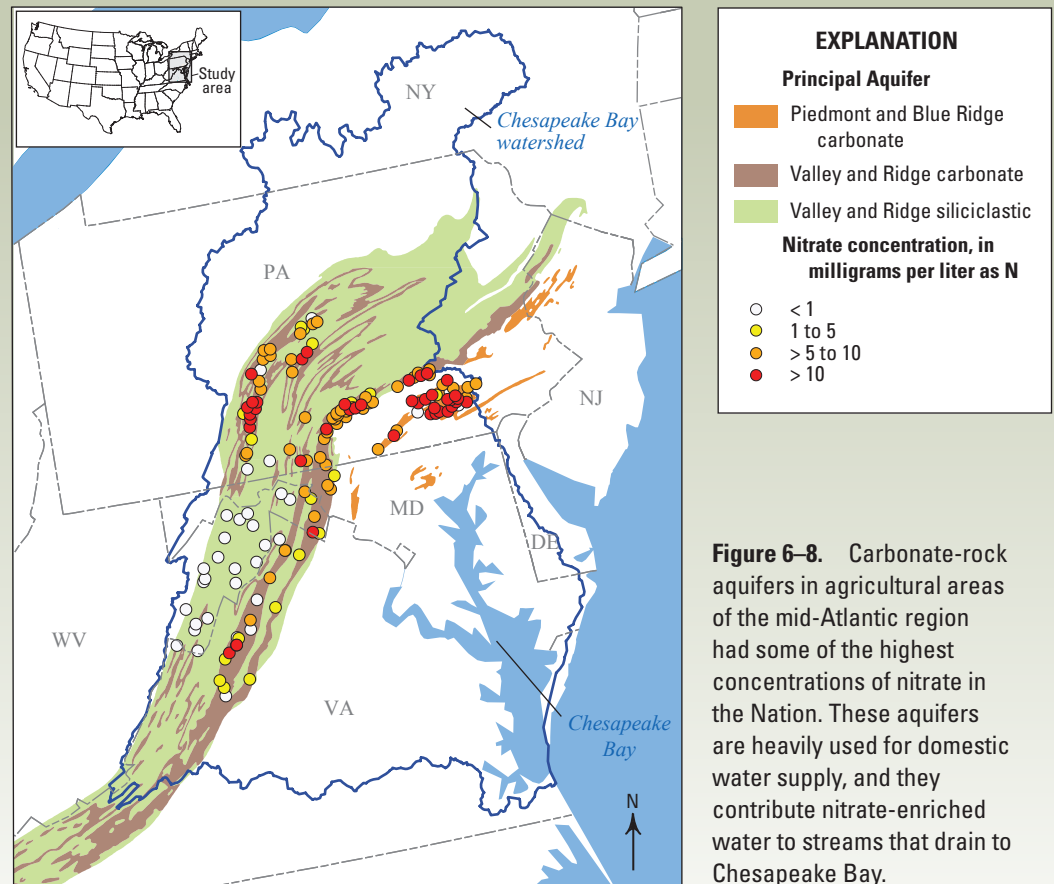


Figure 6–8. Carbonate-rock aquifers in agricultural areas of the mid-Atlantic region had some of the highest concentrations of nitrate in the Nation. These aquifers are heavily used for domestic water supply, and they contribute nitrate-enriched water to streams that drain to Chesapeake Bay.

Modified from Lindsey and others⁽³⁶⁾

High nitrate concentrations in the carbonate-rock aquifers result from three factors—high nitrogen inputs, karst geology (carbonate rocks), and oxic groundwater (fig. 6–9). The carbonate-rock aquifers underlie valleys and low-lying areas where land use typically is agricultural or urban, whereas land that overlies the siliciclastic aquifers is either forested or a mix of land uses. Agricultural and urban areas have higher nitrogen inputs than do forested or mixed-land-use areas. Nitrogen inputs are particularly high near the wells that were sampled in the Piedmont and Blue Ridge carbonate-rock aquifers, even compared with nitrogen inputs near wells sampled in agricultural areas elsewhere in the Nation (fig. 6–9). This difference is largely because of nitrogen inputs from manure from confined animal feeding operations.⁽⁶¹⁾ Permeable karst features in the soil zone overlying the carbonate-rock aquifers allow rapid movement of water and nitrate to the aquifers (see sidebar, Karst features and tile drains—Physical features that affect water infiltration can increase or decrease the susceptibility of aquifers to nitrate contamination, p. 87). Oxic groundwater, which is especially widespread in the Valley and Ridge carbonate-rock aquifers, preserves nitrate by preventing denitrification. In contrast to the carbonate-rock aquifers, concentrations of nitrate in the Valley and Ridge siliciclastic-rock aquifer are low because nitrogen inputs are not as high, karst features are absent, and oxic conditions are much less common compared with the carbonate-rock aquifers (fig. 6–9).

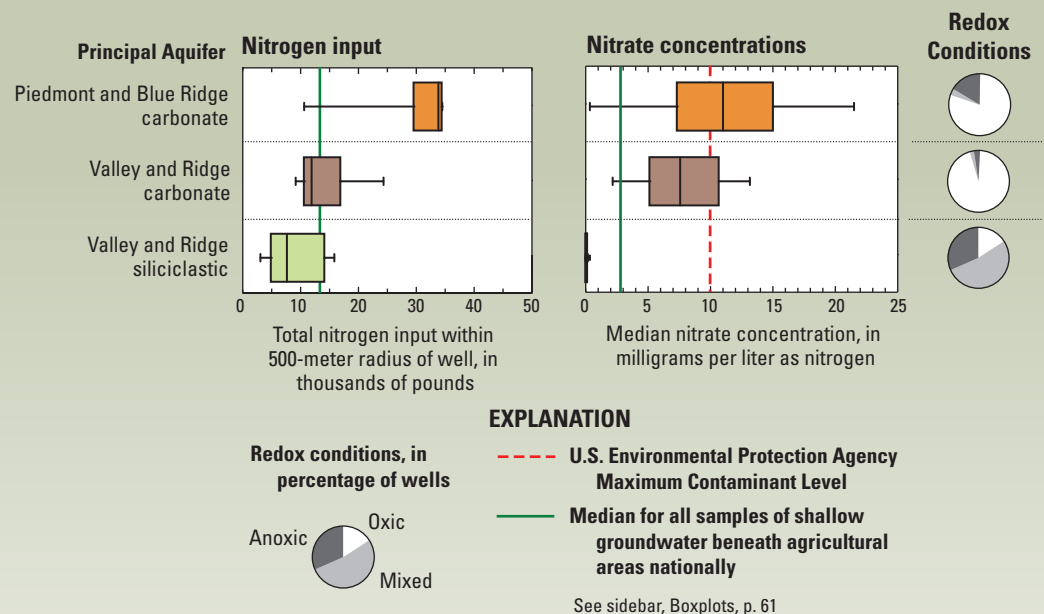


Figure 6–9. High nitrate concentrations in the Piedmont and Blue Ridge and the Valley and Ridge carbonate-rock aquifers result from large inputs of agricultural nitrogen at the land surface, highly permeable karst features in the soil zone that allow rapid movement of nitrate to the aquifer, and oxic groundwater that limits denitrification in the aquifers.

Nitrogen from discharging groundwater contributes to eutrophication in the Chesapeake Bay and delays water-quality improvements

Chesapeake Bay, the largest estuary in the United States, provides a wealth of benefits, including commercial fisheries, recreation opportunities, and wildlife habitat. However, excessive nutrients, sediment, and other contaminants during many decades have degraded the water quality of the bay and threaten this valuable ecosystem.^(146, 147) Each year, large anoxic areas, called dead zones, develop in response to excessive nutrients that stimulate algal blooms, which kill or weaken fish and shellfish. Coordinated efforts of Federal and State agencies, local governments, and other organizations and institutions to reduce nutrients and restore water quality began in the 1980s. Improvements have been slow for a variety of reasons, one of which involves groundwater. Groundwater provides a large part of the water

and nitrogen in streams in the Chesapeake Bay watershed. On average, about 50 percent of the water and nitrogen load in streams in the watershed comes from groundwater.^(22, 25, 148) Transport of nutrients from the land surface through an aquifer to streams can take decades; nitrogen in groundwater discharging to streams today is the result of nitrogen inputs at land surface in years past, when the groundwater was recharged. Consequently, water-quality conditions in the bay respond slowly to reductions in nitrogen from nonpoint sources in the watershed that is delivered to bay waters through groundwater discharge.⁽¹⁴⁸⁾ The delay that groundwater introduces is essential to consider in planning for the restoration of water quality in Chesapeake Bay.⁽²⁴⁾

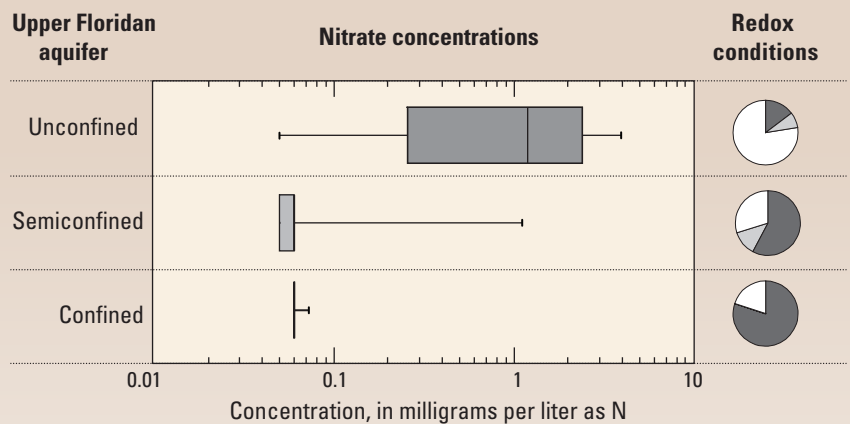
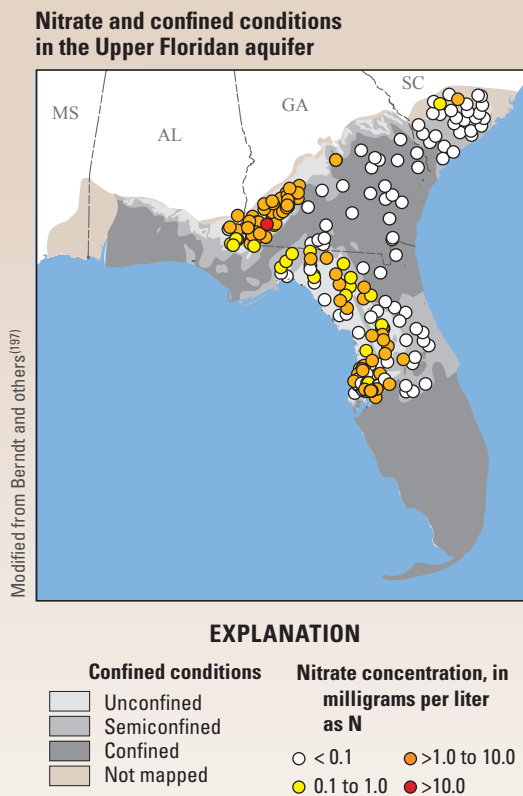


Photographs from top left clockwise: Bridge and heron, Jane Thomas, IAN, UMCES; boat, Ben Longstaff, IAN, UMCES (ian.umces.edu/imagelibrary/), used with permission; soft-shell crabs in barrel, copyright Ken Rygh, istockphoto.com



Upper Floridan Carbonate-Rock Aquifer—*Confined Aquifer Conditions and Anoxic Groundwater Result in Low Concentrations of Nitrate*

The Floridan aquifer system is the fifth most heavily pumped aquifer in the United States, supplying water for irrigation, public supply, and domestic use.⁽⁵⁾ Agriculture—field crops, vegetables, and citrus—covers about 20 percent of the land overlying the aquifer; urban and suburban areas also are extensive. Despite these sources of nitrogen, nitrate concentrations in many parts of the Upper Floridan aquifer are very low (fig. 6–10). The low-permeability confining layers of sand, clay, and sandy limestone that cover much of the Upper Floridan aquifer protect it from contamination from the land surface and from the overlying surficial aquifers. Additionally, anoxic conditions in the confined parts of the Upper Floridan aquifers favor denitrification (fig. 6–10).



See sidebar, Boxplots, p. 61

EXPLANATION
Redox conditions, in percentage of wells

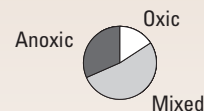


Figure 6–10. The presence or absence of low-permeability confining units is a major hydrogeologic control on the distribution of nitrate in the Upper Floridan carbonate-rock aquifer. In unconfined areas, nitrate from the land surface can enter and move through the aquifer quickly, resulting in higher nitrate concentrations than in confined parts of the aquifer. Anoxic conditions in the confined and semiconfined parts of the aquifer make it less likely that nitrate will persist in these areas.

The presence of a confining layer is a key difference between the Upper Floridan carbonate-rock aquifer and the Piedmont and Blue Ridge and the Valley and Ridge carbonate-rock aquifers in the mid-Atlantic region. Groundwater in large parts of the confined Upper Floridan aquifer is more than 10,000 years old,^(67, 68) whereas groundwater is far younger in the mid-Atlantic carbonate rock aquifers—only 10 to 20 years old in some parts of the Valley and Ridge carbonate-rock aquifer.⁽⁶⁹⁾ The age differences in groundwater between these two aquifer systems demonstrate the effectiveness of the confining layer in limiting water movement and nitrate contamination from the land surface into the Upper Floridan aquifer.

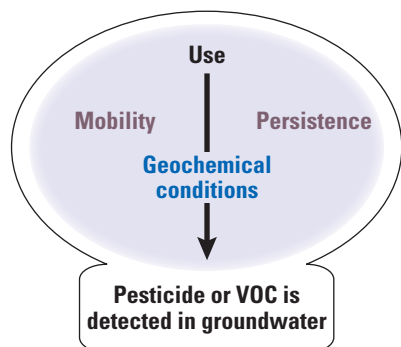
Nitrate concentrations in the unconfined parts of the Upper Floridan aquifer, although much higher than concentrations in the semiconfined or confined parts of the aquifer (fig. 6–10), are low relative to concentrations in other aquifers nationally that also are affected by human activities. Yet concentrations in the unconfined parts of the Upper Floridan aquifer are about 10 times greater than background concentrations in the aquifer and, consequently, pose problems for the springs and streams into which the groundwater discharges. Florida's freshwater springs, which are fed by water from the Floridan aquifer system, are a natural resource of enormous economic, recreational, and ecological value.⁽⁷⁰⁾ Increasing concentrations of nitrate during the past 40 years in many springs threaten the ecological integrity and water quality of these valuable water resources.⁽⁷¹⁾



Photograph by Alan M. Cressler, USGS

Crystal clear springs, such as Rainbow Spring in Marion County, Florida, are fed by groundwater from the Floridan aquifer system and are vulnerable to contamination from increasing concentrations of nitrate.

Pesticides and Volatile Organic Compounds



Pesticides and volatile organic compounds (VOCs) are pervasive in modern life. They are used in agriculture, industry, transportation, and many day-to-day activities around the home. Thousands of different chemicals have been manufactured for use in the United States. Many of these chemicals are toxic and can pose human-health or ecological concerns in drinking water or in the environment. Groundwater samples from the Principal Aquifers were analyzed for about 240 pesticides and VOCs, with a focus on those that are most heavily used.

Pesticides and VOCs can reach groundwater through infiltration in recharge from the land areas where they are applied, through accidental spills or leaks, or through waste disposal. Which chemicals reach groundwater depends to a large extent on their use, but it also depends on the properties of the chemicals. Chemical characteristics—such as water solubility, volatility, density, and sorption properties—determine the mobility of a chemical through soils and aquifers. Many pesticides and VOCs degrade in soils and groundwater into other chemicals; a chemical's resistance to degradation (persistence) also will determine if it is detected in groundwater. Mobility and persistence, in turn, are affected by geochemical conditions in the aquifer.

Volatile organic compounds (VOCs) are a class of chemicals that can easily volatilize (evaporate). They are everywhere in modern life, in gasoline, paints, glues, cleaners, and personal care products. VOCs also are used in the manufacturing of many different products, including automobiles, electronics, wood products, and plastics, in dry cleaning, in refrigeration, and for some types of pest control.



How Often Were Pesticides and VOCs Detected and Are They Health Concerns?

Pesticides and VOCs were frequently detected in groundwater, and all Principal Aquifers are vulnerable to contamination by these chemicals (fig. 6–11; appendix 3). Pesticides were detected in 32 percent and VOCs were detected in 40 percent of wells sampled in the parts of aquifers used for drinking water. Concentrations of individual pesticides and VOCs were mostly low (less than $0.2 \mu\text{g/L}$), however, and human-health benchmarks were rarely exceeded (table 4–1). Detections and benchmark exceedances were more frequent in shallow groundwater beneath agricultural and (or) urban land than in deeper groundwater used for drinking water (figs. 6–11 and 6–12). The shallow groundwater that was sampled represents recently recharged groundwater present in a large part of the United States that will move deeper into aquifers, potentially affecting future drinking-water supplies.

Although they rarely exceeded existing human-health benchmarks as individual chemicals, pesticides and VOCs often occurred in groundwater as mixtures. Mixtures of pesticides or VOCs were present in about 40 percent of groundwater samples from parts of aquifers used for drinking water, in 68 percent of samples of shallow groundwater beneath agricultural land, and in 82 percent of samples of shallow groundwater beneath urban land. Mixtures are a potential concern because the human-health effects of some chemicals may be additive.^(72–74) There are millions of possible chemical mixtures in drinking-water sources, and their interactions are not well understood.^(75, 76)

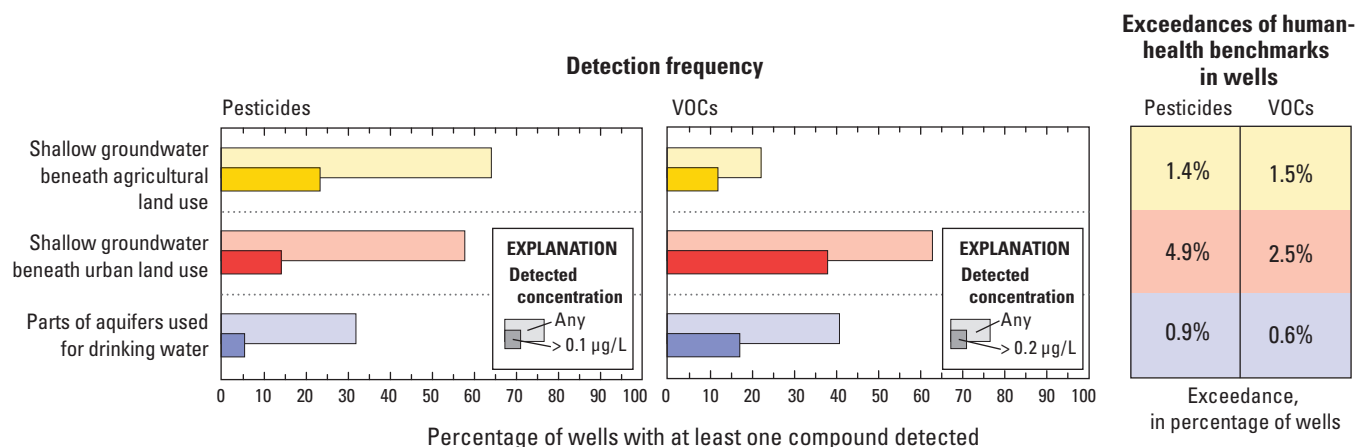


Figure 6–11. Pesticide and VOCs were detected frequently in groundwater but rarely at concentrations greater than human-health benchmarks. Detections and exceedances of human-health benchmarks were more frequent in shallow groundwater beneath agricultural and (or) urban land than in deeper groundwater from parts of aquifers used for drinking water. Although not currently used for drinking water in most areas, shallow groundwater eventually will move deeper into the aquifer and could affect the quality of future drinking-water supplies.



Pesticides are used in agriculture, in homes and businesses, on lawns and gardens, along roads, in recreational areas, and on pets and livestock. There are hundreds of different pesticide chemicals in use in the United States.⁽¹⁹⁰⁾

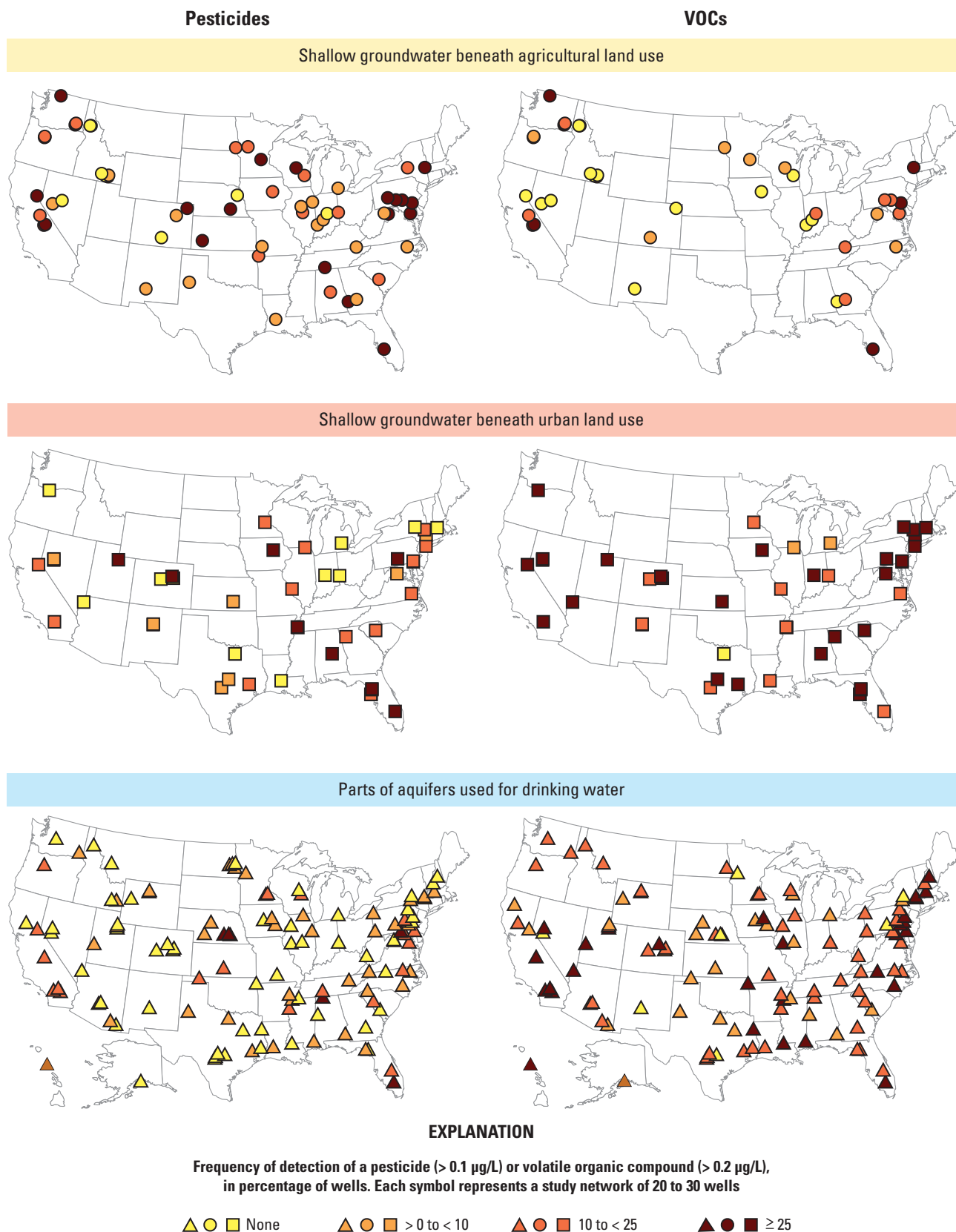


Figure 6–12. Detections of pesticide and VOCs were widespread across the Nation. Detections of pesticides were most frequent and widespread in shallow groundwater beneath agricultural areas, and detections of VOCs were most frequent and widespread in shallow groundwater beneath urban areas.

Which Pesticides and VOCs Were Detected and Why?

Herbicides used in agriculture were the most frequently detected type of pesticide. Atrazine (and its degradates), simazine, prometon, and metolachlor were the herbicides most frequently detected (fig. 6–13; table 6–1). These findings generally reflect patterns of chemical use. Agricultural herbicides account for about 80 percent of the total amount of conventional pesticides used in the United States, and atrazine and metolachlor have been among the most heavily used agricultural herbicides for the past several decades.^(77, 78) Atrazine, simazine, and metolachlor were detected more frequently in shallow groundwater beneath agricultural land than in other settings, whereas prometon, an herbicide used along roads and rights-of-way, was detected more frequently in shallow groundwater beneath urban land (appendix 3).

Trihalomethanes, a group of chemicals that includes byproducts of water chlorination, and solvents were the most frequently detected types of VOCs (fig. 6–13). Trihalomethanes and solvents, along with gasoline hydrocarbons, were detected in some wells in nearly every aquifer (appendix 3). Chemicals used in organic synthesis, gasoline oxygenates, fumigants, and refrigerants were detected less frequently overall and in fewer aquifers. As with pesticides, patterns of chemical use help explain some of the differences in distributions of chemical groups in groundwater. Solvents, trihalomethanes, and gasoline hydrocarbons have been used for many decades throughout the United States.⁽⁷⁹⁾ In contrast, use of fumigants and gasoline oxygenates (additives to enhance fuel octane) has been limited to small areas of the country. Gasoline hydrocarbons are used in larger amounts than any other kind of VOC but were less frequently detected than trihalomethanes and solvents. The lower frequency of detections, despite higher use, is because gasoline hydrocarbons also are among the least soluble of the VOCs, tend to sorb to soil and aquifer solids, and biodegrade under oxic conditions,⁽¹⁴⁾ illustrating the importance of chemical characteristics as well as use patterns in the distribution of chemicals in groundwater.

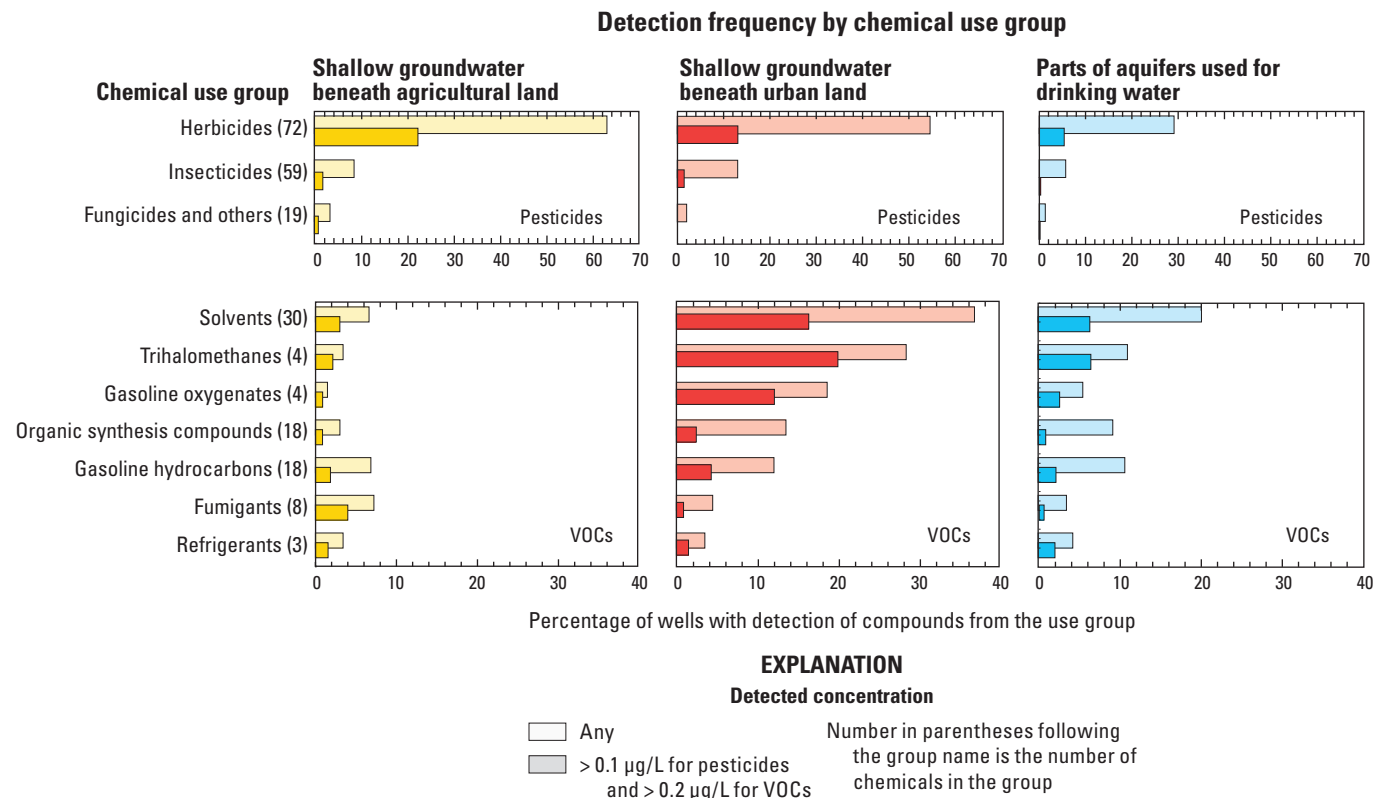


Figure 6–13. Herbicides were the most frequently detected pesticides in groundwater, and trihalomethanes and solvents were the most frequently detected VOCs in groundwater. Many pesticides and VOCs have been widely used across the United States and are mobile and persistent in groundwater.

Table 6–1. Pesticides and VOCs that were detected most frequently in groundwater.

[Based on detections at any concentration in samples from parts of aquifers used for drinking water and in samples of shallow groundwater beneath agricultural and urban land]

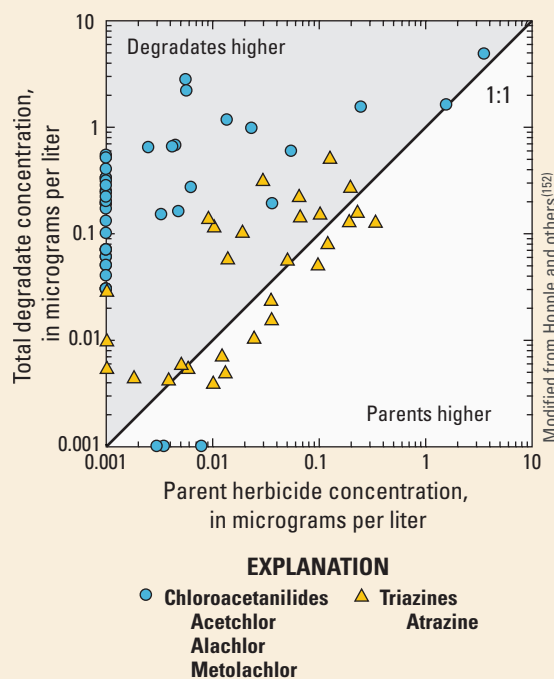
Compound	Description and general use
Pesticides	
Atrazine, deethylatrazine, deisopropylatrazine, and hydroxyatrazine	Herbicide, commonly used to control weeds in corn, sorghum, and soybeans, and its degradation products
Simazine	Herbicide, commonly used to control weeds in corn, orchards, turf and lawns, along roads and rights-of-way, and in nurseries
Prometon	Herbicide, used to control weeds along fences, buildings, roads, railways, and rights-of-way
Metolachlor	Herbicide, commonly used to control weeds in corn and soybeans, in nurseries, on turf and lawns, and along fences
VOCs	
Chloroform	Byproduct of the disinfection of water with chlorine and used in industry to produce other organic compounds; also has natural sources
Carbon disulfide	Used in industry to produce other organic compounds and also used as an agricultural fumigant
Perchloroethene (PCE), Trichloroethene (TCE), and 1,1,1-tricloroethane (TCA)	Solvents with commercial and industrial uses, such as metal degreasing and dry cleaning
Methyl <i>tert</i> -butyl ether (MTBE)	Gasoline additive (oxygenate), used to increase fuel octane and reduce emissions

Pesticides and VOCs use different assessment levels

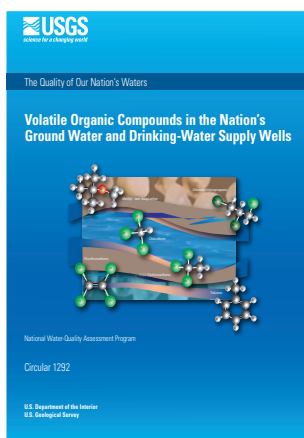
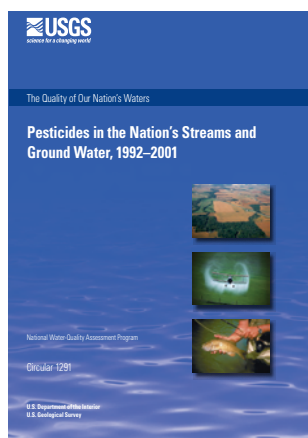
The presence of pesticides and VOCs in groundwater was evaluated in two ways—detections at any concentration (without regard to differences in analytical reporting levels for individual chemicals) and detections at concentrations greater than specified values called common assessment levels. Detection frequencies at any concentration provide the best representation of chemical occurrence in the environment, whereas detection frequencies at common assessment levels provide the best approach for comparisons among different chemicals. The common assessment levels used in this circular are 0.1 µg/L for pesticides and 0.2 µg/L for VOCs. The different assessment levels for pesticides and VOCs reflect the differences in the laboratory methods used to analyze these two groups of chemicals.

Pesticide degradates

Many pesticides degrade in the soil or groundwater through physical, chemical, or biological reactions. This does not mean that the chemicals entirely disappear; rather, they are transformed into different chemicals. Some of these pesticide degradates can be as toxic as their parent chemicals and more mobile or persistent in groundwater.^(149–151) Increasingly, laboratory methods are being developed that give us the ability to detect pesticide degradates in groundwater. The results show that pesticide degradates can be present just as frequently and sometimes at even higher concentrations than the parent chemicals. In a study of the source water to 73 public-supply wells, for example, concentrations of pesticide degradates equaled or exceeded those of the parent chemicals for two groups of herbicides: triazines and chloroacetanilides.⁽¹⁵²⁾ The triazine group includes atrazine, and the chloroacetanilides group includes several other commonly used agricultural herbicides. The chloroacetanilide herbicides break down more quickly in soil than the triazine herbicides.⁽¹³⁾ As a result, concentrations of chloroacetanilide degradates almost always exceeded those of the parent chemicals, whereas concentrations of triazine degradates were about equal to those of the parent compound (atrazine). In some samples, the degradates were present even when the parent chemicals themselves were not detected.



Concentrations of herbicide degradates equaled or exceeded concentrations of the parent chemicals in many samples of source water to 73 public-supply wells in the Cambrian-Ordovician, glacial, High Plains, Piedmont and Blue Ridge crystalline, and Rio Grande aquifers or aquifer systems.



For more information on pesticides and VOCs in the Nation's groundwater, see Gilliom and others⁽¹³⁾ and Zogorski and others.⁽¹⁴⁾

Atrazine

Atrazine is frequently detected in groundwater for several reasons: it has been widely used for several decades, it is moderately soluble, and it has a relatively long half-life in soil (146 days).⁽¹³⁾ Atrazine was detected in 40 percent of shallow wells sampled beneath agricultural land, in 29 percent of shallow wells sampled beneath urban land, and in 16 percent of deeper wells in drinking-water aquifers. Atrazine biodegrades, and its degradates, particularly deethylatrazine,^(80, 81) were also among the most frequently detected pesticides (table 6–1). Few wells contained atrazine at concentrations greater than its USEPA MCL of 3 µg/L, but 4.6 percent of shallow wells beneath agricultural land had atrazine concentrations greater than one-tenth of the MCL (0.3 µg/L).

Atrazine occurs so frequently that scientists can use its occurrence to learn about the factors that influence its distribution in groundwater. Two factors controlling distribution were the most important at the national scale: (1) where and how much atrazine was used, and (2) the age of the groundwater that was sampled.⁽⁸²⁾ Concentrations of atrazine and its degradate, deethylatrazine, were higher in groundwater beneath land areas of intensive atrazine use and in groundwater that had been in the aquifer for shorter periods of time than in groundwater beneath other land uses or in older groundwater. Groundwater age is important because atrazine



Photograph by Stephen Kirkpatrick, USDA, NRCS

Atrazine is an herbicide used in the production of corn, sorghum, and sugarcane; it also is used on lawns, turf, and tree farms. Atrazine has been one of the two most heavily used pesticides in the United States since at least 1987.^(77, 78)

use has increased with time, and older groundwater is less likely to have been recharged at a time when atrazine use was high than is younger groundwater. Several other factors also were related to concentrations of atrazine and deethylatrazine in groundwater. Higher concentrations of atrazine were measured in areas with more permeable soils and higher recharge rates than in areas with less permeable soils and lower recharge rates.⁽⁸²⁾ These factors reflect the ease with which water moves into the aquifer. Atrazine does not degrade readily in groundwater, and there was little evidence that atrazine was degraded once it reached the saturated zone.

Understanding the factors that control atrazine distribution in groundwater aids in predicting concentrations of atrazine and deethylatrazine in areas where no groundwater data are available (fig. 6–14). The highest concentrations are predicted to occur in shallow groundwater beneath agricultural land in parts of the High Plains aquifer, in unglaciated parts of Illinois, Iowa, Wisconsin, and Minnesota, and in southeastern Pennsylvania; concentrations are high in these areas because atrazine use is high, soils are permeable, and recharge rates are high.⁽⁸²⁾ Concentrations of atrazine and deethylatrazine are likely to exceed the atrazine MCL of 3 µg/L, however, in groundwater beneath only 5 percent of the Nation’s agricultural areas. Predicted concentrations such as these can be used to identify areas of potential concern and set priorities for groundwater monitoring.

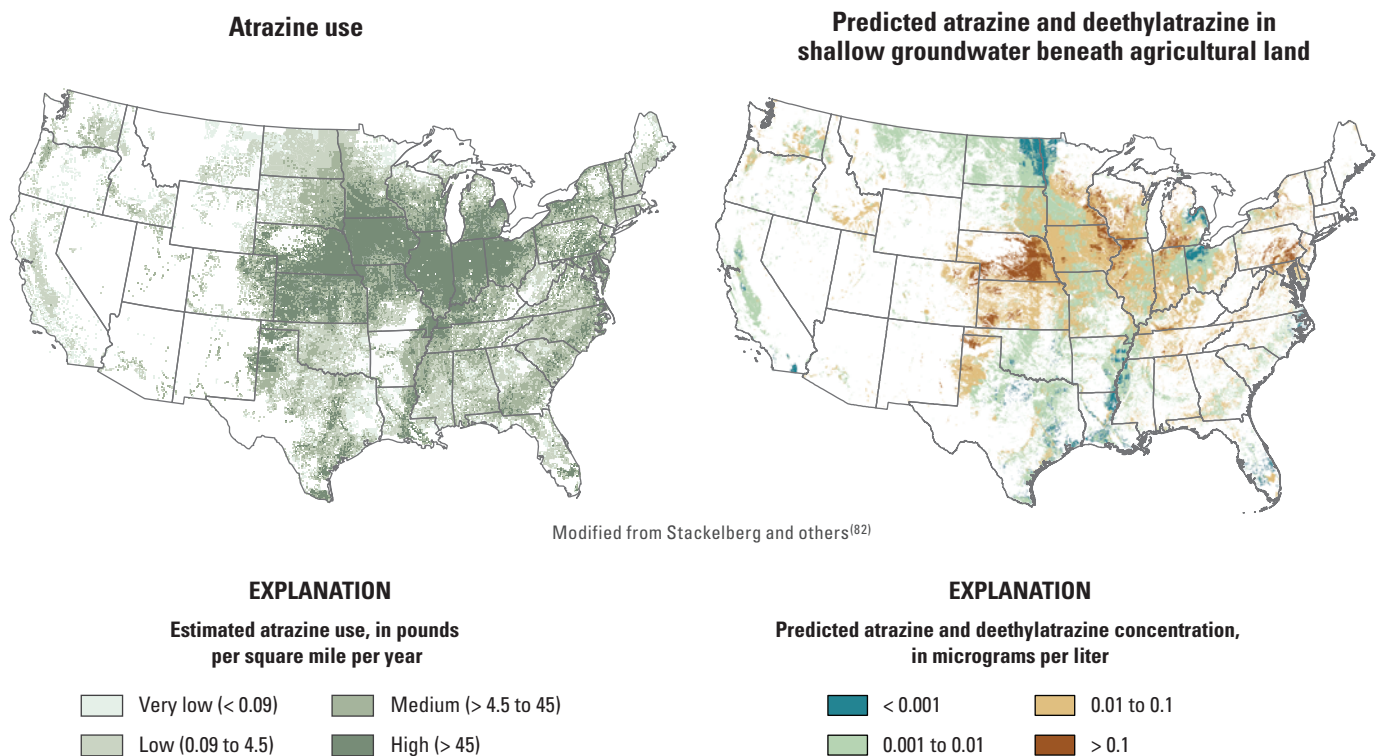


Figure 6–14. Atrazine use (left) is one of the most important factors used to predict atrazine and deethylatrazine concentrations in groundwater (right). Within areas of high atrazine use, groundwater residence time, soil permeability, and other factors explain some of the differences in predicted concentrations.

Chloroform, Perchloroethene, Trichloroethene, and Trichloroethane

Why were chloroform, perchloroethene (PCE), trichloroethene (TCE), and 1,1,1-trichloroethane (TCA) among the most frequently detected VOCs? These chemicals have numerous, widespread sources and a long history of use in the United States.⁽¹⁴⁾ These VOCs also are moderately soluble in water, have a low tendency to sorb to aquifer materials, and are relatively slow to biodegrade, especially in oxic conditions.

Chloroform is used in industry but also formed when water is treated with chlorine—when drinking water, wastewater, or pool water is disinfected, for example. Thus, leaky sewers, wastewater discharge, and landscape watering with chlorinated water are potential sources of chloroform to groundwater; these sources that are ubiquitous in residential and urban areas across the Nation. PCE, TCE, and TCA are chlorinated solvents with many commercial and industrial uses, including degreasing and dry cleaning. These VOCs enter groundwater through waste disposal, spills, and leaks. Chloroform, PCE, TCE, and TCA all were detected more frequently in shallow groundwater beneath urban land than in deeper groundwater used for drinking water or in shallow groundwater beneath agricultural land because sources of these VOCs are more common in urban areas than in other areas (table 6–2).

PCE and TCE were among the few pesticides or VOCs that were measured at concentrations greater than human-health benchmarks in groundwater samples. In fact, PCE and TCE accounted for nearly 20 percent of all instances in which a pesticide or VOC exceeded its human-health benchmark, second only to dieldrin in this regard (table 4–1). In contrast, chloroform was rarely present at concentrations of potential human-health concern; samples from only two wells had chloroform concentrations greater than the USEPA MCL (a combined MCL for chloroform and three other trihalomethanes).

Table 6–2. Frequently detected VOCs.

Chemical	Detection frequency, at concentrations greater than 0.2 micrograms per liter, as percentage of wells		
	Shallow groundwater beneath urban land	Shallow groundwater beneath agricultural land	Aquifers used for drinking water
Chloroform	20	2	6
Perchloroethene (PCE)	8	0.3	2
Trichloroethene (TCE)	4	0.2	1
1,1,1–Trichloroethane (TCA)	4	0.7	0.6

Methyl *Tert*-Butyl Ether

Methyl *tert*-butyl ether (MTBE) is an oxygenate that was added to reformulated gasoline during the 1980s and 1990s to reduce air pollution. MTBE in water supplies quickly became a concern when it was detected in public wells in California and other States in the 1990s.⁽⁸³⁾ Compared with other components of gasoline, MTBE is much more soluble, less likely to sorb to soils or aquifer materials, and more resistant to biodegradation. MTBE enters groundwater from leaking underground storage tanks and other releases of gasoline to the environment. There is no MCL or HBSL for MTBE, but the USEPA recommends concentrations in drinking water less than 20 to 40 $\mu\text{g/L}$ to avoid unpleasant taste and odor.⁽⁶⁰⁾ A number of States have adopted MCLs for MTBE in drinking water that range from 10 to 70 $\mu\text{g/L}$.

Monitoring by the NAWQA Program documented the frequent occurrence of MTBE in groundwater as early as the mid-1990s, and these data helped inform USEPA recommendations to reduce the use of MTBE in gasoline.^(84, 85) In the present study, which includes data collected from 1991 to 2010, MTBE was one of the most frequently detected VOCs in the Principal Aquifers. MTBE occurs mostly in shallow groundwater beneath urban areas, but only about 1 percent of shallow wells beneath urban land had a concentration greater than 20 $\mu\text{g/L}$. The widespread occurrence of MTBE in groundwater (fig. 6–15), despite its relatively short history of intense use (fig. 6–16), illustrates how vulnerable shallow groundwater is to contamination by newly introduced chemicals with physical and chemical properties that make them mobile and persistent in the subsurface.

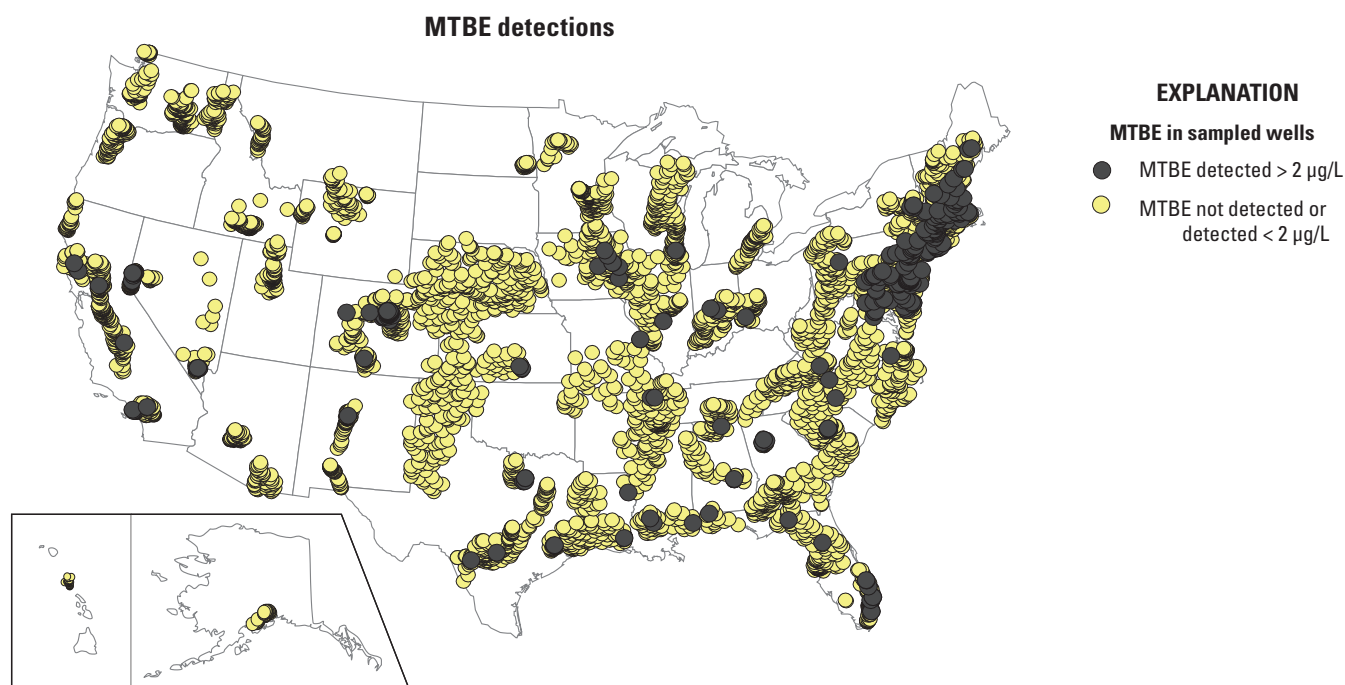


Figure 6–15. Methyl *tert*-butyl ether (MTBE) was widely detected across the United States. Nationally, MTBE was detected in 18 percent of shallow wells beneath urban land, 5 percent of deeper wells in drinking-water aquifers, and 1.4 percent of shallow wells beneath agricultural land. It was detected most frequently, however, in wells in the Northeast, which was one of the areas of high MTBE use in the 1990s.

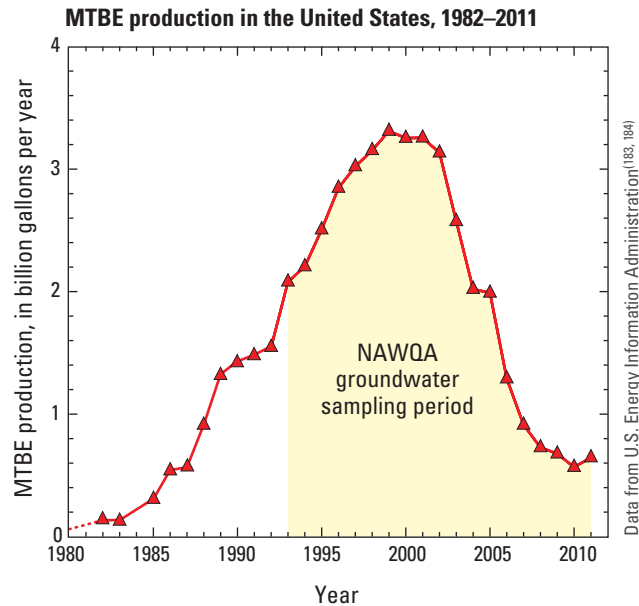


Figure 6-16. Methyl *tert*-butyl ether (MTBE) production in the United States increased rapidly in the 1980s and 1990s because of its use in oxygenated gasoline. In 1998, MTBE ranked fourth in production among organic chemicals produced in the United States.⁽¹⁸²⁾ Production and use have greatly decreased since 2000 partly because of concerns about contamination of drinking-water supplies. The use of MTBE was restricted or banned in 25 States as of 2007.⁽⁸³⁾

MTBE in Santa Monica, California

MTBE contamination in Santa Monica, California, led to the closure in 1996 of supply wells that provided about 50 percent of the city's water supply.⁽⁸³⁾ A new treatment plant was constructed to remove MTBE from the water supply and to restore the wells as a drinking-water source.⁽¹⁵³⁾ Costs of more than \$100 million dollars were incurred, including the costs of the treatment facility, of groundwater remediation and monitoring, and of about \$3 million annually to purchase replacement water during the time the wells could not be used.^(205, 206)



Photograph courtesy of the City of Santa Monica

Fumigants

From a national perspective, agricultural fumigants are detected infrequently in groundwater. In most Principal Aquifers, they were not detected at all. However, in areas where they were used, fumigants such as dibromochloropropane (DBCP) and ethylene dibromide (EDB) are still detected in groundwater, and at concentrations higher than their human-health benchmarks, decades after their use was banned because of health concerns (fig. 6–17).

Fumigants have been applied extensively in several areas of the United States since the 1950s to control soil pests in agriculture. In those early days of pesticide use, groundwater was not thought to be vulnerable to contamination from chemicals applied at the land surface.⁽⁸⁶⁾ This perception changed, however, when DBCP was detected in 1979 in California's Central Valley aquifer system, 2 years after its use had been banned there because of reported sterility among manufacturing workers.^(87, 88) Within a few years, DBCP was detected in groundwater in other States. The fumigants EDB, 1,2-dichloropropane (DCP), and 1,2,3-trichloropropane (TCP) also have long histories of use and were banned or unavailable for pesticide use by the early 1980s.^(89–91) The fumigants DBCP, EDB, and DCP cause cancer and other health problems.⁽²⁰⁶⁾

In the Central Valley aquifer system in California, DBCP was detected in 11 percent of all wells sampled in the NAWQA Principal Aquifer assessments, and nearly three-fourths of the measured DBCP concentrations exceeded the USEPA MCL of 0.2 µg/L (fig. 6–17). In one groundwater study area in the Central Valley aquifer system, DBCP was detected in one-half of the domestic wells that were sampled, and about one-third of the sampled domestic wells had concentrations greater than the MCL.^(29, 92) In the Hawaiian volcanic-rock aquifers underlying Oahu, DBCP and EDB were detected in more than 10 percent of wells, and DCP and TCP were detected in more than 30 percent of wells. Several of the fumigant concentrations measured in the Hawaiian volcanic-rock aquifers exceeded the Hawaii MCLs, which are lower than the USEPA MCLs.⁽⁹³⁾

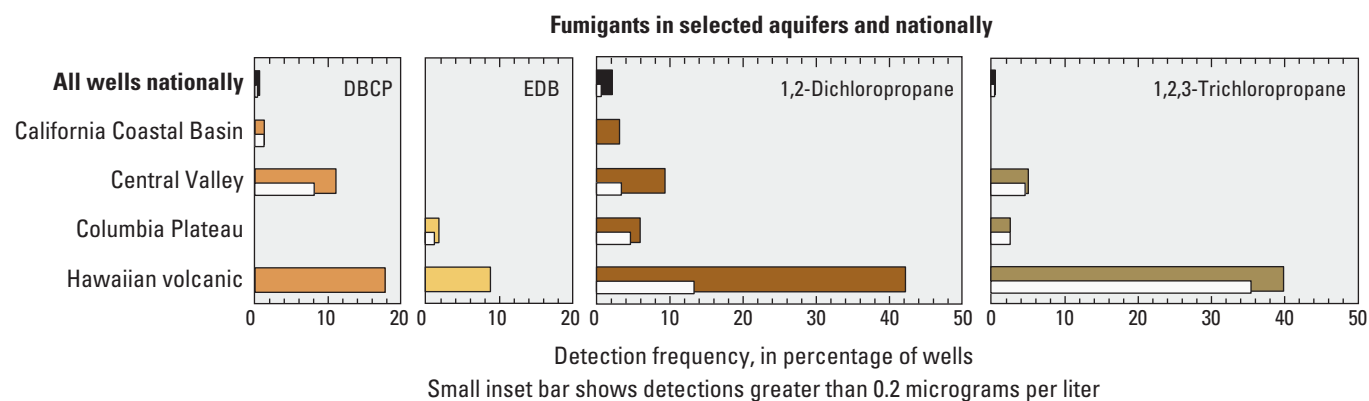
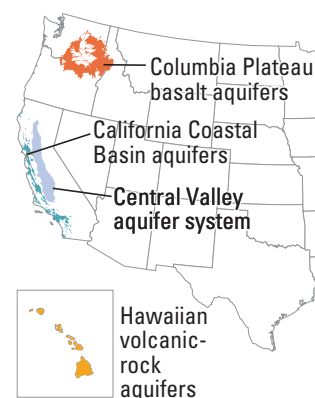


Figure 6–17. Nationally, agricultural fumigants were infrequently detected in groundwater, even at low concentrations. Where fumigant use was extensive, however, including parts of California (California Coastal Basin aquifers and Central Valley aquifer system), Washington (Columbia Plateau aquifers), and Hawaii (Hawaiian volcanic-rock aquifers), these chemicals were much more frequently detected in groundwater, even decades after their use was banned. (DBCP, dibromochloropropane; EDB, ethylene dibromide)

These agricultural fumigants are persistent in groundwater; samples for the NAWQA studies were collected between 1993 and 2002, about 25 years after the use of DBCP, EDB, DCP, and TCP as agricultural fumigants was discontinued. These VOCs remain in groundwater for a long time because they are highly soluble, do not sorb strongly to soils, and degrade very slowly. Forecasting models predict that concentrations of DBCP in Central Valley groundwater could continue to exceed the MCL for 70 years after the DBCP entered the aquifer⁽⁹⁴⁾ and that, similarly, DBCP could remain at detectable concentrations in Oahu groundwater for decades.⁽⁹⁵⁾ In the Central Valley, DBCP and the other fumigants are likely to move deeper into the aquifer, potentially affecting public-supply wells in addition to the domestic wells in which they are currently detected.⁽⁹⁶⁾ Fumigants in source water to public-supply wells can require costly treatment when alternative water supplies are not available. Treatment systems for fumigants in a number of public-supply wells on Oahu, installed in the early 1980s at a cost of approximately \$45 million, are still in operation, with ongoing annual maintenance costs of about \$350,000.⁽⁹⁷⁾



Photographs clockwise from top left: USDA, ARS; U.S. Salinity Laboratory; copyright istockphoto.com

Fumigants are used to control worms, weeds, fungi, and other microorganisms in soil. They are injected as gas into the soil before planting (top left) or are mixed with irrigation water. Fumigants have been used extensively for a variety of crops, including pineapple on the Hawaiian island of Oahu (bottom), potatoes and sugar beets in the Columbia Plateau and Snake River Plain in the northwest, and orchards, vineyards, and other crops in California (top, right).

Chapter 7: *How Does Our Use of Water Affect Groundwater Quality?*

About 80 billion gallons of groundwater is pumped each day from the Nation's aquifers, and 128 billion gallons per day of water is spread across the landscape for irrigation. This movement of water has altered groundwater flow systems—profoundly in some cases, where the flux of water through aquifers has more than doubled relative to natural conditions prior to development. Whenever water is removed or added to an aquifer, groundwater flow directions, flow rates, and often geochemical conditions change. Consequently, when our use of water alters groundwater flow systems, groundwater quality also is affected, sometimes in unexpected ways.

This chapter describes ways in which water use, particularly irrigation and groundwater pumping, have affected constituents in groundwater from geologic and manmade sources in a number of hydrogeologic settings.

How much have we changed groundwater flow systems?

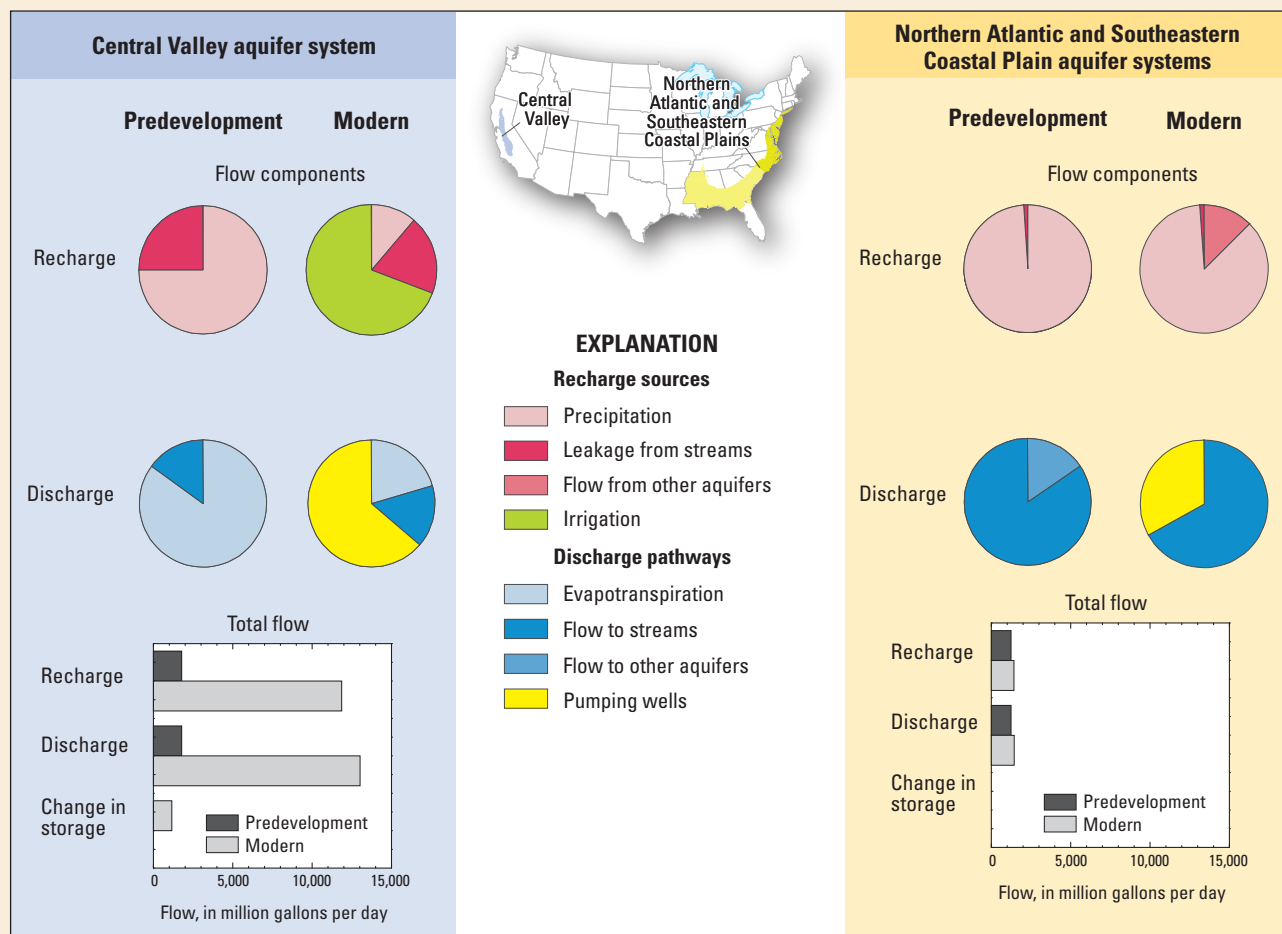
Aquifer water budgets help us understand how much pumping, irrigation, and other activities have changed groundwater flow systems. A water budget quantifies the volumes of water that enter, leave, and are stored in an aquifer during a specified amount of time. Examples of annual water budgets are shown for a western aquifer system—the Central Valley aquifer system in California—and for an area along the east coast that includes part of the Northern Atlantic Coastal Plain and the Southeastern Coastal Plain aquifer systems.^(28, 155, 156) Water use for agriculture, public supply, and other purposes associated with urban and residential development has substantially altered water flows in these aquifer areas.

In the Central Valley, total flows through the aquifer have increased sixfold. Groundwater recharge to the aquifer prior to development was from precipitation and leakage from streams. Discharge was mostly by evapotranspiration in wetlands and other low-lying areas. In modern times, irrigation accounts for nearly two-thirds of the annual recharge. Discharge is now mostly by pumping wells for nearly two-thirds of the annual recharge. Even with the

additional recharge, the amount of groundwater pumped in the Central Valley is much larger than the annual recharge. This situation has led to a large net loss of the water stored naturally in the aquifer. Pumping also has left less water available to support wetland vegetation and wildlife. Groundwater levels have declined by as much as hundreds of feet, and aquifer compaction from the loss of water has led to subsidence of the land surface.⁽¹⁵⁷⁾

In the Coastal Plain aquifer systems, total flows through the aquifer system have not changed greatly, but pumping has induced inflow of groundwater from other aquifers and reduced groundwater discharge to streams. Prior to development, recharge was entirely from precipitation and discharge was mostly to streams. In modern times, pumping accounts for about one-third of total annual discharges. Because groundwater discharge can contribute a large fraction of the flow in streams originating in the coastal plain, reductions in groundwater discharge are a potential concern for stream ecology.

Predevelopment and modern water flows through aquifers



Modified from Bexfield and others,⁽²⁸⁾ Faunt,⁽¹⁵⁵⁾ and Campbell and Coes⁽¹⁵⁶⁾

Large-Scale Flow Alterations in the Western Aquifers

The development of water resources for agricultural, urban, and residential uses in the arid and semiarid West has greatly increased both recharge to and discharge from the aquifers in these areas. Modern rates of recharge and discharge are more than twice the natural, predevelopment rates in some aquifers and basins (fig. 7–1). Infiltration of excess irrigation water and canal leakage are the two major sources of artificial recharge. Other sources of artificial recharge include leakage from water distribution pipes, sewer lines, and storm drains; septic-system effluent; and engineered infiltration of wastewater and stormwater. The increased discharge results primarily from groundwater pumping. Irrigation and pumping can accelerate the downward movement of manmade contaminants and increase concentrations of dissolved solids in groundwater.



Photograph by Jeff Vanuga, USDA, NRCS

When crops and lawns are irrigated, not all the water is used by the plants. Some of the excess irrigation water moves downward into the aquifer, augmenting natural groundwater recharge and potentially carrying contaminants from the land surface. The photograph shows an irrigated wheat field in Yuma, Arizona.

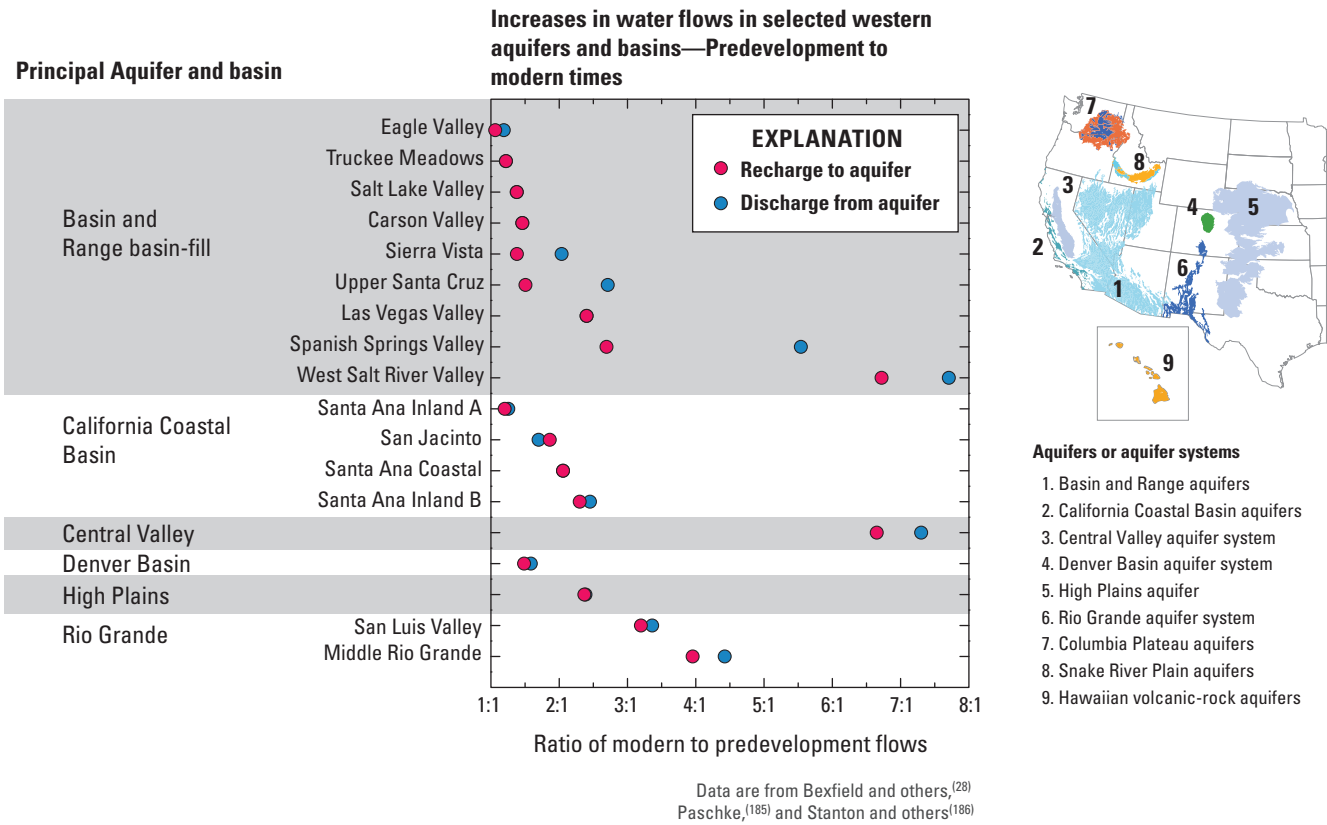


Figure 7–1. Our use of water has drastically changed how water moves in the West. The amount of water that moves through aquifers—both recharge and discharge—has doubled, tripled, or increased by even more in some basins. These large changes in groundwater flow can affect the occurrence of contaminants from both manmade and geologic sources.

Aquifers With Artificial Recharge Are More Vulnerable to Contamination From Human Sources

Artificial recharge from irrigation and other sources increases groundwater flow rates and in many cases adds water to an aquifer in places where there was little or no natural recharge prior to development. This new recharge water can make the aquifers more vulnerable to human sources of contamination because the new recharge water brings contaminants down from the land surface into the aquifer.

The basin-fill aquifer in the San Luis Valley, which is part of the Rio Grande aquifer system in southern Colorado, is an example of where some of these changes have taken place (fig. 7–2). The infiltration of excess irrigation water and leakage from irrigation canals has increased recharge to more than three times the predevelopment rate. The additional recharge occurs across the valley floor in areas of irrigated agriculture that received little natural recharge in predevelopment times. The increased recharge has made the shallow aquifer more vulnerable to contamination from the land surface by providing a pathway for their transport into groundwater. Concentrations of nitrate have increased from less than 3 mg/L as N throughout

San Luis Valley, Colorado

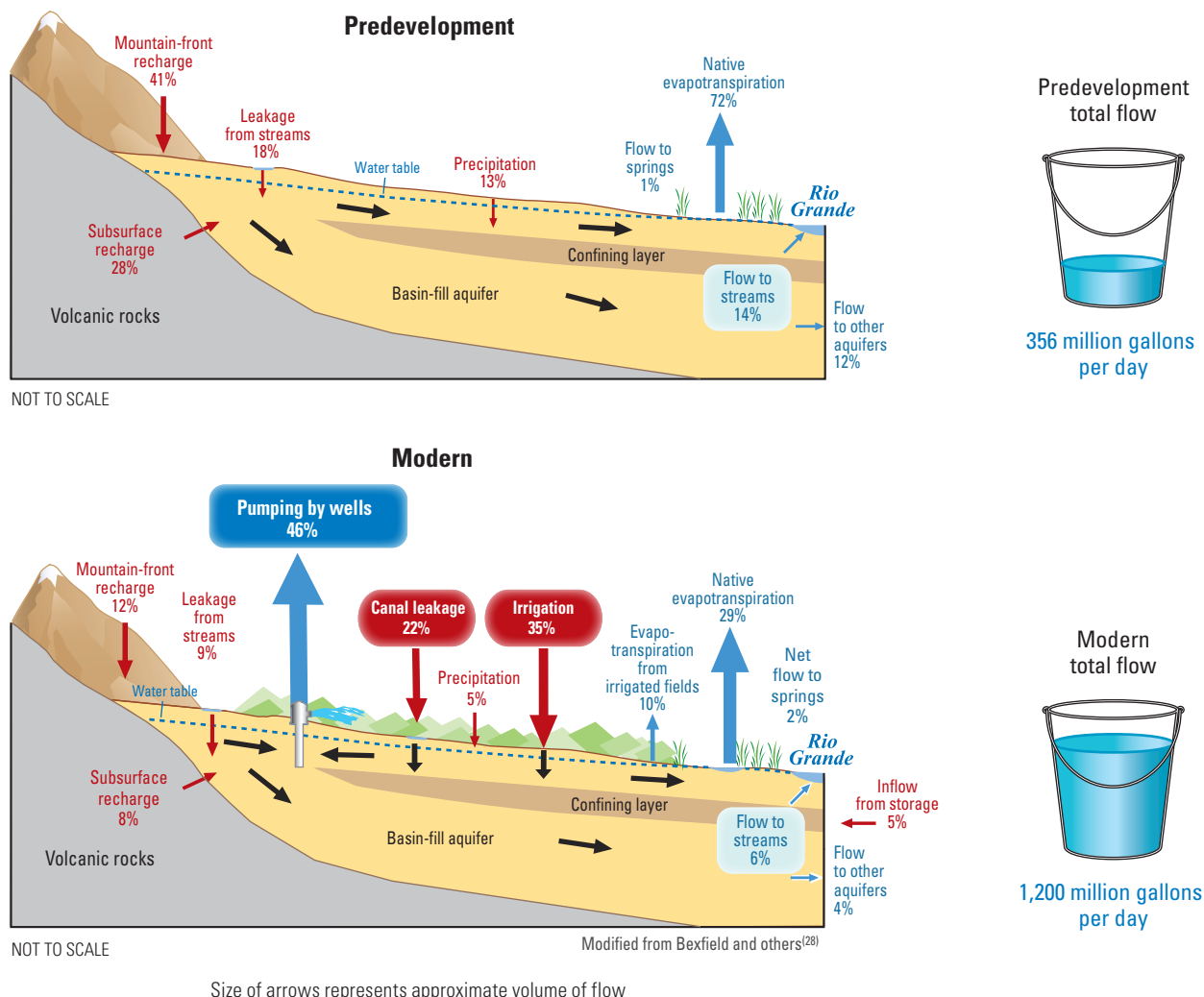


Figure 7–2. In the San Luis Valley basin-fill aquifer, in southern Colorado, irrigated agriculture and groundwater pumping have increased water flow through the aquifer more than threefold relative to predevelopment conditions. As a result, the shallow, unconfined aquifer, which is used for domestic supply, is more vulnerable to human sources of contamination.

the basin before agricultural development to more than 10 mg/L as N over broad areas as the result of leaching of fertilizer applied to crops.⁽⁹⁸⁾ The deeper, confined aquifer, from which public-supply wells pump water, remains relatively unaffected by these changes. However, domestic wells commonly draw water for household use from the shallow, unconfined aquifer, which is affected by the recent human activities on the land surface.

In the Central Valley, California, recharge has increased more than sixfold and discharge has increased more than sevenfold with water and land development. Before development, groundwater flowed upward in the valley center and discharged in wetlands and streams (fig. 7–3).⁽⁹⁹⁾ Infiltration of excess irrigation water and pumping from the deep aquifer have reversed the direction of flow so that groundwater now flows downward throughout the valley. (100, 101) In some areas, groundwater that previously discharged to the San Joaquin River, in the southern Central Valley, now flows laterally beneath the river toward pumping wells on the western side of the valley (fig. 7–3). Downward flow through a confining layer also is enabled by wells that are screened in upper and lower aquifer layers.⁽²⁹⁾ As a result, both shallow and deeper parts of the aquifer in the center of the valley are more vulnerable to contamination by manmade chemicals from the land surface.⁽⁹²⁾

Central Valley, California

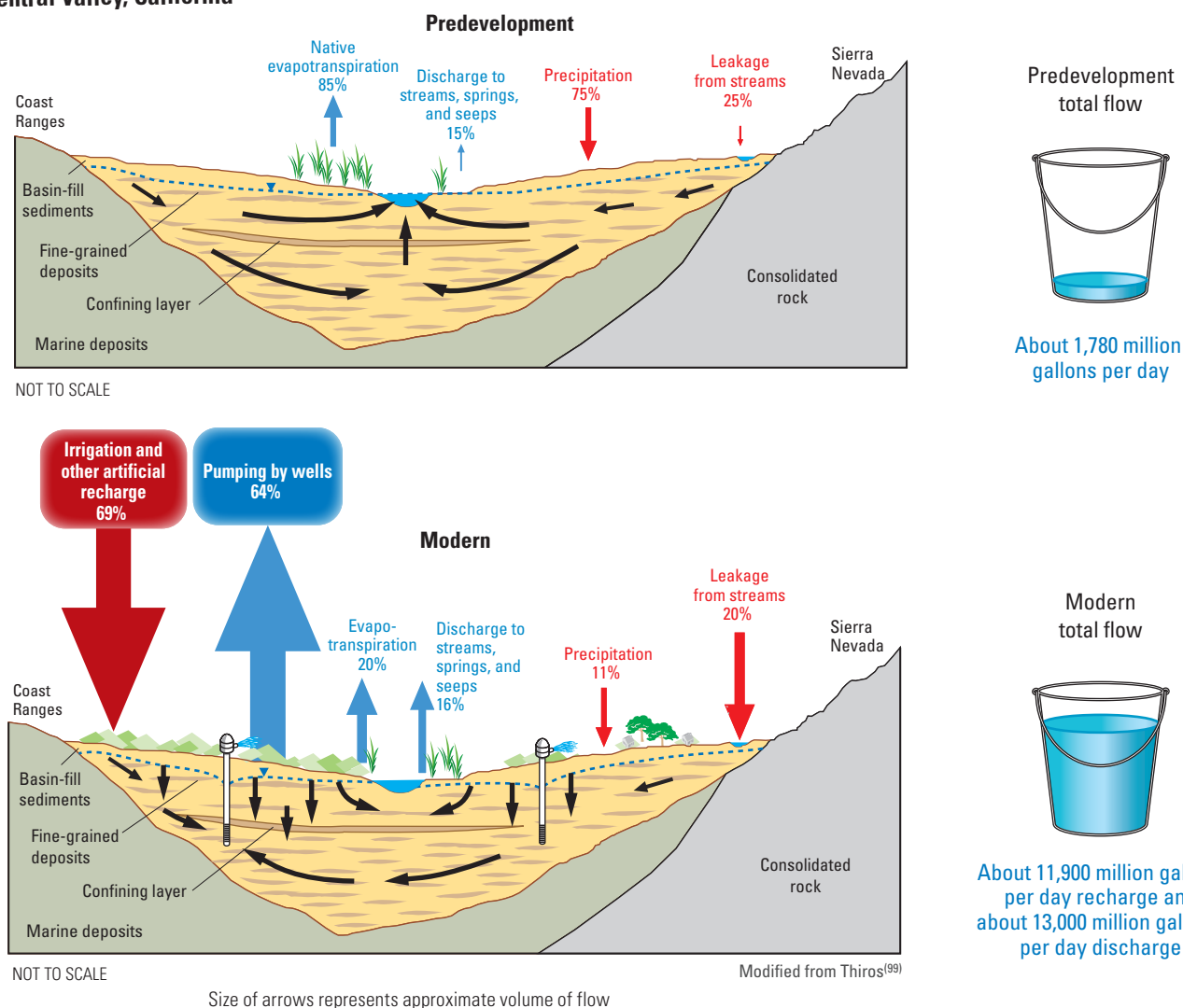


Figure 7–3. Infiltration of excess irrigation water and pumping from the deep aquifer have reversed natural flow directions in the Central Valley, California, so that groundwater flows downward and laterally, where it used to flow upward. As a result, the deeper aquifer, used for public supply and irrigation, is more vulnerable to human sources of contamination.

Dissolved Solids Increase in Aquifers With Artificial Recharge

Concentrations of dissolved solids are naturally high in groundwater and soil water in the arid and semiarid West (see “Dissolved Solids” section in chapter 5). Irrigation and other sources of artificial recharge, however, have increased those concentrations across widespread areas in parts of the Central Valley, California Coastal Basin, Basin and Range basin-fill, Rio Grande, and High Plains aquifers or aquifer systems.^(28, 56) High concentrations of dissolved solids can restrict the use of the groundwater for drinking water or irrigation (see chapter 4). In the Santa Ana Basin in California, intensive water management for dissolved solids is needed to maintain drinking-water supplies (see sidebar, Groundwater in the intensively managed Santa Ana Basin, southern California, p. 115). High dissolved solids in irrigation water can reduce crop yields and contribute to soil salinization.

Concentrations of dissolved solids increase in groundwater as the result of artificial recharge for several reasons. The dissolved salts in irrigation water are left behind when the water evaporates or is taken up by plants, and percolation of excess irrigation water to the water table carries these salts to the groundwater. Excess irrigation water can flush minerals that have accumulated from thousands of years of weathering or evaporative concentration in the unsaturated zone down to the water table. Irrigation or other artificial recharge can raise the water table close to the land surface, so that direct evapotranspiration of shallow groundwater can further concentrate dissolved solids.



Photograph by Gary Bañuelos, USDA, ARS

Salinization—the buildup of salts in soils to levels that are harmful to plants—is a worldwide problem and affects about one-fourth of the irrigated land in the United States.⁽¹⁹¹⁾ Effects include reduced crop yield and restrictions on the kinds of crops that can be grown. Cotton for example (top left) is one of the more salt-tolerant crops grown in California. White salt deposits, from severe salinization, coat fields in the western San Joaquin Valley in California (middle). Salt-encrusted soils from the Colorado River Basin (bottom right).



Photograph by Scott Bauer, USDA, ARS



Ron Nichols, USDA, NRCS

Groundwater in the intensively managed Santa Ana Basin, southern California

Groundwater is a critical resource in the Santa Ana Basin in southern California, supplying two-thirds of the water used by the 5 million people who live there—about 1 billion gallons each day.⁽¹⁵⁸⁾ In parts of the basin, however, concentrations of dissolved solids in groundwater are higher than the SMCL of 500 mg/L. More than 100 years of irrigated agriculture, natural processes such as evaporative concentration, and wastewater discharge contribute to these high concentrations of dissolved solids. Now, groundwater is intensively managed—through artificial recharge, desalination, high-level wastewater treatment, and saltwater intrusion barrier wells—to ensure that there is enough good-quality groundwater to supply the water needs of the population.

Engineered recharge facilities in the upper parts of the basin replenish the basin-fill aquifers with stormwater runoff and treated municipal wastewater to offset groundwater withdrawals. The recharged stormwater and wastewater typically have higher dissolved solids concentrations than the natural recharge, which is from mountain streams. Dissolved solids concentrations in the groundwater in these parts of the basin also are increased by excess irrigation water, especially irrigation water imported from the Colorado River.

Water from the Santa Ana River also is used to replenish the groundwater system. Much of the river's flow is captured in the lower part of the basin and made to infiltrate into the aquifer. The river is the source of almost all the recharge to the aquifer in the lower part of the basin, but the river's flow here is a mixture of treated municipal wastewater, intermittent stormwater runoff from agricultural and urban land, and discharge of groundwater that has been affected by human activities.⁽¹⁵⁸⁾ Pumping wells,

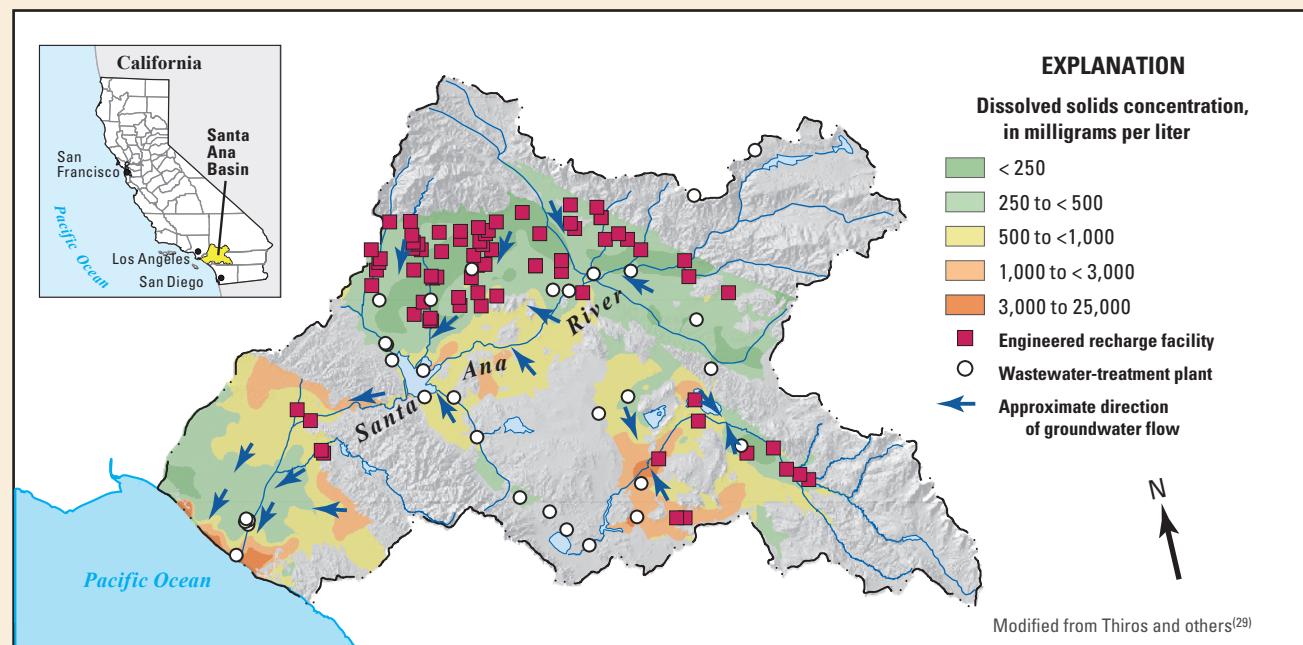


Recharge basins infiltrate Santa Ana River water into the aquifer

desalination plants (for groundwater), and advanced wastewater treatment are being used to manage sources of dissolved solids to the river and to the aquifer.

Since 2008, water from a state-of-the-art advanced-wastewater treatment facility, which reduces dissolved solids in the effluent to less than 100 mg/L, is being used to recharge the aquifer at facilities near the Santa Ana River. This facility is the largest water purification project of its kind in the world and cost \$480 million to build.⁽¹⁵⁹⁾ A \$143 million expansion at the facility is scheduled for completion in 2014.

Dissolved solids and engineered recharge in the Santa Ana Basin, California

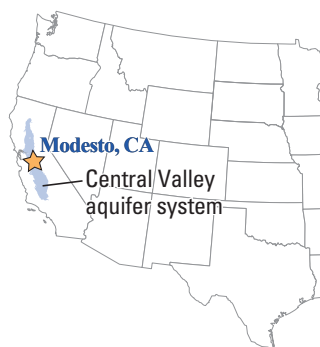


Groundwater Mixing and Geochemical Changes—Trace Elements Are Mobilized in Various Hydrogeologic Settings

Pumping, irrigation, and other flow alterations can mix waters from different sources or from different depths within an aquifer. If the compositions of the mixed waters are different, dissolved constituents can react with one another and with aquifer materials to release naturally occurring trace elements into the groundwater, potentially affecting human or ecosystem health.

Uranium in the Central Valley and High Plains Aquifers

In the Central Valley aquifer system near Modesto, California, uranium is mobilized (fig. 7–4) because of geochemical changes that result from agricultural and urban irrigation.^(102, 103) Irrigation increases plant growth and microbial activity, which produce carbon dioxide. The carbon dioxide reacts with mineral solids to form bicarbonate in the soil water and shallow groundwater. Uranium occurs naturally in the aquifer; it comes from the granite rocks of the Sierra Nevada Mountains to the east, which are the source of the aquifer sediments in the valley. The uranium is more soluble in groundwater that contains bicarbonate because the bicarbonate chemically binds with the uranium to keep it in solution (see “Radionuclides”



Uranium in the Central Valley aquifer system

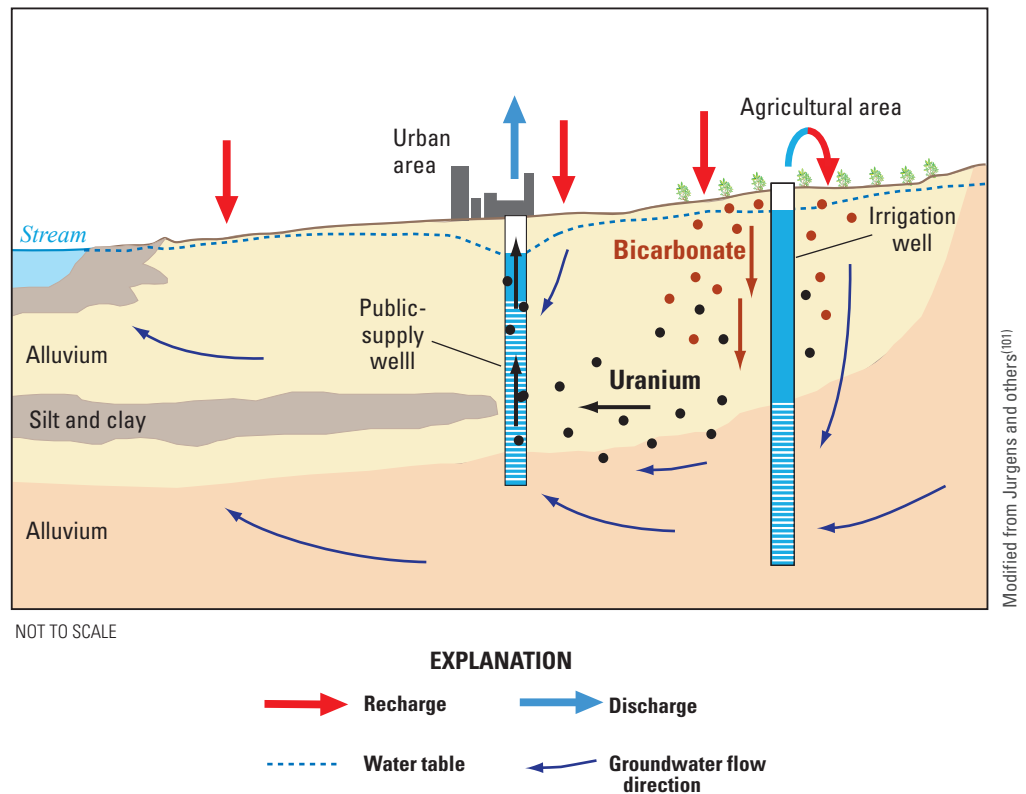
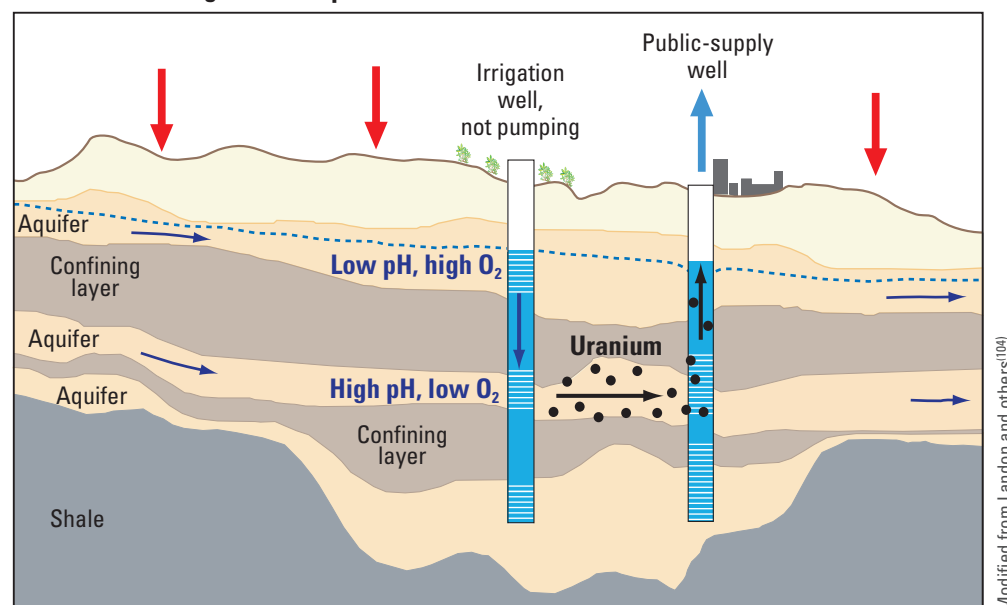


Figure 7–4. Uranium is mobilized in groundwater by irrigation recharge that contains high concentrations of bicarbonate in the Central Valley aquifer system, Modesto, California.

section in chapter 5). The combination of irrigation and groundwater pumping increases the movement of the shallow, uranium-rich groundwater deeper into the aquifer. As a result, concentrations of uranium greater than the MCL are present in groundwater across the eastern San Joaquin Valley, and uranium in groundwater threatens the long-term sustainability of the aquifer as a source of drinking water.⁽¹⁰²⁾

In the High Plains aquifer in York, Nebraska, pumping mixes water from shallow and deep aquifers,^(103, 104) changing redox conditions and mobilizing uranium in the deep aquifer (fig. 7–5). The High Plains aquifer in this area is a layered sequence of aquifers separated by confining layers. The aquifer is heavily pumped to provide water for irrigation, and the pumping wells commonly are screened in more than one aquifer layer. Hydraulic head in the upper aquifer is higher than in the lower aquifer, so groundwater would flow downward if the confining unit were not present. When wells are not pumping, water can flow from the shallow, unconfined aquifer down through the well and into the deep, confined aquifer. Groundwater in the shallow, unconfined aquifer and groundwater in the lower, confined aquifer are chemically distinct; water in the shallow aquifer is oxygenated and has slightly acidic to neutral pH, whereas water in the lower aquifer is nearly anoxic and has slightly alkaline to neutral pH. When these waters mix in the deep aquifer, uranium is released from aquifer sediments into the groundwater. The mixed water with elevated uranium is pumped from a public-supply well that is screened in the deep aquifer.

Uranium in the High Plains aquifer



NOT TO SCALE

EXPLANATION



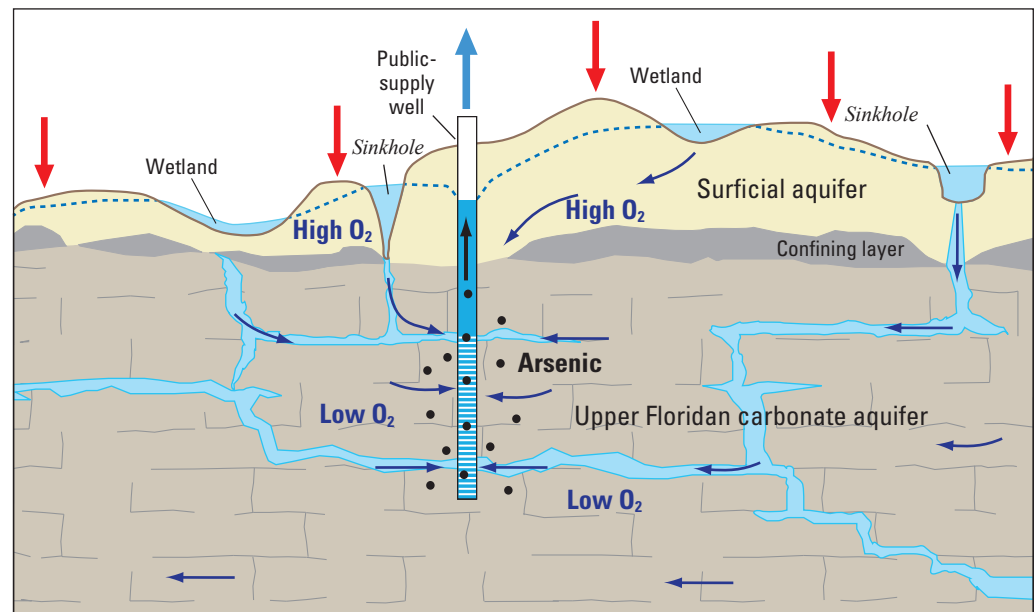
Figure 7–5. Uranium is mobilized in groundwater by the mixing of groundwater from different depths through long-screened wells in the High Plains aquifer, York, Nebraska. O₂, dissolved oxygen.

Arsenic in the Upper Floridan Aquifer

The limestones that make up the Upper Floridan aquifer contain small crystals of pyrite, a mineral that can contain arsenic. Pyrite is stable in anoxic water, but dissolves when exposed to oxic water, releasing the arsenic to groundwater. Mixing of anoxic and oxic water can occur inadvertently during high-volume pumping and during aquifer storage and recovery. High-volume pumping of a deep public-supply well in the Upper Floridan aquifer near Tampa, Florida, causes oxic water from the overlying surficial aquifers to be pulled down into anoxic water of the Upper Floridan aquifer (fig. 7–6). When the well was not being pumped, concentrations of arsenic were about 3 µg/L, but when the well was being pumped, concentrations were as much as 19 µg/L, which is almost twice the MCL of 10 µg/L.⁽¹⁰⁵⁾ Water from this well is blended with water from other public-supply wells so that arsenic concentrations in the distribution system remain below the MCL.



Arsenic in the Upper Floridan and overlying surficial aquifers



NOT TO SCALE

Modified from Ayotte and others⁽¹⁰³⁾ and Katz and others⁽¹⁰⁵⁾

EXPLANATION

- Recharge
- Discharge
- Water table
- ↺ Groundwater flow direction

Figure 7–6. Arsenic in the carbonate rocks of the Upper Floridan aquifer is released to groundwater when recently recharged oxic groundwater is drawn down into the Upper Floridan aquifer by a high-volume pumping well near Tampa, Florida.

Selenium in the Denver Basin Aquifer System and Across the Irrigated Western States

Application of oxygenated irrigation water has enhanced the mobility of selenium in the shallow Denver Basin aquifer system and in parts of the West where selenium occurs in rocks and sediments. Selenium is particularly problematic for livestock and wildlife because it bioaccumulates and can be toxic at elevated levels.⁽¹⁰⁶⁾ Since the 1930s, selenium has been known to cause sickness in cattle and horses where it is present in soils and plants. The association of high selenium levels and irrigation was first recognized in the 1980s, when waterfowl deaths and deformities at the Kesterton National Wildlife Refuge in California were linked to selenium in irrigation drainage water from Central Valley agricultural lands.^(107–109)

In the shallow aquifers of the Denver Basin aquifer system, oxygenated recharge mobilizes selenium from rocks and sediments by converting the reduced form selenite to the more soluble and biologically available oxidized form selenate. Selenium concentrations in groundwater are higher in the shallow sandstone layers and overlying alluvial aquifer, where redox conditions are mostly oxic or mixed, than in the deeper sandstone layers (fig. 7–7). Irrigation in agricultural and urban areas has increased recharge of oxygenated groundwater to the aquifer, and pumping from the sandstone aquifers has increased downward flow of the oxygenated water.^(7, 110)



Photograph by Paul Diaz, Jr., USGS

Sign posted at Sweitzer Lake State Park in the lower Gunnison River Basin in western Colorado.

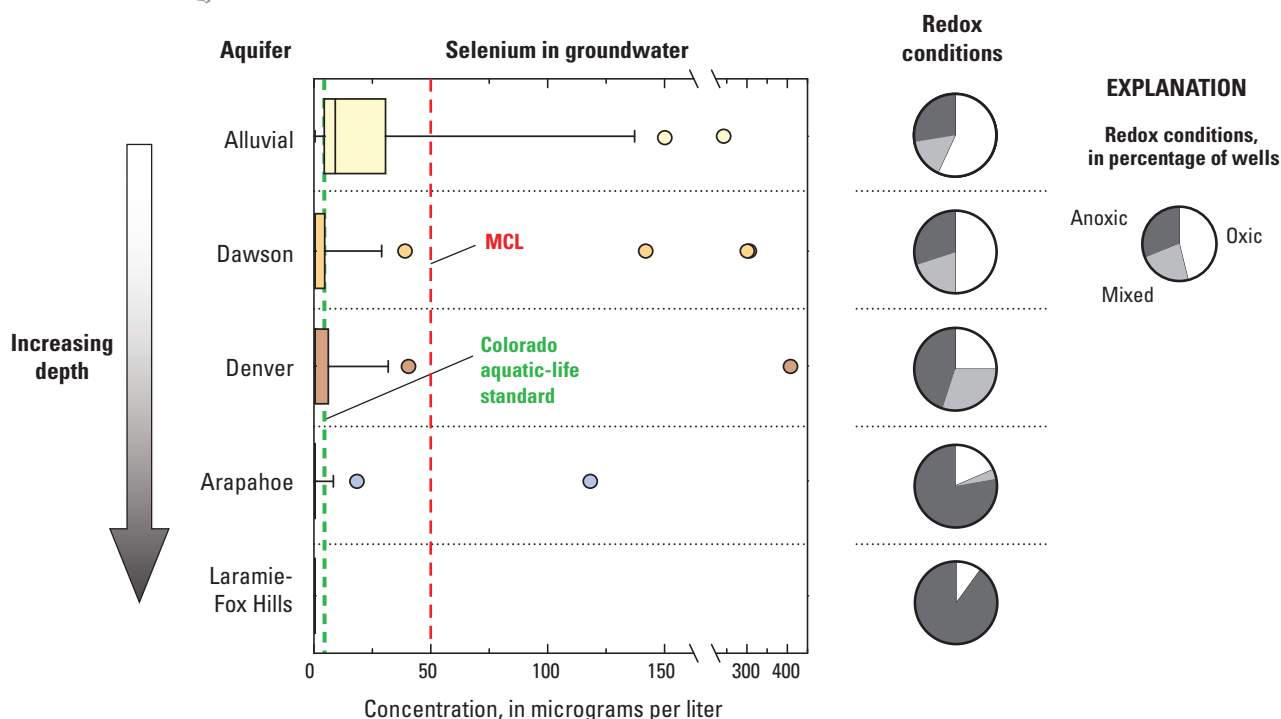


Figure 7–7. Selenium concentrations in the Denver Basin are much higher in the alluvial and shallow sandstone aquifers than in the deeper sandstone aquifers. Selenium in the rocks and sediments that make up the shallow aquifers is released when it interacts with oxygenated recharge from precipitation and irrigation. As a result, concentrations of selenium exceed the MCL for selenium much more frequently in the shallow Denver Basin aquifer system than nationally.

These changes have the potential to move the selenium down into the deeper aquifers that are used for drinking-water supply. The shallow aquifers provide base flow to nearby streams and, in some areas, deliver concentrations of selenium that exceed the Colorado State standard (4.6 µg/L) for the protection of aquatic life (fig. 7–7).



Photograph from USGS

Salt deposits along the banks of Toll Gate Creek in Aurora, Colorado, contain selenium from the underlying bedrock and aquifer sediments. When streamflow levels and the water table rise during storm events and periods of groundwater recharge, the salts dissolve and release selenium to the streamwater. As a result, concentrations of selenium in Toll Gate Creek have been consistently above the Colorado aquatic-life standard since the early 2000s.^(7, 110)

Radium in the Northern Atlantic Coastal Plain Aquifer System

In the Northern Atlantic Coastal Plain aquifer system in southern New Jersey, radium mobility is enhanced by the application of ammonia-based fertilizers and by recharge of septic-system effluent (fig. 7–8).^(46, 103) The ammonia in these sources is oxidized to nitrate (a process called nitrification; see chapter 3) by microbes in the unsaturated zone and in oxic, shallow groundwater. Nitrification generates acidity, further lowering the naturally low pH in the aquifer. At low pH values (less than 5), the quartz-rich sediments of the coastal plain aquifers have little capacity to sorb cations, such as radium. Consequently, radium that occurs naturally in aquifer sediments is released to groundwater. Groundwater with elevated radium concentrations is drawn deeper into the aquifer by the pumping of public-supply wells, which withdraw large volumes of water. Although the aquifer materials do not contain large amounts of radium or its radioactive parent elements, the change in the groundwater chemistry is sufficient to mobilize the radium that is present. As a result, concentrations of radium in 21 percent of the public-supply wells sampled in the southern New Jersey study area were above the MCL for combined radium (see chapter 5).⁽⁴⁶⁾



Radium in the Northern Atlantic Coastal Plain aquifer system

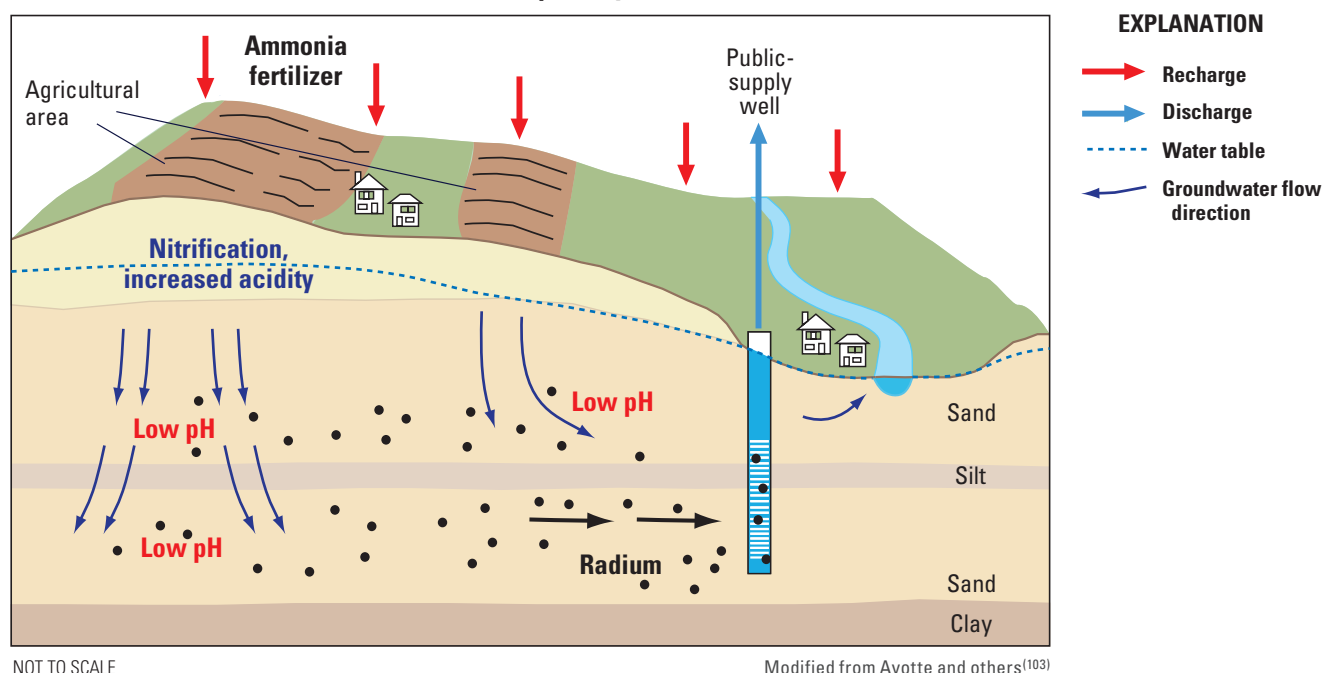


Figure 7–8. In the Northern Atlantic Coastal Plain aquifer system in southern New Jersey, fertilizer application and septic-system effluent lead to decreases in pH that enhance radium mobility in the groundwater.

Groundwater Mixing Across Aquifer Boundaries—*Induced Infiltration and Saltwater Intrusion*

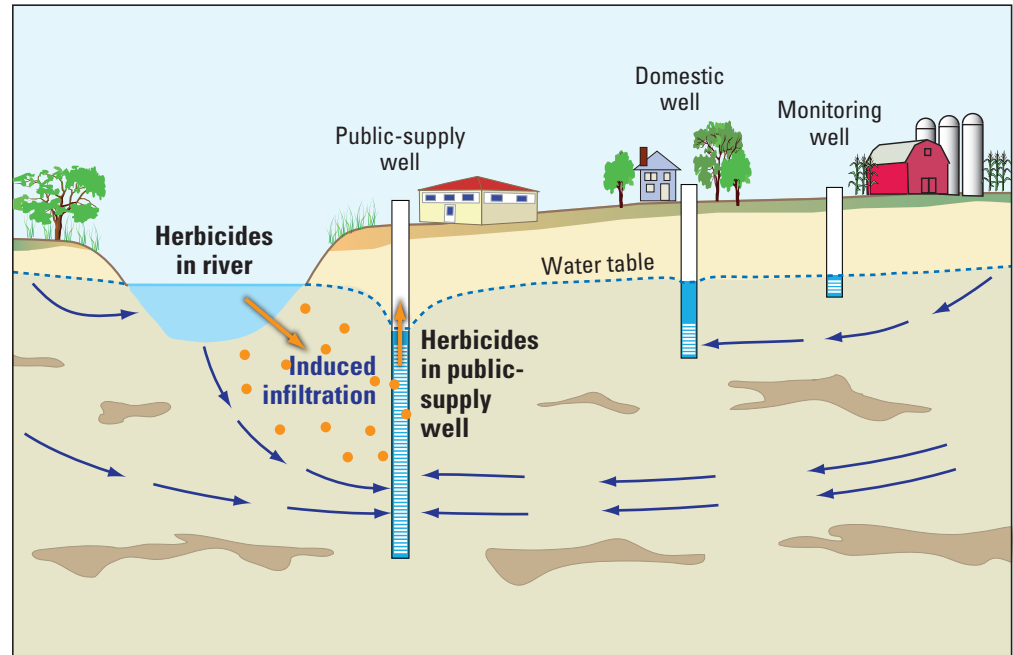
Streams and the ocean are natural boundaries for groundwater flow systems. When flow systems are altered by pumping, flow directions can change, allowing groundwater to mix with seawater or river water. Pumping also can draw deep, saline groundwater up into parts of aquifers used for water supply.

Movement of Pesticide Compounds From Rivers To Aquifers in the Glacial Aquifer System

Many public-supply wells in the glacial aquifer system are near rivers. Thick, permeable glacial deposits in river valleys make these locations favorable for groundwater pumping. Pumping can reverse the natural direction of flow toward rivers, causing water to move from the river into the aquifer, a process called induced infiltration. When this process happens, the aquifer becomes vulnerable to contamination from chemicals in the river. One area where induced infiltration occurs is in the glacial aquifer system along the Great Miami River in southwestern Ohio.⁽¹¹⁾ Agricultural chemicals, including herbicides such as atrazine, are present in the river, especially during rainstorms during the times of year when the chemicals are used. Pumping of high-capacity public-supply wells can draw the river water and contaminants through the riverbed into the groundwater (fig. 7–9); river water can reach the wells within weeks or even days. As a consequence, pesticide compounds are detected more frequently and at higher concentrations in public-supply wells near streams than in domestic wells or shallow groundwater beneath agricultural areas in this part of the glacial aquifer system.⁽⁸⁾



Herbicides in the glacial aquifer system



NOT TO SCALE

Modified from Rowe and others⁽¹¹⁾

EXPLANATION

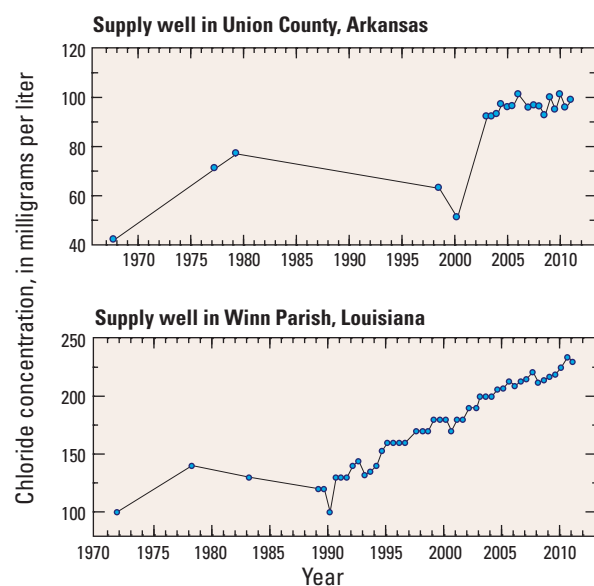
- Water table
- ← Groundwater flow direction

Figure 7–9. In the glacial aquifer system in southwestern Ohio, public-supply wells along the Great Miami River induce the infiltration of river water into the aquifer. Pesticides in the river can be drawn into the aquifer and mix with groundwater that is pumped by the supply wells.

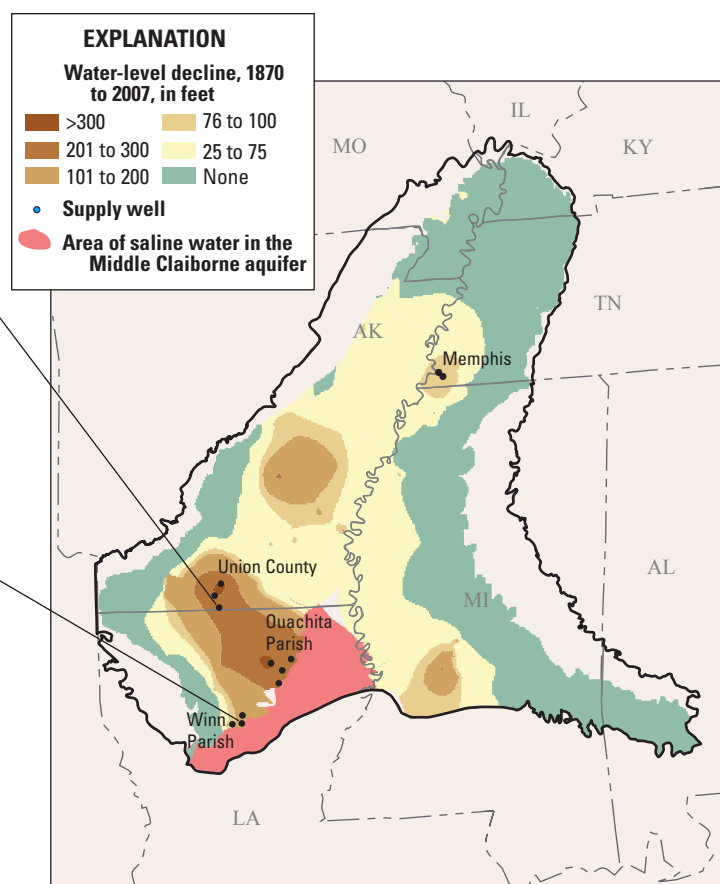
Upward Movement of Saline Water in the Mississippi Embayment–Texas Coastal Uplands Aquifer System

Deep, saline groundwater has moved upwards and inland in parts of the Mississippi embayment–Texas coastal uplands aquifer system as the result of pumping-induced declines in water levels. The freshwater in this aquifer system is underlain by saline groundwater that originated as seawater when the sediments were deposited. Large amounts of groundwater pumping since the early 1900s for public supply and industry have lowered groundwater levels by as much as 300 ft in parts of the aquifer system (fig. 7–10).^(33, 112) When hydraulic heads are lowered by pumping in the freshwater aquifer, the saltwater can move upward or inland to parts of the aquifer used for water supply. This process is called saltwater intrusion. In supply wells in southern Arkansas and northern Louisiana, saltwater intrusion has caused chloride levels to more than double during the past 40 years (fig. 7–10). Saltwater intrusion also has affected groundwater supplies along the Atlantic coast from Maine to Florida⁽¹¹³⁾ and along parts of the Pacific coast (see sidebar, Groundwater in the intensively managed Santa Ana Basin, southern California, p. 115).

Chloride in supply wells



Water-level decline



Modified from Clark and others⁽¹⁸⁷⁾ and Kingsbury and others⁽³³⁾

Figure 7–10. Large amounts of groundwater pumping during the past century have lowered water levels and caused saline water to move into areas of freshwater used for water supply in the Middle Claiborne aquifer, which is part of the Mississippi embayment–Texas coastal uplands aquifer system. Since the late 1990s, management actions to reduce groundwater withdrawals have reversed the water-level declines in some parts of the aquifer.



Photograph from USGS

Rangeland in the Nebraska Sandhills overlies the northern part of the High Plains aquifer.

Chapter 8: *How Is Groundwater Quality Changing?*

Concentrations of chemical constituents in natural waters—even in groundwater—can vary because of year-to-year climatic differences and because natural processes are inherently variable. In contrast, consistent change over time in a particular direction is a trend, and trends in contaminant concentrations raise concerns about the sustainability of groundwater use in future decades. Studying trends in groundwater quality at national or even regional scales is a large undertaking because of the expense of collecting consistent long-term data over large areas and because changes in response to contaminant inputs might not be apparent for many years. Identifying trends in groundwater quality and investigating their causes, however, is essential to helping water managers prepare for the future. Once contaminants in groundwater reach levels that impair its use, it takes a long time for reductions in contaminant inputs to restore the groundwater to its original quality, if such restoration is possible.

This chapter describes trends in groundwater quality and their implications for future groundwater-quality conditions.



A trend is a consistent change over time in a particular direction, distinct from the short-term changes that can result from seasonal effects, year-to-year climatic differences, or the inherent variability of natural processes.

Decadal Trends in Groundwater Quality, Early 1990s to 2010

Upward trends in concentrations of dissolved solids, chloride, and nitrate are indications of human influence on groundwater quality. Concentrations of all three of these constituents are increasing in many parts of the United States.^(2, 3) Two-thirds of groundwater study areas had upward trends for concentrations of dissolved solids, chloride, and (or) nitrate (fig. 8–1); these trends were based on repeated sampling of the wells in groundwater study areas at 10-year intervals (fig. 8–1). Most changes in concentrations were measured in young groundwater (groundwater that was recharged since the early 1950s) because young, shallow groundwater is more likely to be affected by recent activities at the land surface than is older, deeper groundwater.⁽¹¹⁴⁾

The largest changes in concentrations of dissolved solids and chloride occurred in urban areas of the Northeast and upper Midwest and, for dissolved solids only, in agricultural areas in the Southwest and Florida (fig. 8–1). Urban sources of dissolved solids and chloride include wastewater disposal, stormwater runoff, and road-salt application. Irrigation contributes to increasing concentrations of dissolved solids in a number of aquifers in the West and Southwest (chapter 7). Upward trends in dissolved solids are of particular concern in arid areas of the western United States, where water supplies are scarce and dissolved solids concentrations in groundwater are naturally high, because of the potential limitations that high dissolved solids concentrations may place on future uses of groundwater. Upward trends in chloride concentration are a concern where groundwater discharges to streams because of the potential effects of high chloride concentrations on aquatic ecosystems.^(115–118)

The largest changes in concentrations of nitrate occurred in shallow groundwater beneath agricultural areas. Increases in nitrate concentrations were mostly in oxic groundwater, in which denitrification cannot effectively reduce nitrate.^(114, 119–121) In oxic groundwater, nitrate is similar to dissolved solids and chloride, generally—there are many natural and human sources that add these constituents to groundwater, but there are few natural processes that remove them. Upward trends in nitrate are a concern because of the limitations that elevated nitrate concentrations may place on drinking-water uses and because of the effects of nitrogen loads contributed by groundwater discharge to coastal waters.

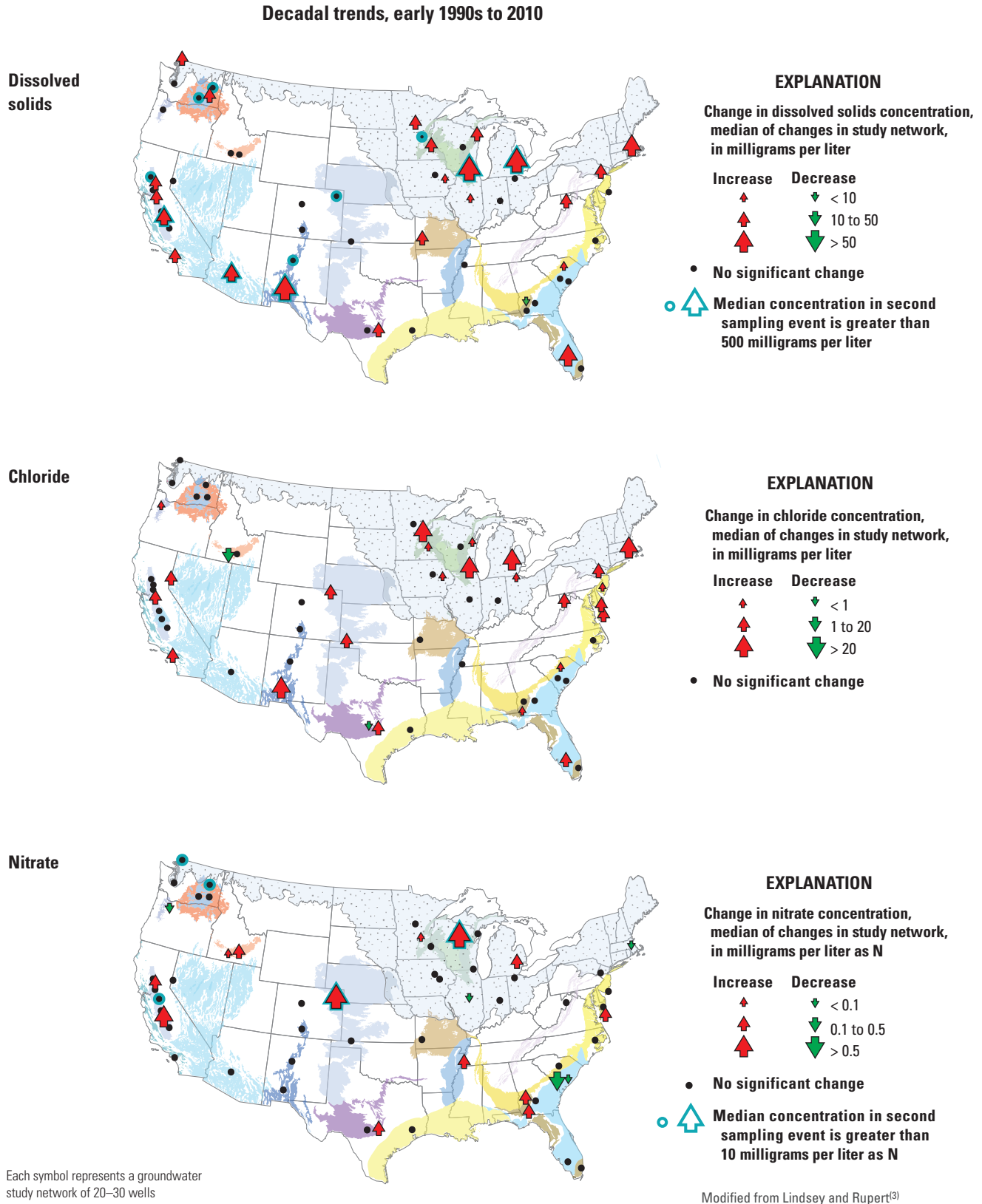


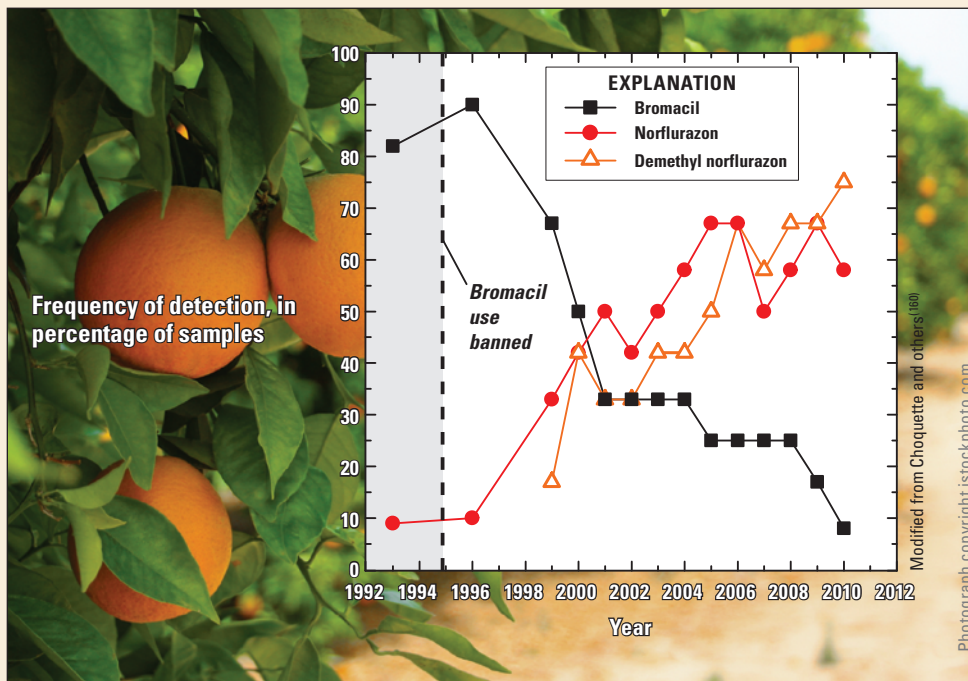
Figure 8–1. Concentrations of dissolved solids, chloride, and (or) nitrate in groundwater increased between the early 1990s and 2010 in two-thirds of the groundwater study areas across the Nation. The studies targeted shallow groundwater beneath urban and agricultural areas (about two-thirds of studies) and deeper groundwater from drinking-water aquifers (about one-third of studies). Trends were determined statistically on the basis of samples collected from the same wells in the study area at 10-year intervals.

Although most changes in groundwater quality between the early 1990s and 2010 were in shallow, young groundwater, similar changes are likely to occur in deeper parts of some aquifers in the future as the shallow groundwater moves downward over time. The deep groundwater in permeable, unconfined aquifers is especially vulnerable to change, for example, in the Central Valley aquifer system in California and in the surficial deposits of the Northern Atlantic Coastal Plain aquifer system (fig. 8–2).

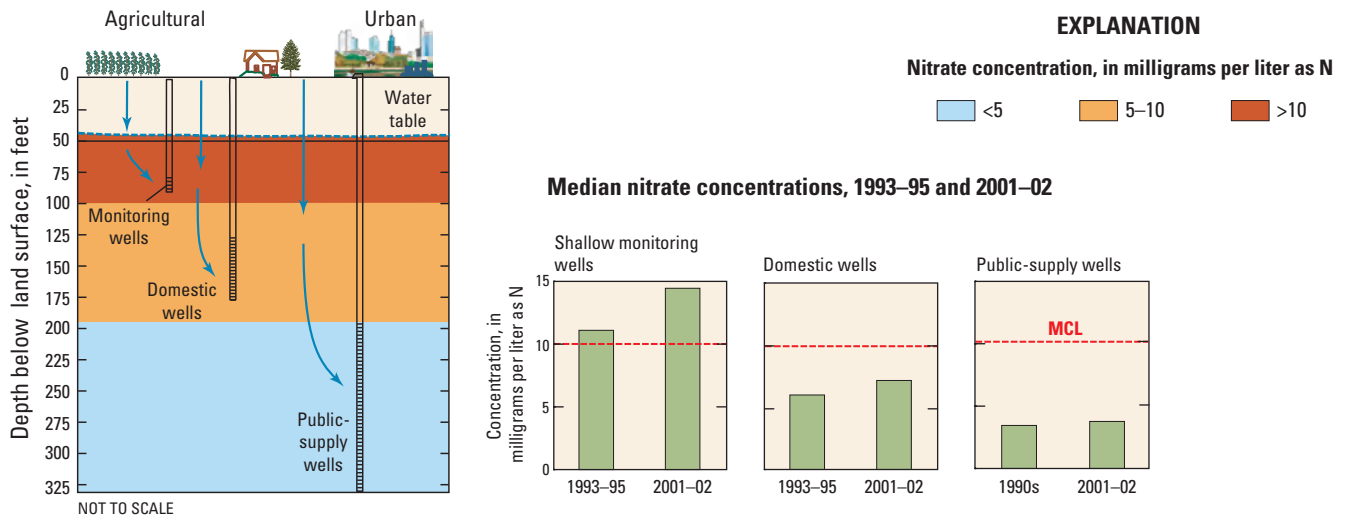
Changes in concentrations of manmade chemicals, such as pesticides and VOCs, in groundwater are closely related to their use. Data on chemical use are needed to understand the causes of these kinds of changes (see sidebar, Pesticide detections in groundwater in response to changing pesticide use, this page). However, information on historical use of pesticides and other manmade chemicals is not often available, either for specific areas or at the national scale, making it difficult to determine why concentrations have changed. At the national scale, three frequently detected pesticides—atrazine, deethylatrazine (a breakdown product of atrazine), and prometon—decreased in concentration from the early 1990s to the early 2000s, although the frequencies at which the compounds were detected in groundwater did not change.⁽¹²²⁾ The decrease in atrazine and deethylatrazine concentrations could be related to product changes in the early 1990s that resulted in less atrazine applied per unit area, but there is not enough information to know for sure.

Pesticide detections in groundwater in response to changing pesticide use

Detections of bromacil, a herbicide applied to citrus crops, decreased in the 1990s and 2000s in the unconfined surficial aquifer in central Florida. These changes followed restrictions on bromacil use that began in 1994. Growers began to replace bromacil with norflurazon, a newer herbicide, in citrus orchards. Within a few years, norflurazon and its degradate desmethyl norflurazon were detected in groundwater more frequently than was bromacil.^(160, 201) These changes in groundwater would be difficult to interpret without knowledge of the changing patterns of pesticide use.



Central Valley aquifer system, eastern San Joaquin Valley, California



Northern Atlantic Coastal Plain surficial aquifer system, Delmarva Peninsula, Maryland and Virginia

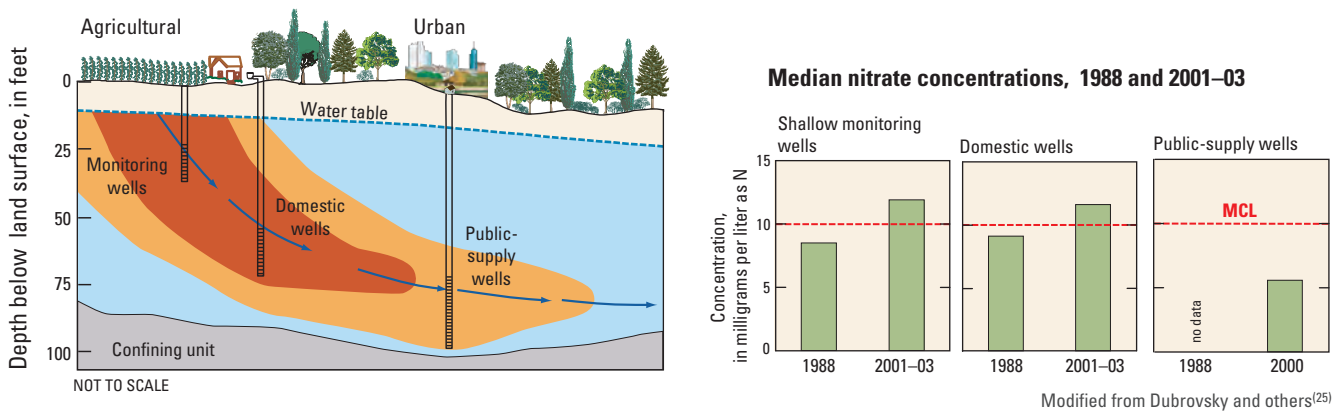


Figure 8–2. Nitrate concentrations increased more in groundwater from shallow monitoring wells than in groundwater from domestic or public-supply wells in the Central Valley and Northern Atlantic Coastal Plain surficial aquifer systems, but over time, changes in shallow groundwater are likely to become apparent in deeper groundwater along the flow path.

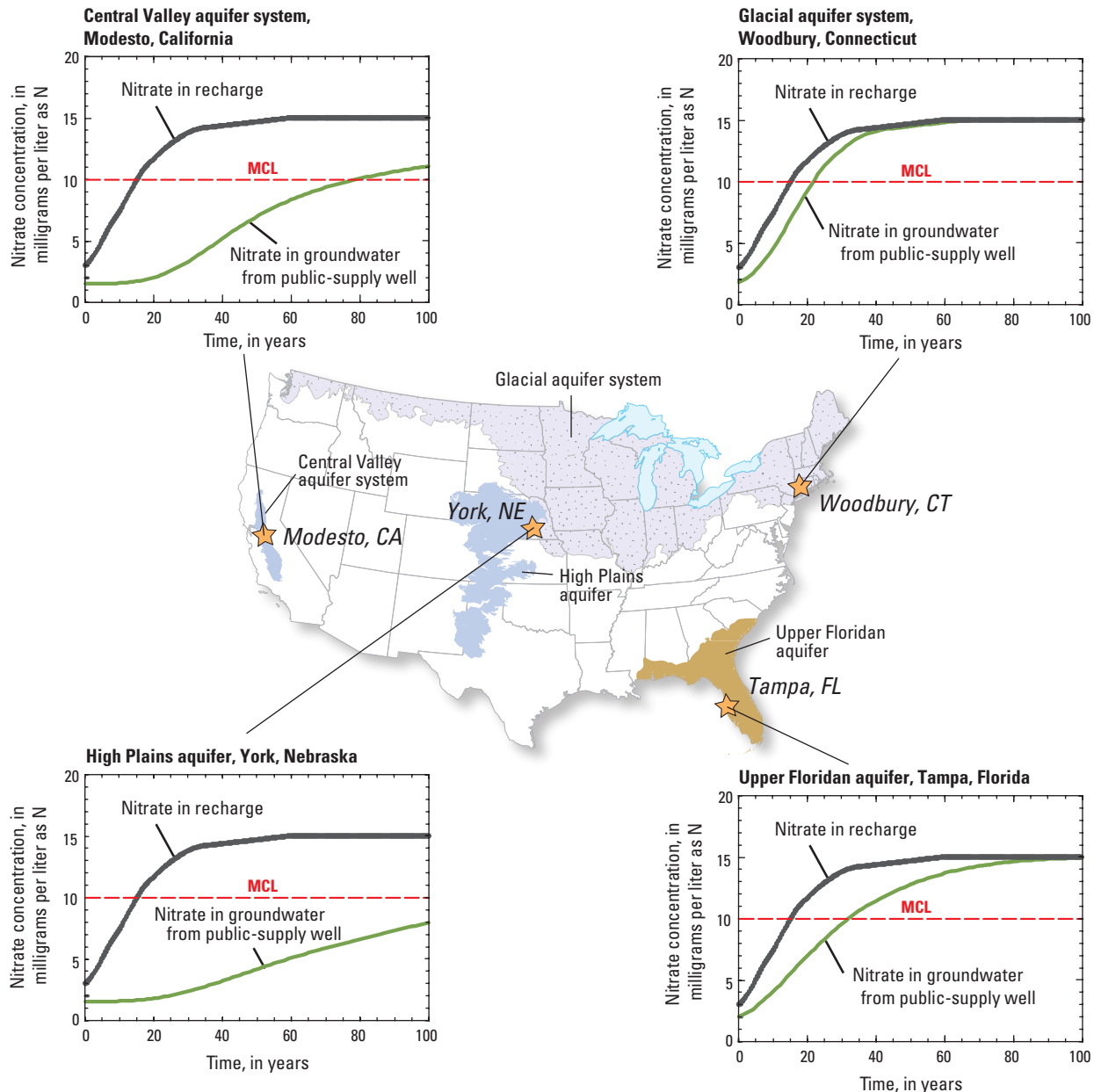
Forecasting Future Changes in Groundwater Quality

Because groundwater moves slowly, there is a lag time, years to centuries in length, between contaminant inputs at land surface and effects on water quality in supply wells.

How will groundwater quality change in the future if we change our use and management of contaminants? In most aquifers, the slow movement of groundwater results in a lag time between contaminant inputs at the land surface and effects on water quality in supply wells and in streams that receive groundwater discharge. This lag time can be years to centuries long.

Forecasting models, based on detailed field studies, can show how aquifers respond to changing contaminant inputs. Thin, shallow aquifers and those with physical features that promote rapid infiltration and flow respond more quickly than do thick, deep aquifers or those that are less permeable. Response times of simulated public-supply wells to increasing nitrate concentrations in the High Plains aquifer or Central Valley aquifer system, which are thick sequences of unconsolidated sediments, were three or more times as long as the response times of simulated public-supply wells in the thin glacial aquifer system or the karstic Upper Floridan aquifer (fig. 8–3). Developing models to accurately forecast future conditions requires a thorough understanding of the processes that might affect contaminant concentrations in groundwater. For example, when denitrification, a process that reduces nitrate concentrations in the aquifer, is included, the maximum nitrate concentrations predicted by the models are reduced by about half or more for all four aquifers.

Simulated nitrate concentrations in groundwater in four aquifers or aquifer systems



Modified from Burow and Green,⁽¹⁸⁸⁾ McMahon and others,⁽¹⁸⁹⁾ and Dubrovsky and others⁽²⁵⁾

Figure 8–3. Forecasting models show how different aquifers respond to the same nitrogen inputs in recharge. In a thin glacial aquifer in Connecticut and in the Upper Floridan aquifer near Tampa, Florida, it takes only about 10 to 20 years for nitrate concentrations to reach the MCL of 10 mg/L as N after nitrogen concentrations reach this level in recharge. In contrast, it would take more than 60 years for nitrate concentrations to reach the MCL in the thick unconsolidated sand and gravel aquifers of the Central Valley aquifer system and High Plains aquifer. The location of the supply well in the aquifer also affects the response times.

Forecasting models allow us to evaluate how our future actions, such as reducing or even eliminating contaminant inputs, might affect groundwater quality. Forecasting models for several aquifers predict that, even if nitrogen inputs were stabilized or eliminated, decades would be required for nitrate concentrations to stop increasing or to decrease to background levels. For example, models of nitrate concentrations in public-supply wells in the Northern Atlantic Coastal Plain aquifer in southern New Jersey indicate that concentrations would continue to increase until 2060, even if nitrogen inputs were held constant at the same levels as in 2000 (fig. 8–4). Similar projections are made for nitrate concentrations in the streams overlying the Northern Atlantic Coastal Plain aquifer system that receive groundwater discharge⁽¹²³⁾ and at sites in basaltic-rock and unconsolidated sand and gravel aquifers in the western United States.^(124, 125)

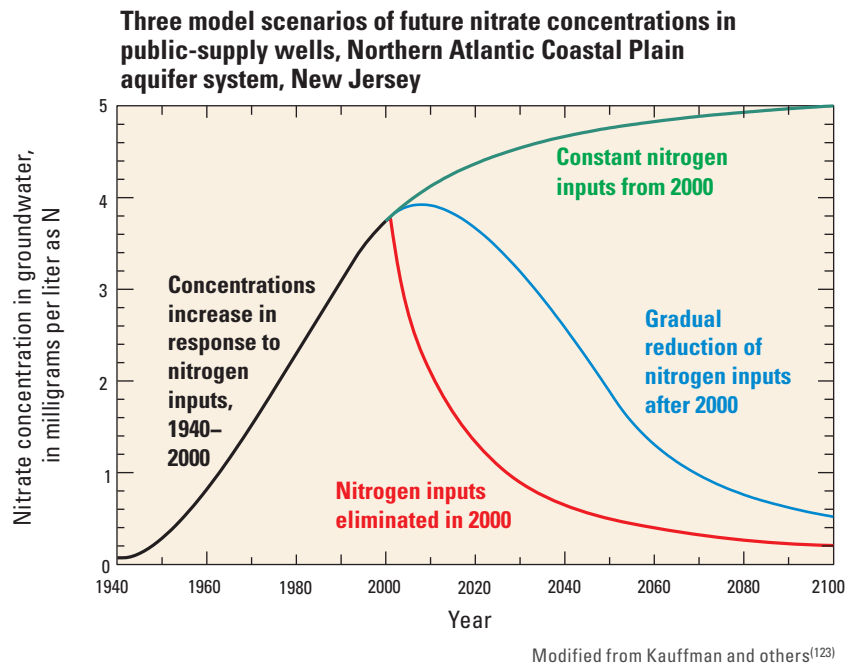


Figure 8–4. Models simulating nitrate concentrations in public-supply wells in the Northern Atlantic Coastal Plain aquifer system in southern New Jersey indicate that concentrations would increase for decades (green line), even if nitrogen inputs to shallow groundwater were held constant at the same levels as in 2000 because of the lag time between changes in contaminant inputs and the response of deep groundwater. Similarly, model simulations indicate that nitrate concentrations would be greater than background levels for decades after either gradual (blue line) or complete (red line) reductions in nitrogen inputs.

Looking Forward

Water-quality trends observed since the early 1990s, the distribution of contaminants in shallow and deep groundwater, and groundwater forecasting models suggest that concentrations of contaminants from human sources are likely to increase in many parts of the Nation's Principal Aquifers. Some of these changes will be the result of past actions—contaminant inputs in past years and decades that are not yet reflected in the quality of groundwater pumped from supply wells or discharged to springs, streams, and estuaries. Other changes will result from the management decisions made and actions taken today and in the future. Information on where contaminants occur, what are the sources of contaminants, and how contaminants are transported through groundwater is critical to understanding the limitations that contaminants may place on future water availability.

For more information about NAWQA Principal Aquifer studies

This report characterizes groundwater quality for many of the Nation's Principal Aquifers.

Links to this and other circulars on the quality of groundwater in the Nation's Principal Aquifers are available at

<http://water.usgs.gov/nawqa/pasumm/>.

More than 2,000 NAWQA Program reports are available at

<http://water.usgs.gov/nawqa/bib/>.

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Glossary

A

alluvial aquifer An aquifer composed of unconsolidated material, such as sand and gravel, deposited by a river or other flowing water.

anoxic Water with no dissolved oxygen or a very low concentration (less than 0.5 milligram per liter) of dissolved oxygen.

aquifer A geologic formation, group of formations, or part of a formation that contains a sufficient amount of saturated permeable material (for example, soil, sand, gravel and (or) rock) to yield substantial quantities of water to wells and springs.

artificial recharge Replenishment of an aquifer through human effort, for example, spreading water, recharge wells, or ditches; recharge through human activities that occurs at a rate greater than that of naturally occurring activities; the water artificially recharging an aquifer.

B

background concentration A concentration of a substance in a particular environment that corresponds to minimal influence by human (anthropogenic) sources or activities.

base flow Groundwater seepage into a stream or river. The continual contribution of groundwater to streams and rivers is an important source of streamflow between rain events.

bedrock General term for consolidated (solid) rock that underlies soils or other unconsolidated material.

C

carbonate rock or bedrock Rocks, such as limestone or dolostone, that are composed primarily of minerals, such as calcite and dolomite, containing the carbonate ion (CO_3^{2-}).

cation An ion or group of ions that has acquired a positive charge by loss of one or more electrons.

closed basin An enclosed area having no drainage outlet, from which water escapes only by evaporation, as in an arid region.

common assessment level A single concentration threshold used to establish an equal basis for comparing detection frequencies among multiple chemicals. Use of a common assessment level avoids biases in detection frequencies caused by one compound having a lower detection level than another. Also sometimes referred to as a “common detection level.”

conduit Pipe-like or channel-like openings in bedrock. Conduits control the direction of water flow and greatly increase the speed at which water travels through an aquifer.

confined aquifer (artesian aquifer) An aquifer in which the groundwater is bounded between layers of relatively impermeable material, such as clay or dense rock. When tapped by a well, water in a confined aquifer is forced up, sometimes above the land surface, by pressure within the aquifer.

confining layer Geologic material with little or no permeability or hydraulic conductivity. Water does not pass through this layer or the rate of movement is extremely slow.

confining unit A hydrogeologic unit of impermeable or distinctly less permeable material within an aquifer or bounding one or more aquifers.

constituent A chemical or biological substance in water, sediment, or biota that can be measured by an analytical (laboratory) method.

contaminant For the purposes of this report, any manmade compound at any concentration or any constituent with a geologic source measured at a concentration exceeding the designated human-health benchmark.

crystalline rocks Igneous or metamorphic rocks consisting wholly of crystals or fragments of crystals. Granite and schist are examples of crystalline rocks.

D

degradate A compound formed by the transformation of a parent compound, typically an organic contaminant or another degradate, by chemical, photochemical, or biological reactions.

degradation The breakdown of a compound to a chemically simpler compound by abiotic or biotic processes.

denitrification The bacterial reduction of dissolved nitrate to nitrogen gas. Denitrification is the primary process by which nitrate can be eliminated naturally in groundwater.

desorption The release of a sorbed material from the solid to which it was sorbed. Opposite process of adsorption.

discharge The rate of flow of surface water or groundwater past a given point at a given moment, expressed as volume per unit of time. Also, the outflow from an aquifer, spring, or well or up through a streambed.

dissolution The process of dissolving a solid (mineral) into a homogeneous solution (water). Dissolution reactions result in the addition of ions to water as minerals react with water. Common dissolution reactions include dissolution of carbonate rock (limestone or dolomite) and incongruent dissolution of silicate minerals (feldspar) by carbonic acid (H_2CO_3).

domestic well A privately owned well that typically serves one home and supplies water for human consumption and other homeowner uses.

drinking-water standard or guideline A threshold concentration in a public drinking-water supply designed to protect human health or to identify acceptable concentrations of constituents that cause unpleasant taste, odor, or color in the water.

E

eutrophication The enrichment of water by nutrients, most commonly phosphorus and nitrogen. During eutrophication, respiration processes that use organic matter cause a marked decline in dissolved-oxygen concentrations of water.

evapotranspiration Loss of water from soil by evaporation and plant transpiration combined.

F

flow path The route or pathway of water flowing through the hydrologic system. Typically refers to subsurface (groundwater) flow.

fumigant A pesticide in the volatile organic compound (VOC) chemical class that is applied to soils to reduce populations of plant parasitic nematodes (harmful rootworms), weeds, fungal pathogens, and other soil-borne microorganisms.

G

gradient *See* hydraulic-head gradient.

groundwater Water that exists beneath the land surface, but most commonly refers to water in fully saturated soils and geologic formations.

groundwater age The time elapsed since the recharge water became isolated from the atmosphere. The term “age” is normally qualified with the word “apparent” to signify that the accuracy of the determined age depends on many variables.

groundwater discharge The flow of water from the saturated zone, for example, from a spring or a well or as seepage to surface water.

groundwater flow path *See* flow path.

groundwater recharge The infiltration of water to the saturated zone. Also refers to water that reaches the water table by infiltration of precipitation or irrigation water through the unsaturated zone or by seepage of water from surface-water bodies, such as streams and lakes.

groundwater residence time The average amount of time it takes for groundwater to move from the point where it enters the aquifer to a specific point of discharge such as a well or stream.

groundwater sustainability The amount of groundwater that will be available to support future uses of a particular aquifer or groundwater resource. The development and use of groundwater in a manner that can be maintained for an indefinite time without causing unacceptable environmental, economic, or social consequences.

H

half-life The time required for the concentration of a compound in a given environ-

mental medium to be reduced to one-half of its original value by one or more processes, such as degradation or transport into another environmental medium.

Health-Based Screening Level (HBSL) An estimate of concentration (for a noncarcinogen) or concentration range (for a carcinogen) in water that (1) may be of potential human-health concern, (2) can be used as a threshold value against which measured concentrations of contaminants in ambient groundwater samples can be compared, and (3) is consistent with U.S. Environmental Protection Agency Office of Water methodologies.

herbicide A chemical pesticide designed to control or destroy plants, weeds, or grasses.

human-health benchmark A threshold concentration above which the concentration of a contaminant in drinking water could have adverse effects on human health. Treatment or other measures can be used before the water is consumed to lower the concentration of the contaminant below the benchmark.

hydraulic-head gradient In an aquifer, the rate of change of total head (water-level elevation in a well) per unit of distance of flow at a given point and in a given direction. Water will flow from higher hydraulic head to lower hydraulic head.

hydrogeologic setting A unit with common hydrogeologic characteristics and therefore common susceptibility to contamination; a composite description of all the major geologic and hydrologic factors that affect and control the movement of groundwater into, through, and out of an area.

hydrogeologic unit A body of rock distinguished and characterized by its porosity and permeability. Also called a hydrostratigraphic unit.

hydrogeology The geologic and hydrologic features that control the movement of water, solutes, and small particles through the subsurface.

hydrologic system The assemblage of pathways by which water travels as it circulates beneath, at, and above the Earth's surface during precipitation, runoff, evaporation, infiltration, transpiration, and groundwater discharge.

I

igneous rock Rock that solidified from molten (melted) or partly molten material. Granite is an example of an igneous rock.

induced infiltration Recharge to groundwater by infiltration of water from the land surface as a result of the lowering of the groundwater head below the surface-water level, for example, by pumping.

infiltration Movement of water, typically downward, into soil or porous rock.

intrinsic susceptibility A measure of the ease with which a contaminant in water enters and moves through an aquifer; a characteristic of the aquifer and overlying material and hydrologic conditions independent of the chemical characteristics of the contaminant and its sources.

ion exchange The replacement of ions attached to the surface of a solid by ions that were in water. Ion-exchange reactions commonly occur between water and ions attached to clay particles.

isotope Each of two or more forms of the same element with the same atomic number (the same number of protons) but a different number of neutrons and therefore different atomic weights.

K

karst Surface and subsurface terrane that is formed on and in soluble rocks, such as limestone and gypsum, primarily by dissolution and collapse, and that is characterized by sinkholes, caves, and underground drainage.

karst aquifer A body of soluble rock that conducts water principally by way of a connected network of tributary conduits formed by the dissolution of the rock, which drains a groundwater basin and discharges to at least one perennial spring.

L

land-use study A study by the U.S. Geological Survey National Water-Quality Assessment (NAWQA) Program to assess the effects of a specific land-use type (generally agricultural or urban) on groundwater quality, in most cases by sampling groundwater from monitoring wells that tap water from or near the water table.

M**Maximum Contaminant Level**

(MCL) Maximum permissible level of a contaminant in water that is delivered to any user of a public water system. MCLs are enforceable standards established by the U.S. Environmental Protection Agency.

median The middle or central value in a distribution of data ranked in order of magnitude such that one-half of the data are higher than the median and one-half are lower. The median is also called the 50th percentile.

metamorphic rock Rock derived from mineralogical, chemical, or structural changes to preexisting rocks in response to marked changes in temperature, pressure, shearing stress, and chemical environment, generally at depth in the Earth's crust. Gneiss and schist are examples of metamorphic rocks.

methemoglobinemia A health condition characterized by reduced ability of the blood to carry oxygen. Infants are most affected. One of the most common causes is nitrate in drinking water. Also called “blue baby syndrome.”

milligrams per liter (mg/L) A unit expressing the concentration of a chemical constituent as weight (milligrams) of constituent per unit volume (liter) of water; equivalent to one part per million in most streamwater and groundwater. One thousand micrograms per liter ($\mu\text{g/L}$) is equivalent to 1 mg/L.

monitoring well A well used to measure water quality or groundwater levels continuously or periodically. Not typically used as a source of drinking water. Sometimes referred to as an “observation well.”

N

natural attenuation The reduction in constituent concentration in the environment caused by naturally occurring physical, chemical, and (or) biological processes.

nitrate An ion consisting of one nitrogen atom and three oxygen atoms (NO_3^-). Nitrate is a plant nutrient and is very mobile in soils.

nitrification The formation of nitrate by the oxidation of ammonium to nitrite followed by oxidation of nitrite to nitrate.

nonpoint source A contaminant source that is not a discrete point, such as a pipe, ditch, or tunnel. Areas of fertilizer and pesticide applications, atmospheric deposition, and

stormwater runoff are examples of sources of nonpoint contamination.

nutrient An element or compound essential for animal and plant growth. Common nutrients include nitrogen, phosphorus, and potassium, such as are found in fertilizer.

O

organic carbon Carbon that originates from plants or animals and is bound in an organic compound.

organic matter Matter resulting from the decay of a plant or an animal and containing organic carbon compounds. Organic matter is rich in nutrients and is an essential component of soils.

organic compound A chemical compound containing the element carbon. A few types of carbon-containing compounds, including oxides of carbon (such as carbon dioxide, or CO_2), are not considered to be organic. Organic compounds include petroleum products, solvents, and many pesticides.

oxic Water with a concentration of dissolved oxygen greater than or equal to 0.5 milligram per liter.

oxidation The loss of electrons by a chemical species as a result of transfer to another chemical species, typically dissolved oxygen. The species donating electrons is “oxidized.”

P

permeability A measure of the relative ease with which a porous or fractured medium can transmit groundwater. Rock formations that transmit fluids readily are described as permeable.

permeable Capable of transmitting liquids or gases through pores or openings.

pesticide Any substance, organic or inorganic, used to kill plant or animal pests.

pH A measure of the acidity (pH less than 7) or alkalinity (pH greater than 7) of a solution; a pH of 7 is neutral. Formally defined as the logarithm of the reciprocal of the hydrogen ion concentration (activity) of a solution.

point source A stationary location or fixed facility from which contaminants are discharged, for example, a pipe, ditch, ship, ore pit, or factory smokestack.

precipitation Any or all forms of water particles that fall from the atmosphere such as

rain, snow, hail, and sleet. Also, the process in which a solid is formed from a fluid supersaturated with dissolved ions.

predevelopment The time prior to substantial groundwater development by humans or effects of agricultural, urban, suburban or other human-related land uses.

Principal Aquifer A regionally extensive aquifer or aquifer system that has the potential to be used as a source of potable water. A Principal Aquifer can be composed of one or more major aquifers.

public-supply well A privately or publicly owned well that provides water for public use to (1) a community water system, (2) a transient noncommunity water system, such as a campground, or (3) a nontransient, noncommunity system, such as a school.

R

radioactive decay The spontaneous emission of particles (alpha or beta) and gamma rays from an atom with an unstable nucleus (radionuclide).

recently recharged groundwater Groundwater that was recharged after 1952, as indicated by tritium concentrations greater than 0.5 tritium unit.

recharge The addition of water to the saturated zone, naturally, by precipitation or runoff, or artificially, by spreading or injection. Also, the water that is added.

reduction The gain of electrons by a chemical species, typically dissolved oxygen, as a result of transfer from another chemical species. The species accepting electrons is “reduced.” Once all of the dissolved oxygen has been reduced, other chemical species can accept electrons, following the most energetically favorable order.

reduction-oxidation (redox) Chemical reactions that involve the transfer of electrons from one chemical species to another, resulting in a change in the valence state of the species. Redox processes in groundwater often are microbially facilitated.

residence time The average amount of time that a solute, particle, organism, or other entity spends within a given environmental medium, such as a lake, groundwater, and the atmosphere.

runoff Excess rainwater or snowmelt that is transported to streams by flow over the land surface.

S

saturated The condition in which all the pores (voids, interstices) within a material are filled with a liquid, typically water.

saturated zone The region in the subsurface in which all the spaces (pores and fractures) are filled with water and are under pressure greater than atmospheric pressure.

Secondary Maximum Contaminant Level (SMCL) Guidelines set by the U.S. Environmental Protection Agency for concentrations of “nuisance” constituents in drinking water that may cause unwanted effects, such as unpleasant taste, color, or odor; discoloration of skin or teeth; or corrosion or staining of plumbing fixtures. Public drinking-water systems are recommended but not required to comply with these guidelines.

sedimentary rocks Rocks composed of particles derived from the erosion or weathering of preexisting rocks or from chemical precipitation from water. Sandstone and limestone are examples of sedimentary rocks.

siliciclastic rocks Rocks formed by the compaction and cementation of quartz-rich mineral grains. Sandstone and shale are examples of siliciclastic rocks.

sinkhole Any closed depression in soil or bedrock formed by the erosion and transport of earth material from below the land surface. A sinkhole typically has a closed topographic contour, drains to the subsurface, and occurs in karst terrane.

sorption The general process by which solutes, ions, and colloids become attached to solid matter.

subsurface The region of earth materials beneath the land surface that encompasses the soil and unsaturated and saturated zones.

susceptibility *See* intrinsic susceptibility.

T

tile drain A drain installed to collect subsurface water and route it to a drainage ditch, stream, or wetland. Originally constructed using short segments of clay or cylindrical concrete “tiles” and installed manually, modern tile drains typically are corrugated, perforated plastic pipes installed 3 to 6 feet

below the soil surface by mechanical trenches.

trace element An element found in only minor amounts (concentrations less than 1.0 milligram per liter) in water or sediment; includes arsenic, cadmium, chromium, copper, lead, mercury, nickel, and zinc.

tritium unit (TU) A measure of the concentration of tritium (^3H), equal to one ^3H atom in 1,018 atoms of hydrogen (H), or 3.24 picocuries per liter.

U

unconfined aquifer An aquifer that has a water table; an aquifer containing unconfined groundwater.

unconsolidated deposit Deposit of loosely bound sediment that typically fills topographically low areas.

unsaturated zone A subsurface zone containing both water and air. The unsaturated zone is limited above by the land surface and below by the water table.

V

volatile organic compound (VOC) An organic chemical that has a high vapor pressure relative to its water solubility. VOCs include components of gasoline, fuel oils, lubricants, organic solvents, fumigants, some inert ingredients in pesticides, and some by-products of chlorine disinfection.

vulnerability The tendency or likelihood for contaminants to reach a specified position in the groundwater system after introduction at some location above the uppermost aquifer. The vulnerability of a groundwater resource to contamination depends both on the intrinsic susceptibility of the resource and on the locations and types of human and geologic sources of contaminants, locations of wells, and the characteristics of the contaminant(s).

W

watershed The upper surface of the saturated zone below which all voids (spaces) are filled with water.

water table The upper surface of the saturated zone below which all voids (spaces) are filled with water.

Appendixes 1–4

Appendix 1. Water-Quality Constituents Included in This Study

Appendix 2. Concentrations Exceeding Human-Health Benchmarks and Non-Health Guidelines in Principal Aquifers

Appendix 3. Detections of Pesticides and Volatile Organic Compounds in Principal Aquifers

Table A3–A. Pesticides detected at any concentration.

Table A3–B. Pesticides detected at concentrations greater than 0.1 microgram per liter.

Table A3–C. VOCs detected at any concentration.

Table A3–D. VOCs detected at concentrations greater than 0.2 microgram per liter.

Appendix 4. Groundwater Quality in Principal Aquifers in a National Context —Concentrations by Study and Well Type

The appendixes for this report and the national dataset are available at <http://pubs.usgs.gov/circ/1360/>.

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