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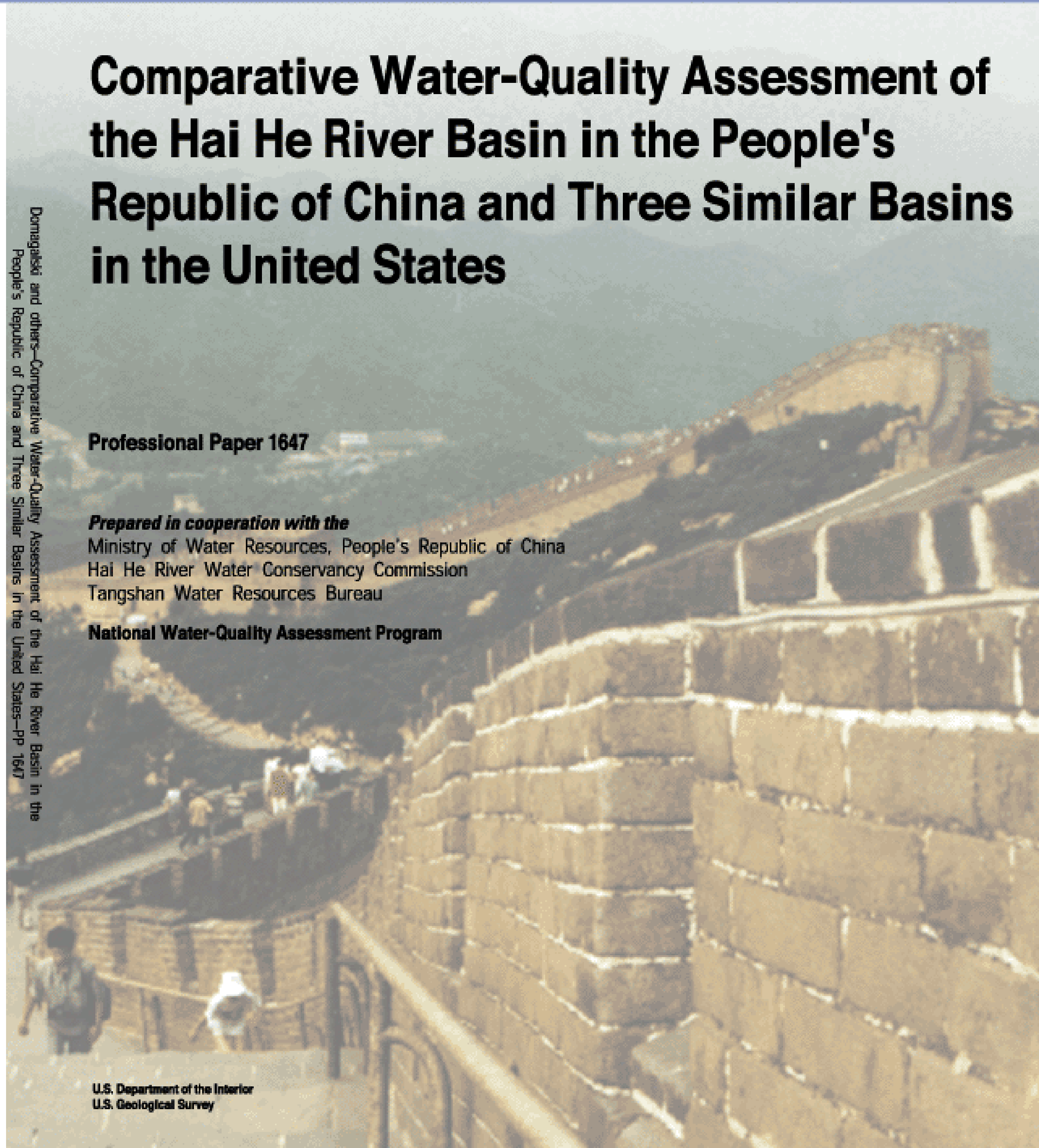
Comparative Water-Quality Assessment of the Hai He River Basin in the People's Republic of China and Three Similar Basins in the United States



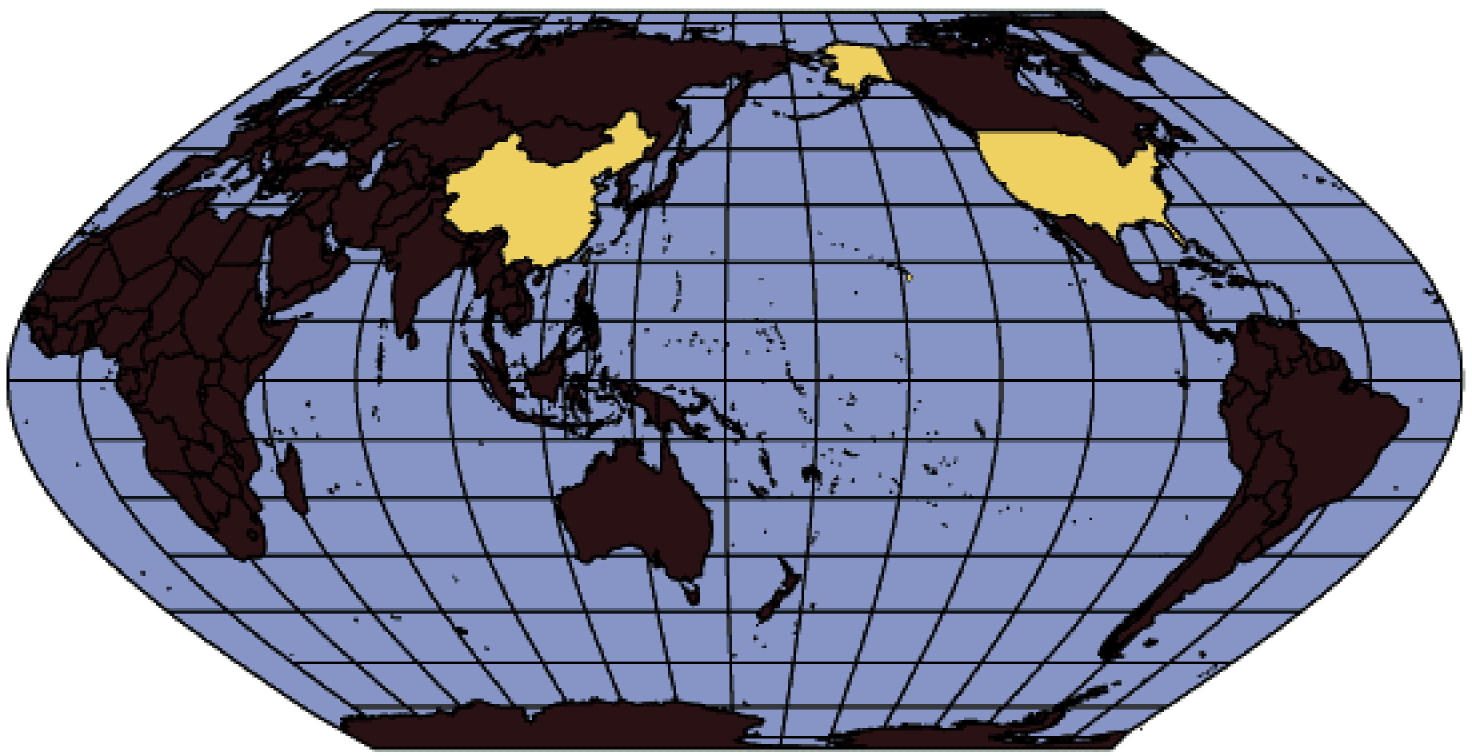
Professional Paper 1647

Prepared in cooperation with the
Ministry of Water Resources, People's Republic of China
Hai He River Water Conservancy Commission
Tangshan Water Resources Bureau

National Water-Quality Assessment Program

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

Domagalski and others—Comparative Water-Quality Assessment of the Hai He River Basin in the People's Republic of China and Three Similar Basins in the United States—PP 1647



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U.S. GEOLOGICAL SURVEY PROFESSIONAL PAPER 1647

NATIONAL WATER-QUALITY ASSESSMENT PROGRAM

Prepared in cooperation with the

Ministry of Water Resources, People's Republic of China
Hai He River Water Conservancy Commission
Tangshan Water Resources Bureau

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FOREWORD

The U.S. Geological Survey (USGS) is committed to serve the Nation with accurate and timely scientific information that helps enhance and protect the overall quality of life, and facilitates effective management of water, biological, energy, and mineral resources. Information on the quality of the Nation's water resources is of critical interest to the USGS because it is so integrally linked to the long-term availability of water that is clean and safe for drinking and recreation and that is suitable for industry, irrigation, and habitat for fish and wildlife. Escalating population growth and increasing demands for the multiple water uses make water availability, now measured in terms of quantity and quality, even more critical to the long-term sustainability of our communities and ecosystems.

The USGS implemented the National Water-Quality Assessment (NAWQA) Program to support national, regional, and local information needs and decisions related to water-quality management and policy. Shaped by and coordinated with ongoing efforts of other Federal, State, and local agencies, the NAWQA Program is designed to answer: What is the condition of our Nation's streams and ground water? How are the conditions changing over time? How do natural features and human activities affect the quality of streams and ground water, and where are those effects most pronounced? By combining information on water chemistry, physical characteristics, stream habitat, and aquatic life, the NAWQA Program aims to provide science-based insights for current and emerging water issues. NAWQA results can contribute to informed decisions that result in practical and effective water-resource management and strategies that protect and restore water quality.

Since 1991, the NAWQA Program has implemented interdisciplinary assessments in more than 50 of the Nation's most important river basins and aquifers, referred to as Study Units. Collectively, these Study Units account for more than 60 percent of the overall water use and population served by public water supply, and are representative of the Nation's major hydrologic landscapes, priority ecological resources, and agricultural, urban, and natural sources of contamination.

Each assessment is guided by a nationally consistent study design and methods of sampling and analysis. The assessments thereby build local knowledge about water-quality issues and trends in a particular stream or aquifer while providing an understanding of how and why water quality varies regionally and nationally. The consistent, multi-scale approach helps to determine if certain types of water-quality issues are isolated or pervasive, and allows direct comparisons of how human activities and natural processes affect water quality and ecological health in the Nation's diverse geographic and environmental settings. Comprehensive assessments on pesticides, nutrients, volatile organic compounds, trace metals, and aquatic ecology are developed at the national scale through comparative analysis of the Study-Unit findings.

The USGS places high value on the communication and dissemination of credible, timely, and relevant science so that the most recent and available knowledge about water resources can be applied in management and policy decisions. We hope this NAWQA publication will provide you the needed insights and information to meet your needs, and thereby foster increased awareness and involvement in the protection and restoration of our Nation's waters.

The NAWQA Program recognizes that a national assessment by a single program cannot address all water-resource issues of interest. External coordination at all levels is critical for a fully integrated understanding of watersheds and for cost-effective management, regulation, and conservation of our Nation's water resources. The Program, therefore, depends extensively on the advice, cooperation, and information from other Federal, State, interstate, Tribal, and local agencies, non-government organizations, industry, academia, and other stakeholder groups. The assistance and suggestions of all are greatly appreciated.

Robert M. Hirsch

Robert M. Hirsch
Associate Director for Water

Editor's Note

This report is based on a research study in the People's Republic of China. The report was edited for an international technical audience and for Chinese readers with English as a second language (ESL). For example, the term "Tangshan study area" is used prior to defining "Tangshan study unit," which is used thereinafter to denote the specific Tangshan area under study. The term "physiographic provinces" was changed to "physiographic regions" to prevent possible miscommunication with the Chinese geographic term "Provinces." Other similar assessments were made during the language editing phase of the editorial process.

The style used for site names and well locations in the area studied outside the United States—the Tangshan region of the People's Republic of China—was taken from unpublished data and from correspondence with the Chinese coauthors. The "Atlas of the People's Republic of China," produced and published in the People's Republic of China (see the "Xiudong" listing in the References Cited section at end of this report), was used to verify spellings of Chinese cities, rivers, and other geographic features. Style editing included appropriate use of syntax of Chinese phrases, diacritical marks, and syllable boundary markers (for example, "the two-syllable "Xi'an" for two Chinese characters is distinguished from the single syllable "xian" for a single Chinese character). In some places in the report, "People's Republic of China" was respectfully replaced with "China" to reduce repetition or because of limited space such as in table cells; the United States of America is referred to in shortened fashion as well.

Some USGS standards for style of illustrations have been customized as well. In the bar graph figures—figures 30, 31, 32, and 33—the Legend, or Explanation box, does not include the word "Explanation." This word was eliminated to maintain consistency with the boxes of similar figures in which "Explanation" is not required when the box appears within the illustration, as with figures 21–25 and 34–36. In the "Piper diagrams" (figures 13–20), the term "trilinear graph" replaces the term "Piper diagram." Some slight variation in graphical elements on maps of areas in the People's Republic of China and the United States is the result of different digital sources.

The References Cited section includes no references pertaining to Chinese data on the study because, though available, this information has not been published in the international scientific literature. Representatives from various water agencies in the People's Republic of China (Hai He River Water Conservancy Commission, Tangshan Water Resources Bureau, and the Chinese Ministry of Water Resources) have worked extensively with the U.S. Geological Survey on the content of this report. This collaboration is noted in the authorship on the title page.

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CONVERSION FACTORS, VERTICAL DATUM, AND ABBREVIATIONS

Multiply	By	To obtain
cubic meter (m^3)	0.0008107	acre-foot
kilogram (kg)	2.205	pound avoirdupois
kilometer (km)	0.6214	mile
megagram (Mg)	1.102	ton (2,000 lb)
megagram per square kilometer (Mg/km^2)	2.855	ton (2,000 lb) per square mile
meter (m)	1.094	yard
milligram per liter (mg/L)	8.345	pound per million gallon
millimeter (mm)	0.03937	inch
square hectometer (hm^2)	2.471	acre
square kilometer (km^2)	0.3861	square mile

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

$$°F = (1.8)°C + 32$$

Sea level: In this report "sea level" refers to the National Geodetic Vertical Datum of 1929 (NGVD of 1929)—a geodetic datum derived from a general adjustment of the first-order level nets of both the United States and Canada, formerly called Sea Level Datum of 1929.

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

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

1 megagram = 1 metric ton = 1 tonne = 1,000 kilogram

Abbreviations and Acronyms

μg/L, microgram per liter
μm, micrometer
μS/cm, microsiemens per centimeter
pCi/L, picocurie per liter

CFC, chlorofluorocarbon
DBCP, 1,2-dibromo-3-chloropropane
δ, delta
EPA, U.S. Environmental Protection Agency
GIS, Geographic Information System
H, hydrogen
^2H, deuterium
^3H, tritium
^3He, helium-3
N, nitrogen
NAWQA, National Water-Quality Assessment (Program)
O, oxygen
p, level of statistical significance
per mill, parts per thousand
PRC, People's Republic of China
RASA, Regional Aquifer Systems Analysis
ρ, Spearman's rho
U.S., United States
USGS, U.S. Geological Survey
yr, year

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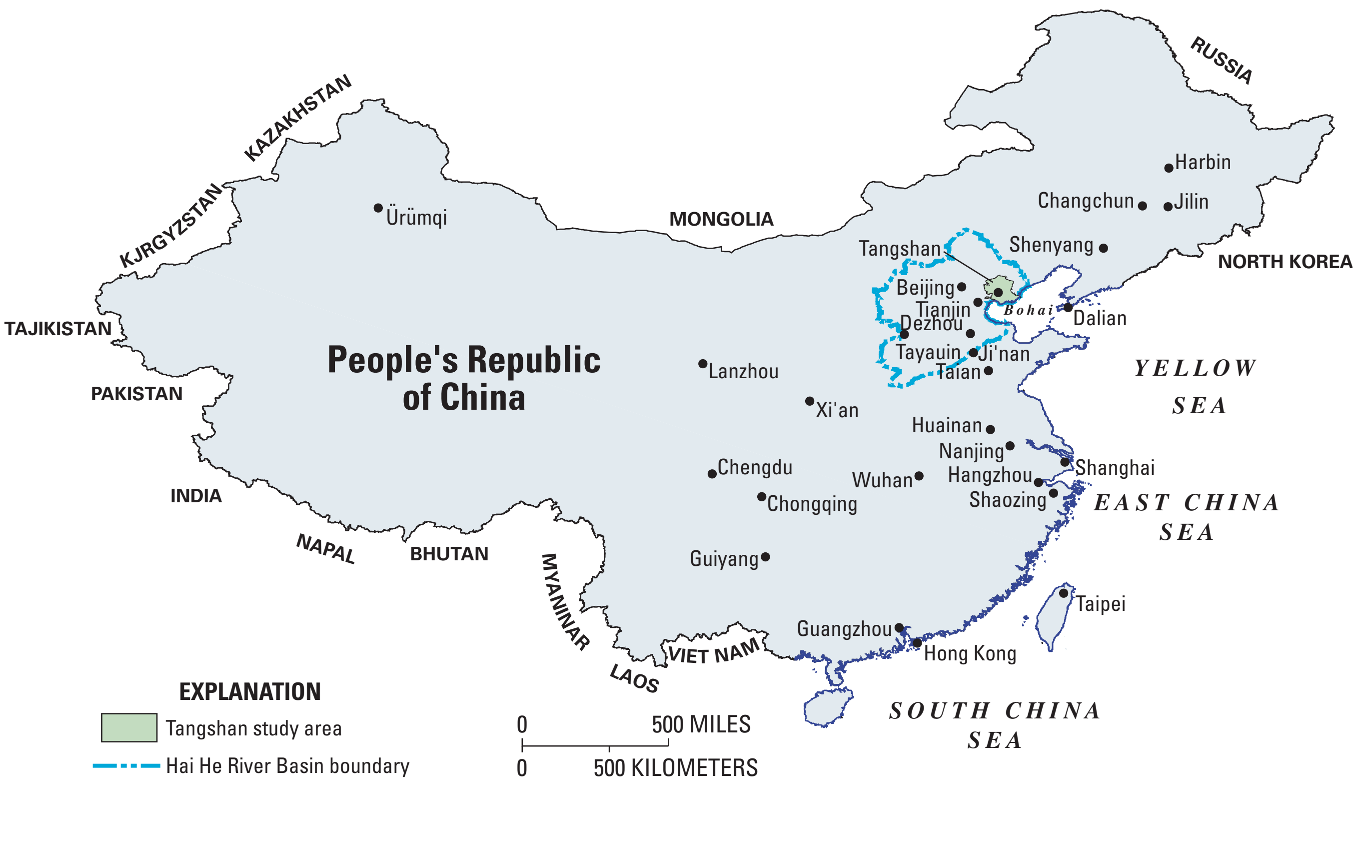
ABSTRACT

Ground-water quality with respect to nitrate, major inorganic constituents, pesticides, stable isotopes, and tritium was assessed in the agricultural Tangshan region in the Hai He River Basin of the People's Republic of China and compared with three similar regions in the United States: the Delmarva Peninsula of the states of Delaware, Maryland, and Virginia; and the San Joaquin and Sacramento Valleys of the state of California. These four regions are considered similar with respect to size, land use, or climate. Although the Tangshan region has been in agricultural production for a much longer time, probably several centuries, than the three regions of the United States, the widespread use of synthetic fertilizers and other soil amendments probably started at a similar time in all four regions. Median nitrate concentrations were found to be similar in the four regions in most instances, and those median concentrations were below the American nitrate drinking water standard of 10 milligrams per liter; however, higher concentrations, and a greater range of concentrations, were evident for the Tangshan region. In some water samples collected from a shallow aquifer in Tangshan, nitrate concentrations exceeded the Chinese standard of 20 milligrams per liter, whereas few comparative samples collected in the United States exceeded that standard. In Tangshan, recently recharged (early 1960s) water that was detected in wells drilled as deep as 150 meters was found to correlate with the elevated nitrate concentrations. Relatively low nitrate, which is indicative of natural water, was measured in older water of deeper wells. In addition to elevated nitrate concentrations, the agricultural area of the Tangshan region has been affected by an increase in the concentrations of total dissolved solids and iron. The increase in total dissolved solids of the Tangshan study unit could not be attributed to any one process. Increases in iron concentrations may be partly attributable to the widespread application of animal wastes and sewage as fertilizer, which could deplete oxygen concentrations in ground water and lead to dissolution of iron from various minerals. In contrast to the United States, pesticides were not detected in aquifers of the Tangshan region, which could be attributed to lower pesticide use in the People's Republic of China. Alternatively, pesticide use may be increasing in the People's Republic of China, but the pesticides would not yet have been detected in ground water because of the lag in travel time from soil horizons to the aquifer.

INTRODUCTION

In 1986, the U.S. Geological Survey (USGS) initiated a pilot program, the National Water-Quality Assessment (NAWQA), designed to assess the current water-quality conditions, to identify trends, and to describe the natural and anthropogenic factors affecting water-quality conditions on regional and national levels. Full-scale implementation of the NAWQA Program began in 1991. The goals and design of the NAWQA Program are described by Hirsch and others (1988) and by Gilliom and others (1995). The NAWQA Program has successfully described and identified the extent and causes of nitrate and other contamination in ground water and surface water on regional and national levels. This success is attributed to a uniform approach to study design, through understanding of the hydrological factors that affect contaminant concentrations and transport in aquifers and rivers, and to an adherence to strict quality control practices in the field and laboratory. Currently, the NAWQA Program is focusing on nonpoint sources of contamination, including nitrogen fertilizer and pesticides. To address these contamination problems in ground water, studies are designed on various spatial scales. Three types of ground-water studies are used in NAWQA ground-water investigations. The first is a study-unit survey whereby a randomly selected population of wells, in a defined part of a study unit and normally within a continuous aquifer system, is sampled for natural water and contaminant chemistry. The second is the land-use survey, which targets specific types of land uses within an aquifer setting. The third is the flow-path study, which addresses ground-water and surface-water interactions.

As a result of a rapidly developing economy and intensive agricultural land-use practices, some areas of the People's Republic of China have shown evidence of ground-water and surface-water quality degradation. In the People's Republic of China, water quality and availability can affect future economic growth, and the lack of clean water can have serious consequences for human health and agricultural production. To help address and better understand these problems, as well as to provide a framework for effective management, a cooperative research project was initiated in 1995 to utilize parts of the NAWQA approach to study the reasons for nitrate and other agricultural contamination problems within the region surrounding the city of Tangshan in the Hai He River Basin (Zhang, Suo Zhu, Hai He River Water Conservancy Commission, written commun., 1996) of the People's Republic of China (fig. 1). This project, hereinafter referred to as the "joint agreement," included an assessment of nitrate and other water-quality constituents of an agricultural region north of the city of Tangshan along with a comparative assessment of three similar agricultural regions of the United States—the Delmarva Peninsula, the San Joaquin–Tulare Basins, and the Sacramento River Basin (fig. 2). The joint agreement was designed to introduce methodologies of ground-water assessment not widely available in the People's Republic of China, such as stable isotope chemistry and methods of dating



map data: Environmental Systems Research Institute, 1998

Figure 1. People's Republic of China including the Hai He River Basin and the Tangshan study area (Xiudong, 1989).

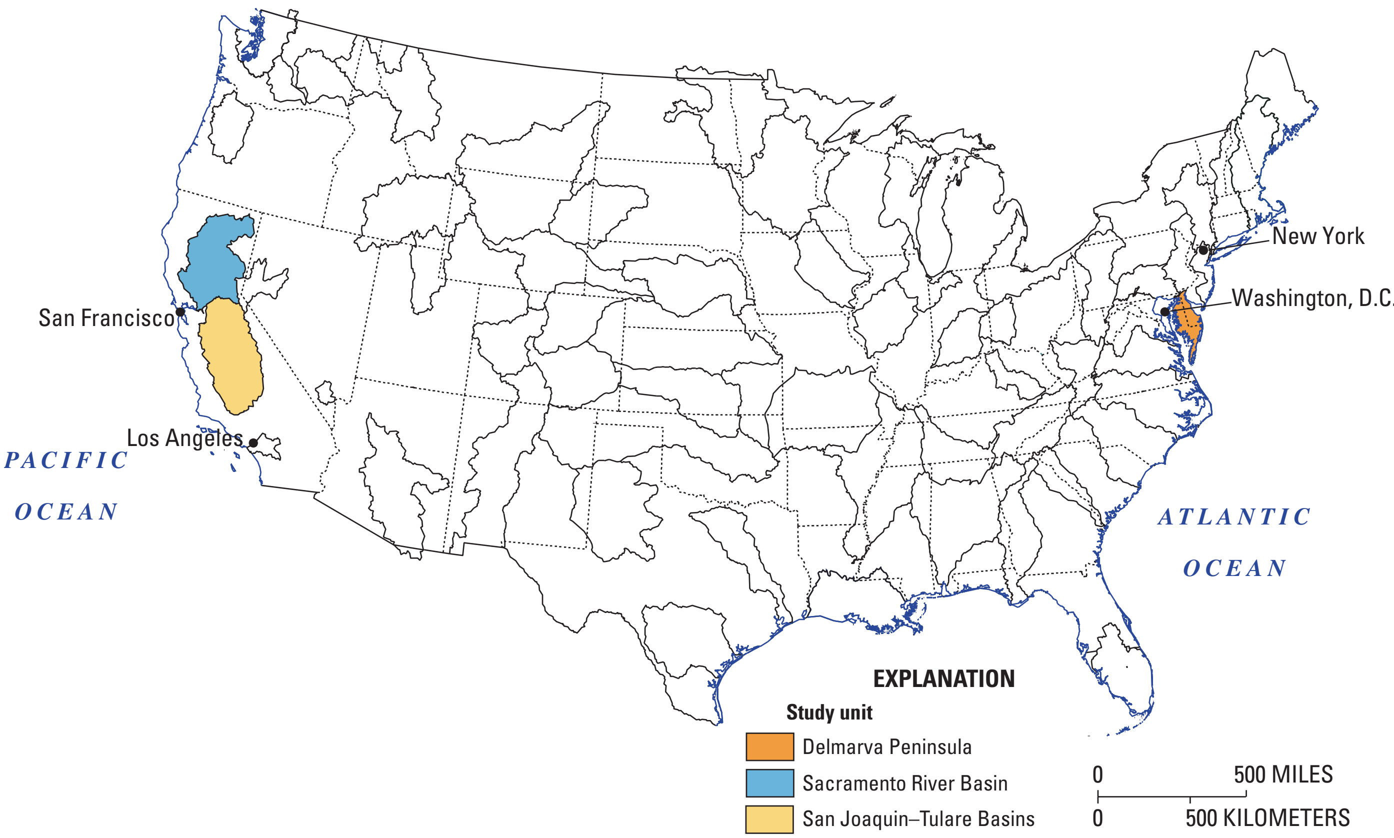


Figure 2. United States including the Delmarva Peninsula, the Sacramento River Basin, and the San Joaquin–Tulare Basins study units. Other NAWQA study units are shown by the solid contours for comparison.

ground-water recharge. At the time of the writing of the joint agreement, the stable isotope and dating studies were considered to be among the most important work elements of the agreement. The joint agreement was also designed to introduce water-quality scientists in the People's Republic of China to the methods of land-use analysis using a Geographic Information System (GIS). It was anticipated that a similar approach to study design would allow for a direct comparison of the geochemical and hydrological conditions in the four study areas, and that this comparison would benefit researchers and scientists both in the United States and in the People's Republic of China.

Although information was available on the chemistry of ground water in the Tangshan region, information about Tangshan's ground-water flow system was scarce. Whereas the general direction of flow of predevelopment ground water was known or assumed, little was known about the effect of agricultural development and pumpage on the flow system and the areas of the aquifer that were most susceptible to contamination. Knowledge of the age distribution of ground water, and possibly the use of stable isotopes, could enable scientists and water managers of the People's Republic of China to determine these effects and to plan effective control strategies to protect water quality.

Three dating methods, tritium (^3H), tritium/helium-3 ($^3H/^3He$), and the chlorofluorocarbons (CFCs), were selected—in the joint agreement—to determine the age of recently recharged (less than 50 years) ground water. ^3H analysis is used to determine if recharge occurred before or after the 1950s (Plummer and others, 1993). $^3H/^3He$ analysis provides better temporal resolution than ^3H, especially for recharge that occurred in the decade after the 1950s. CFCs are organic compounds used as refrigerants and are globally distributed in the atmosphere. The partitioning of CFCs in rainwater is known, and the amounts of specific CFCs in the atmosphere, as a function of time, are known or have been calculated (Plummer and others, 1993). CFC analyses can provide even better temporal resolution on recharge date, but the method does not work for all ground-water systems. The method works best for sandy aquifers where dissolved oxygen is present. Complicating factors that arise when using CFC analysis include microbial degradation of the CFCs or contamination of the ground water with excess

CFCs, as happens near landfills. Therefore, a combination of dating techniques was used for the Tangshan region.

Stable isotope studies were restricted to hydrogen and oxygen isotopes (ratio of ^{2}H to ^{1}H, and the ratio of ^{16}O to ^{18}O) in water molecules, and nitrogen (ratio of ^{14}N to ^{15}N) and oxygen (ratio of ^{16}O to ^{18}O) isotopes in nitrate molecules. These isotopes can be related to precipitation and ground-water recharge flow paths and to the type or source of nitrogen in ground water (Coplen, 1993).

The purpose of this report is to compare data and interpretations of ground-water chemistry and agricultural contaminant chemistry for the Tangshan region of the People's Republic of China and three study units in the United States: Delmarva Peninsula, which includes parts of the states of Delaware, Maryland, and Virginia; and the San Joaquin and Sacramento Valleys in the central region of the state of California. This report presents new data collected in the Tangshan region during 1996 and 1997, and also includes a reexamination of data previously published for the three regions of the United States. The original data on the United States regions, or "study units," were collected between 1985 and 1997.

DESCRIPTION OF STUDY UNITS

The following sections describe the general environmental and land-use characteristics of the study units chosen for this joint agreement.

Hai He River Basin

The Hai He River Basin (figs. 1 and 3) is located in the northern part of the People's Republic of China (35°N to 41°N, and 112°E to 120°E). The basin consists of mountains and plateaus in the northern and western parts, and the North China Plain in the eastern and southern parts. The Hai He River Basin belongs to the semihumid climate in the monsoon region of the East Asia warm Temperate Zone (Edmonds, 1998). The winters are dry and cold, with low rainfall in the spring and heavy rainfall in the summer. The average annual precipitation is 548 mm, about 80 percent of which falls during June to September. The Hai He River Basin is composed of two large river systems: the Hai He River system and the Luan He River system. The Hai He River system includes the Hai He River and several major tributaries, and part of the South Grand Canal, a major canal. The Luan He River system includes the Luan He River and several tributaries. The Hai He River Basin includes two very large cities—Beijing and Tianjin—and numerous other cities, including Tangshan. The drainage basin is 318,800 km^{2}, of which 189,000 km^{2} is mountainous and the remainder is plain (Lin Chao, Hai He River Water Conservancy Commission, written commun., 1998). The basin population is 118 million people and there are 110 million square hectometers of farmland (Lin Chao, Hai He River Water Conservancy Commission, written commun., 1998). The cropping patterns in the Tangshan study unit are diverse, and the major crops are wheat, rice, corn, sorghum, cotton, and peanuts. The population density is 370 people per square kilometer. Water resources, which are deficient in the basin, average 40.4 billion (40.4×10^{9}) cubic meters per year (Lin Chao, Hai He River Water Conservancy Commission, written commun., 1998). Surface runoff is 26.4 billion cubic meters. The average surface water per capita use is 251 m^{3}/yr (Lin Chao, Hai He River Water Conservancy Commission, written commun., 1998). This can be compared to a per capita usage in the United States (based on data collected in 1990) of 9,913 m^{3}/yr (Population Action International, 2000). As a result of the large population and the large amount of land in agriculture, water resource projects have been constructed to control floods, improve drainage, and provide for irrigation and water supply. Serious water contamination problems also exist in the basin. The annual amount of wastewater is about 4.71 billion megagrams, about 4 billion megagrams of which is discharged into rivers (Lin Chao, Hai He River Water Conservancy Commission, written commun., 1998). The combined problems of water shortage and water contamination limit economic and agricultural development.

The region chosen for the ground-water investigation, hereinafter called the "Tangshan study unit," is located within an area known as the North China Plain, about 160 km southeast of Beijing (fig. 3) (Xiudong, 1989). The 13,472 km^{2} study unit is about 130 km from east to west and 150 km from north to south, and has 180 km of coastline. The study unit slopes from the front of the mountain region southward to the Bohai Sea, resulting in a general predevelopment direction of ground-water flow to the ocean (Zhang, Suo Zhu, Hai He River Water Conservancy Commission, written commun., 1996). Three physiographic regions are defined for this study: the mountain region of the north, the plain region in the center, and the coast region to the south (fig. 4) (Xiudong, 1989). The mountain region covers 4,620 km^{2}, the plain region 4,884 km^{2}, and the coast region 3,968 km^{2}. Several geomorphic zones are recognized (fig. 5) within these physiographic regions. The Tangshan study unit is characterized by the monsoon climate of the Asian warm Temperate Zone, with cold winters and hot wet summers. The average annual temperature is 10.5°C (Zhang, Suo Zhu, Hai He River Water Conservancy Commission, written commun.,

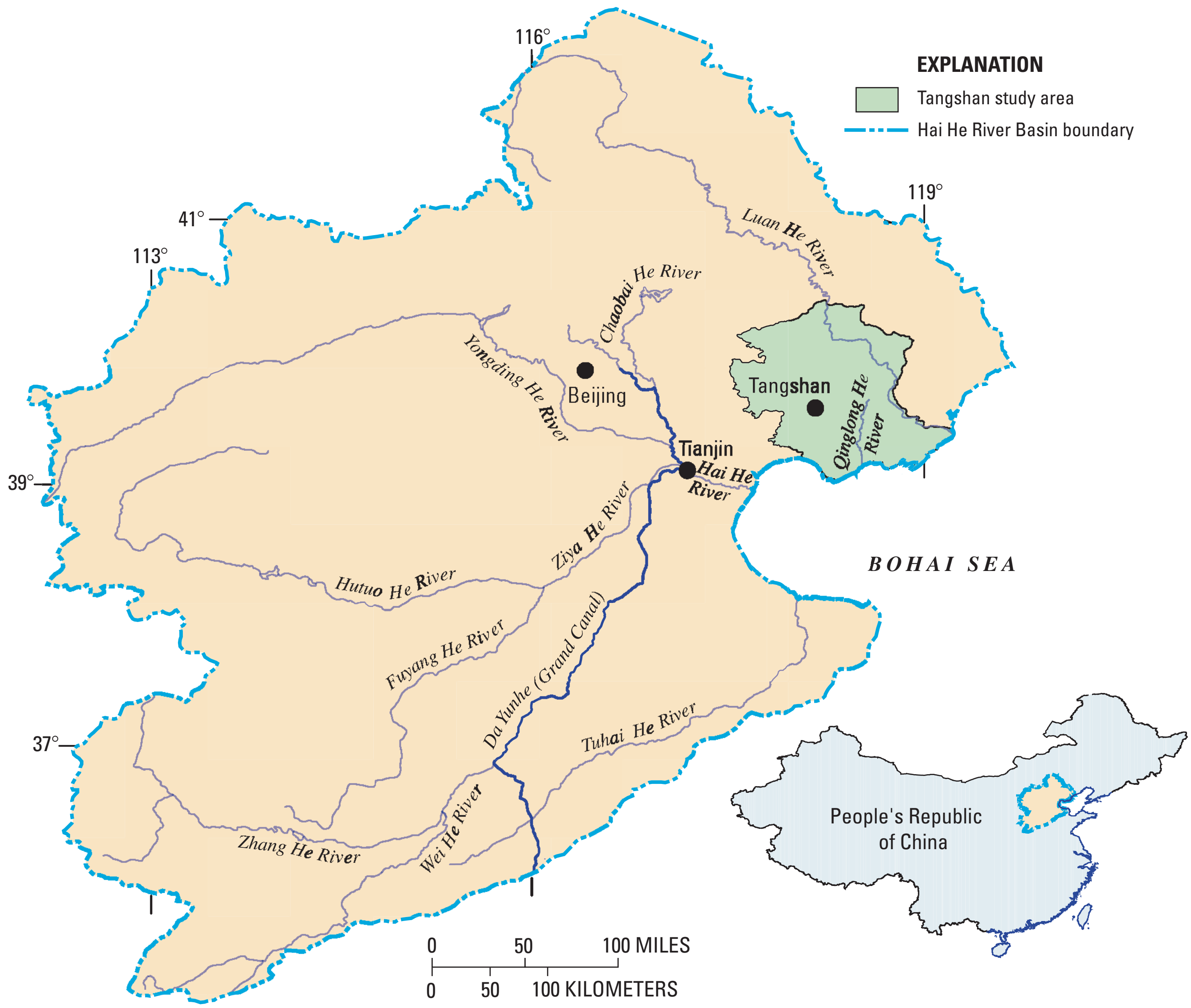


Figure 3. Hai He River Basin and Tangshan study area in the People's Republic of China.

1996). Annual precipitation decreases from 750 mm in the northern mountain region to 600 mm in the southern plain. The average precipitation in the study unit is 645 mm, most of which falls between June and September (Zhang, Suo Zhu, Hai He River Water Conservancy Commission, written commun., 1996). The Luan He River is the largest river in the study unit and has perennial flow. The study unit also includes many smaller rivers with seasonal or very low base flow. All rivers flow into the Bohai Sea from the north, southwest, and southeast. Water resources development is very important in the study unit, which includes 162 reservoirs with a total storage capacity of 4,361 billion cubic meters (Lin Chao, Hai He River Water Conservancy Commission, written commun., 1998).

Geologically, the Tangshan study unit lies at the corner of the North China Platform (Yang and others, 1986). This area has a complex geologic history, including folding and faulting of the nearby mountains. The area is also influenced by distant tectonic processes, including the movements of the Himalaya Mountains, which raised the mountains of the Tangshan study unit during the Cenozoic era. Movement along faults has resulted in serious earthquakes, including a devastating impact on the city of Tangshan during the 1970s. In the east, the bedrock comprises Archaean metamorphic and igneous rock (Yang and others, 1986). The mineralogy includes feldspars, quartz, and dolomite. The western and middle areas of the study unit have arenaceous rocks of the Permian,

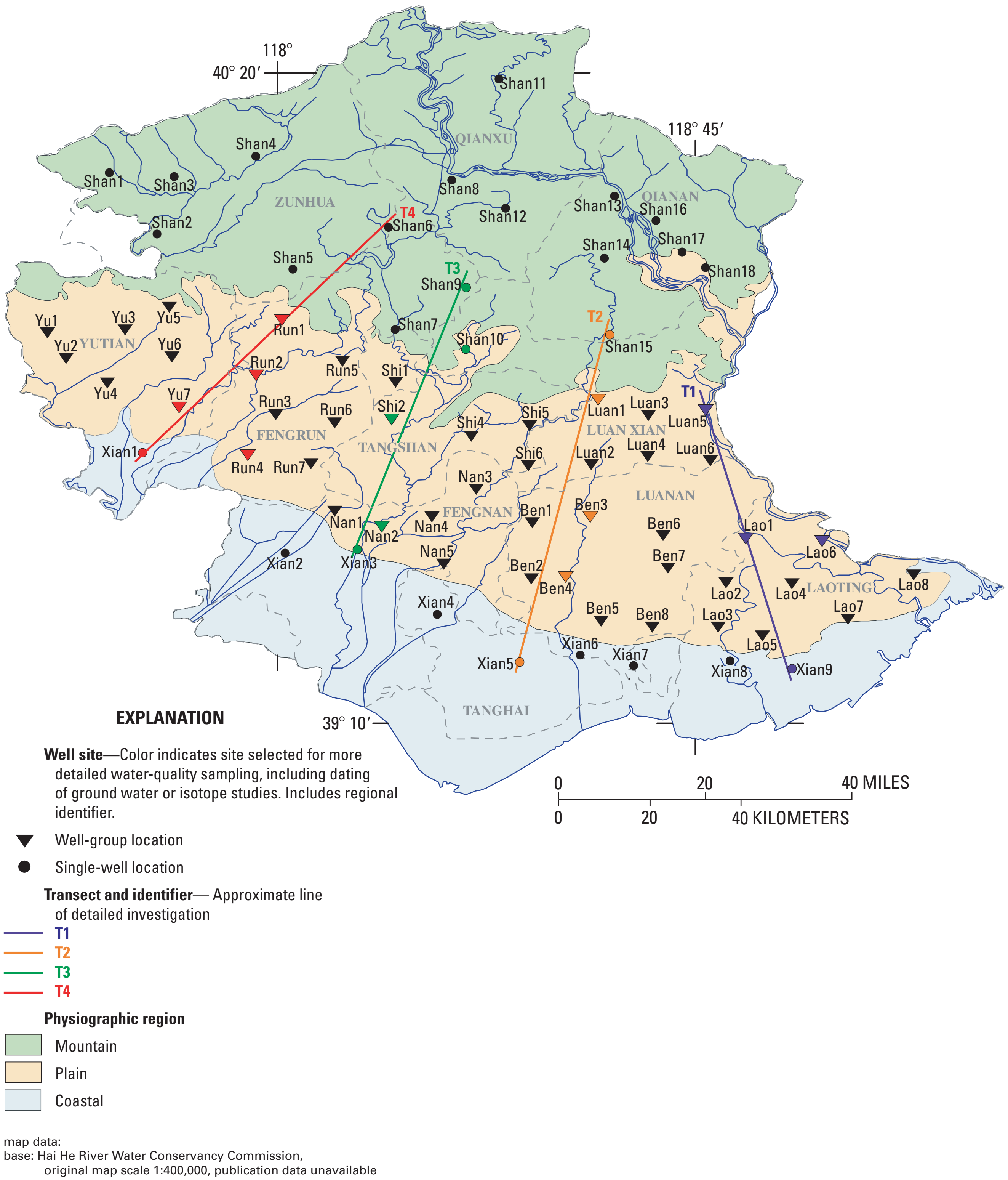
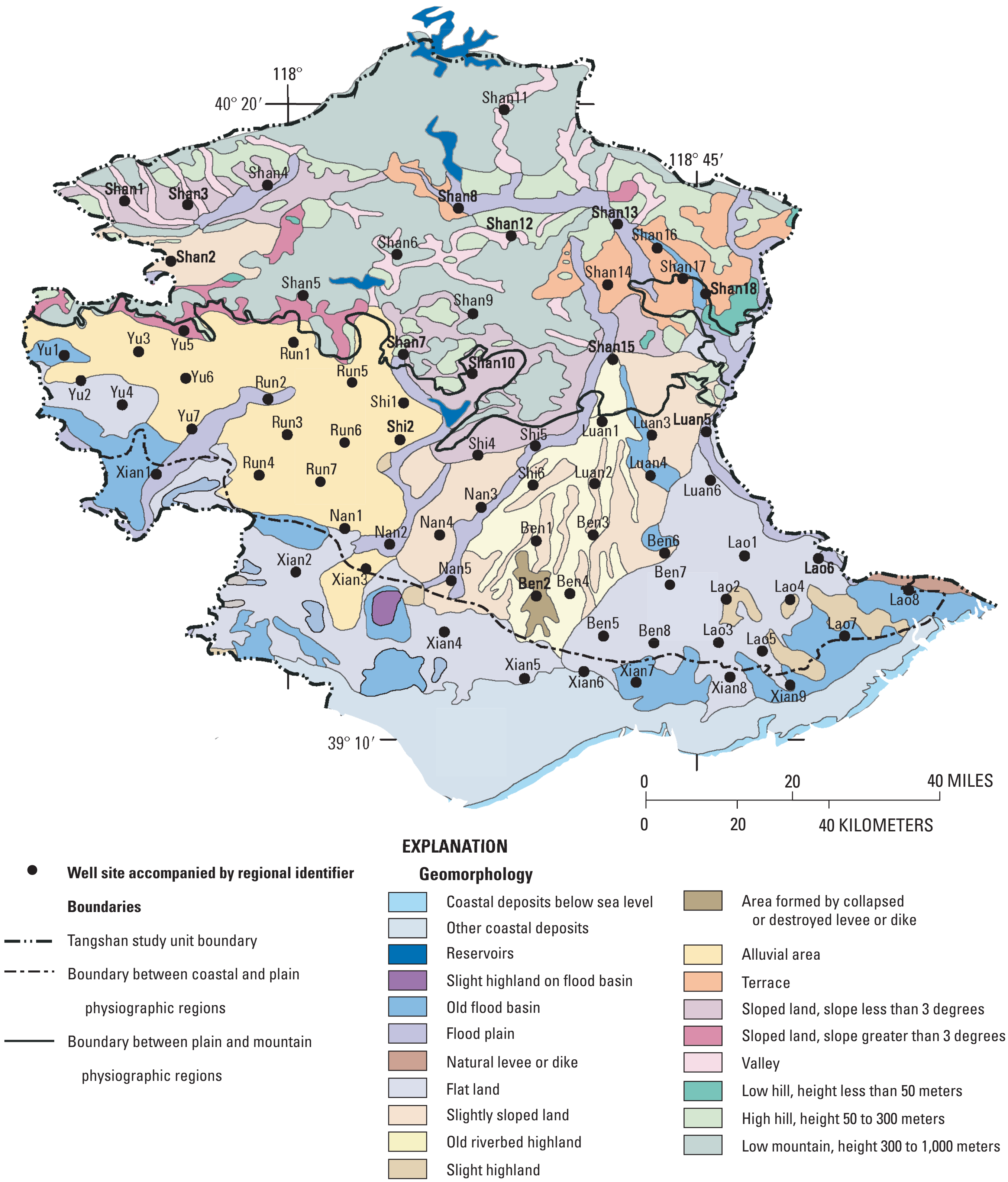


Figure 4. Tangshan study area, or "study unit," and locations of wells, transects (T1 through T4) for detailed investigations, county boundaries, and physiographic regions, People's Republic of China. A well group consists of two or more wells. Well sites show the regional identifier (Ben1, Lao1, Nan1, etc.), which corresponds to the Chinese naming convention.



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base: Hai He River Water Conservancy Commission,
original map scale 1:400,000, publication data unavailable
geomorphology: Hai He River Water Conservancy Commission,
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Figure 5. Geomorphic regions of the Tangshan study unit, People's Republic of China. Well sites show the regional identifier (for example, Ben1, Lao1, and Nan1), which corresponds to the Chinese naming convention.

Mississippian, and Pennsylvanian Periods and tuffs of the Tertiary Period. The western parts of the study unit also include Ordovician limestone. The southern part of the study unit includes primarily coastal deposits. The surficial deposits of the plain area are composed of primarily Quaternary deposits, including gravels, sands, clayey sands, and clays.

Four aquifer systems are recognized in the Tangshan study unit, Aquifers 1–4. Aquifers 1 and 2 are shallow and have good recharge characteristics, whereas aquifers 3 and 4 are deeper and separated from the overlying aquifers by clayey sand or clay layers, although those layers are probably not continuous (Zhang, Suo Zhu, Hai He River Water Conservancy Commission, written commun., 1996). Aquifer 1 is not continually saturated under the present conditions of recharge and water use and has generally been lost as a water-producing unit. The thickness of Aquifer 1 is 20–140 m. The thickness of Aquifer 2 is 40 to 240 m. The sediments are alluvial, diluvial, or lacustrine. Aquifer 3 is about 20 to 140 m thick. The sediments are composed of alluvial, diluvial, and marine sediments. Aquifer 4 is about 10 to 20 m thick. All of the upper sedimentary material is from the Quaternary period and is composed mainly of alluvial, diluvial, or lacustrine sediments. Information on the saturated thickness of these aquifers was provided by the Hai He River Water Conservancy Commission (Lin Chao, Hai He River Water Conservancy Commission, written commun., 1998).

Delmarva Peninsula

The general environmental setting of the Delmarva Peninsula has been described in Hamilton and others (1993). The Peninsula has an oval shape that extends about 241 km north to south and about 113 km east to west at its widest point and its physiography consists mostly of the Coastal Plain with a small amount of the Piedmont upland in the north (fig. 6). The Delmarva Peninsula is a flat to gently rolling upland, which is flanked by low plains that slope toward the Chesapeake Bay, the Delaware Bay, and the Atlantic Ocean. Tidal wetlands are located close to the coastline.

A wedge of unconsolidated sediments, which thickens to the south and east, underlies the Delmarva Peninsula. The thickness of the sediment varies considerably: it is more than 2,400 m along the Atlantic Coast of Maryland, whereas no sediment is located along the boundary of the Coastal Plain and Piedmont upland physiographic regions (fig. 6). The sediments range from Cretaceous to Quaternary (Holocene) in age and are comprised primarily of sand, clay, silt, gravel, and variable amounts of shells. The wedge of sediments is underlain by Precambrian igneous and metamorphic rocks, and sedimentary rocks of the Cretaceous Period. Previous studies in Cushing and others (1973) identified a series of nine confined aquifers and associated confining units, whereas Harsh and Laczniak (1990) identified only six confined aquifers and associated confining units. In either case, the series of confined aquifers is overlain by an extensive surficial aquifer that is under unconfined conditions in most of the study unit. This surficial aquifer is the focus of the water-quality studies for this study unit because it supplies water to the confined underlying aquifers and also because it is used extensively. About one half of the 643,000 m^3 of water that is pumped daily from wells is withdrawn from the surficial aquifer.

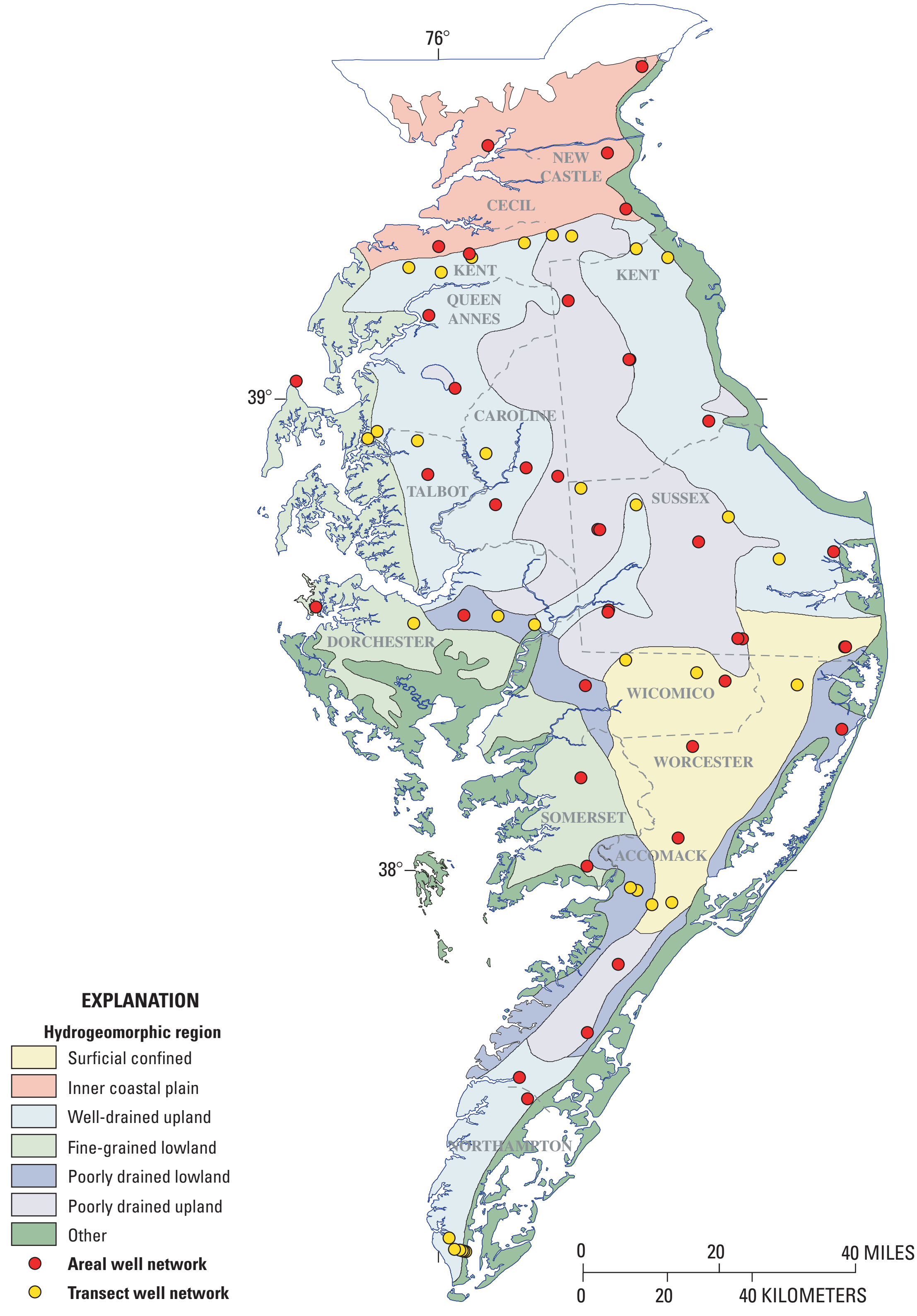
A description of the surficial aquifer of the Delmarva Peninsula has been provided in Hamilton and others (1993). Previous authors who also have reported on this aquifer include Rasmussen and others (1955), Jordan (1962, 1964), Hansen (1966), Cushing and others (1973), Owens and Denny (1978, 1979a,b), Denny and others (1979), Owens and Minard (1979), Hansen (1981), Bachman (1984), Owens and Denny (1984), Mixon (1985), and Andres (1986). Briefly, the sediments that compose the surficial aquifer represent several time-stratigraphic units, and those sediments were deposited in fluvial, estuarine, and marine and marginal marine environments. Most investigators consider the deposits to be from the Pleistocene Epoch. The mineralogy of these sediments consists of quartz sand and varying amounts of plagioclase, orthoclase, feldspars, and glauconitic sand. Minor amounts of heavy minerals are also present.

The Delmarva peninsula includes primarily one major physiographic region, the coastal plain, but comprises seven hydrogeomorphic regions within the plains (described in Hamilton and others, 1993): the poorly drained upland, the well-drained upland, the surficial confined region, the poorly drained lowland, the fine-grained lowland, the inner coastal plain, and “other” (fig. 7). Knowledge of these hydrogeomorphic regions is critical in understanding major element chemistry and contaminant transport. The surficial aquifer has been described as “under water table conditions throughout most of the study unit” (Hamilton and others, 1993, p. 8). The shallow water table is about 0–3 m below land surface in the central uplands. The water table is deeper in the well-drained uplands (as deep as 12 m below land surface). The flow in the surficial aquifer is from local water-table highs to streams and the coast. The ground-water flow paths are generally shorter than a few kilometers (Hamilton and others, 1993). Within these regions, agriculture is the major land use, woodlands constitute about 31 percent of the land area, and residential or urban development constitutes about 13 percent.

The average annual precipitation for the Delmarva Peninsula is 1,143 mm/yr. More than half of

map data: U.S. Geological Survey, 1981a,b; 1983 c,e,f,g; 1984a,b,e,i; 1999

Figure 6. Physiographic regions of the Delmarva Peninsula, United States. Includes state and county boundaries.



map data: Hamilton and others, 1993.
U.S. Geological Survey, 1981a,b; 1983c,e,f,g; 1984a,b,e,i; 1999

Figure 7. Hydrogeomorphic regions and locations of well networks of the Delmarva Peninsula, United States. Includes county boundaries.

this precipitation falls as rain during the spring and summer, but most of the recharge from the surface to the surficial aquifer occurs in the winter and spring nongrowing seasons when evapotranspiration is low. Much of the agricultural land in the Delmarva Peninsula is used for soybeans and corn, which are used for poultry feed (Hamilton and others, 1993; Shedlock and others, 1999). In addition to grain crops, other crops such as fruits, vegetables, and nursery stock are grown for local and regional markets. Large poultry farms are found across the peninsula, which is one of the leading production areas of broiler chickens in the United States (Hamilton and others, 1993; Shedlock and others, 1999).

San Joaquin Valley

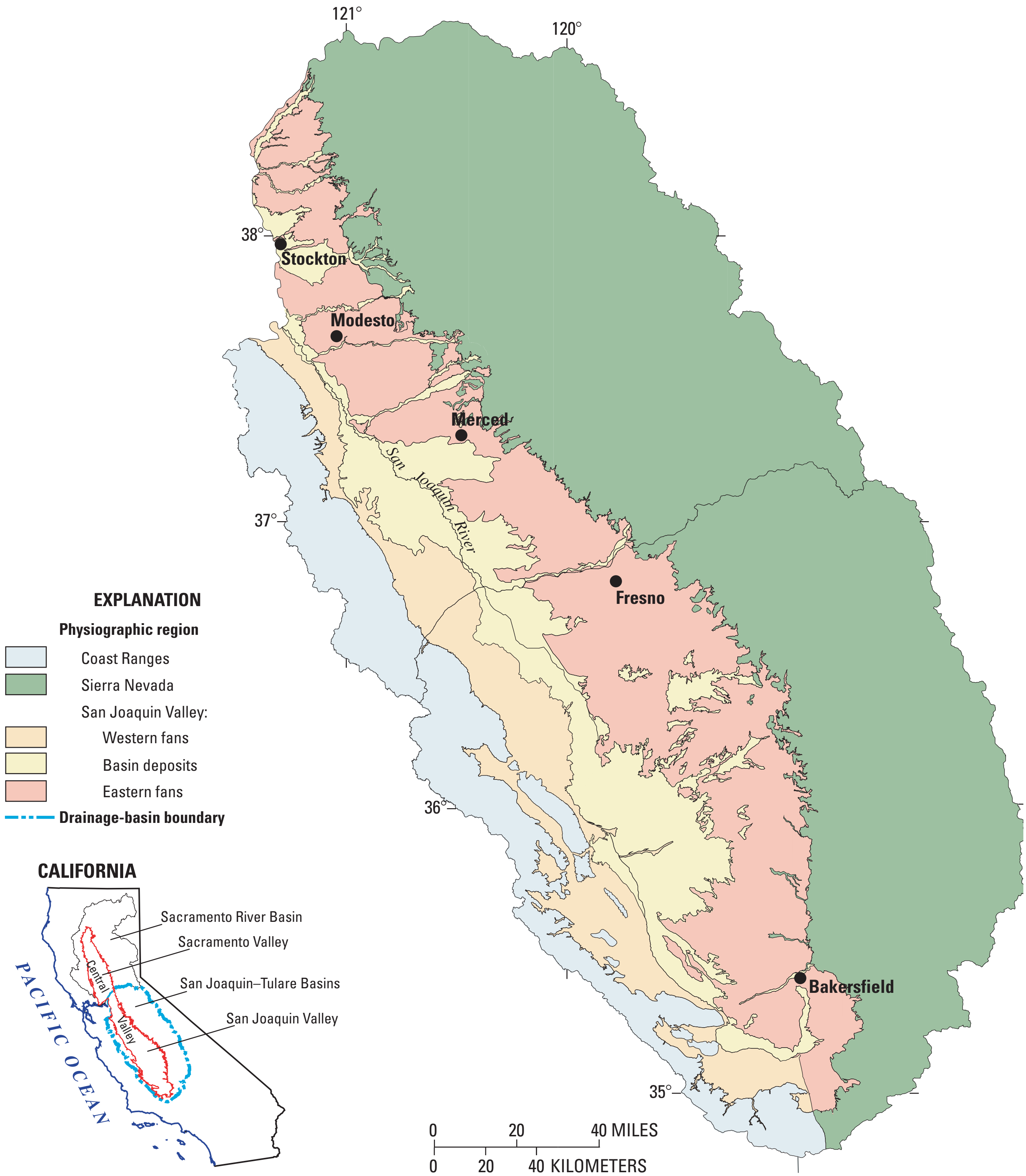
The San Joaquin Valley is the low-lying part of what is commonly referred to in the USGS as the San Joaquin–Tulare Basins (two separate basins that combine to form a larger basin). The San Joaquin–Tulare Basins are composed of three major physiographic regions—the Coast Ranges, the San Joaquin Valley, and the Sierra Nevada (fig. 8). The San Joaquin Valley, which is part of the Central Valley of California (fig. 8), is subdivided into three physiographic regions: the western fans, basin deposits, and eastern fans. Because most of the ground-water use, and potential impacts on ground water, occur within the valley's physiographic region, that part of the study unit was selected for detailed investigation. The valley, which consists of the San Joaquin and Sacramento Valleys, is a structural and topographic trough more than 805 km long. The San Joaquin Valley is the lower two-thirds of the Central Valley (fig. 8). A low east-west trending structural high in the valley floor just south of the Kings River area separates the southern part of the San Joaquin Valley into an area dominated by closed drainage. The climate in the San Joaquin Valley is Mediterranean with mild winters and hot summers. The average annual precipitation ranges from 127 to 406 mm (Page, 1986), most of which falls from November to April. As a result of the small amount of precipitation, ground-water recharge probably is almost exclusively acquired from infiltration of irrigation water. Most of the valley floor is irrigated.

A generalized geohydrologic section through the central part of the San Joaquin Valley is shown in figure 9. The regional freshwater aquifer system is in the Tulare Formation of the Pliocene and Pleistocene Epochs and in more recently deposited overlying alluvium. Because the Tulare Formation and overlying alluvium are lithologically similar, it is difficult to distinguish the boundary between them (Davis and others, 1959; Page, 1986), and so, it is not shown in figure 9. The Corcoran Clay Member of the Tulare Formation is an areally extensive fine-grained lacustrine deposit throughout the western part of the valley and the western part of the southern valley. It is used in this report to define the boundary of an upper and lower zone of the regional aquifers. The part of the Tulare Formation above the Corcoran Clay Member consists of Coast Ranges sediments on the west that interfinger eastward with sediments derived from the Sierra Nevada.

Alluvial, Pleistocene nonmarine, and other nonmarine deposits of the eastern part of the valley were derived primarily from the weathering of granitic intrusives of the Sierra Nevada, with fewer contributions from sedimentary and metasedimentary rocks of the foothills. The Sierran deposits are primarily highly permeable, medium to coarse-grained sands with low total organic carbon. The deposits generally are coarsest near the upper parts of the alluvial fans in the eastern part of the valley and finest near the valley trough. The depth to ground water below land surface varies greatly in these deposits (6 to 61 m). The combination of coarse-grained deposits and the relatively shallow water table results in a high potential for transport of nitrate or pesticides in irrigated areas of the eastern part of the valley (Domagalski and Dubrovsky, 1991, 1992).

The alluvial deposits of the western part of the valley tend to be of finer texture relative to those of the eastern part of the valley because of their origin in the Coast Ranges. The Coast Ranges to the west of the San Joaquin Valley are a complex mixture, consisting primarily of marine shales with smaller amounts of continental sediments and volcanic rocks. Ground water is less than 6 m below land surface over much of the western part of the valley, particularly in the lower parts of the alluvial fans. The unsaturated zone is primarily fine grained in these areas.

The southern part of the valley has closed drainage except in the wettest years, and lacustrine sediments have been deposited in the lowest topographic areas. These fine-grained sediments may tend to inhibit the transport of agricultural chemicals such as nitrate and pesticides. Stream-channel deposits of coarse sands are present along the San Joaquin River and its major east-side tributaries. In the valley trough, flood-basin deposits of varying extent flank the stream-channel deposits. The flood-basin deposits are interbedded lacustrine, marsh, overbank, and stream-channel sediment deposits generated by the numerous sloughs and meanders of the major rivers. The soils that have developed on these deposits generally are clays with low permeability (Davis and others, 1959). The stream-channel and flood-basin deposits are variable in nature with generally shallow water tables. The potential for contaminant transport may be high in places where the coarse-textured deposits are present.



map data: Fenneman and Johnson, 1946. California Division of Mines and Geology, 1958; 1959; 1964; 1965a,b; 1966; 1967; 1969. U.S. Geological Survey, 1978a. Page,1986

Figure 8. Physiographic regions of the San Joaquin–Tulare Basins, California, United States.

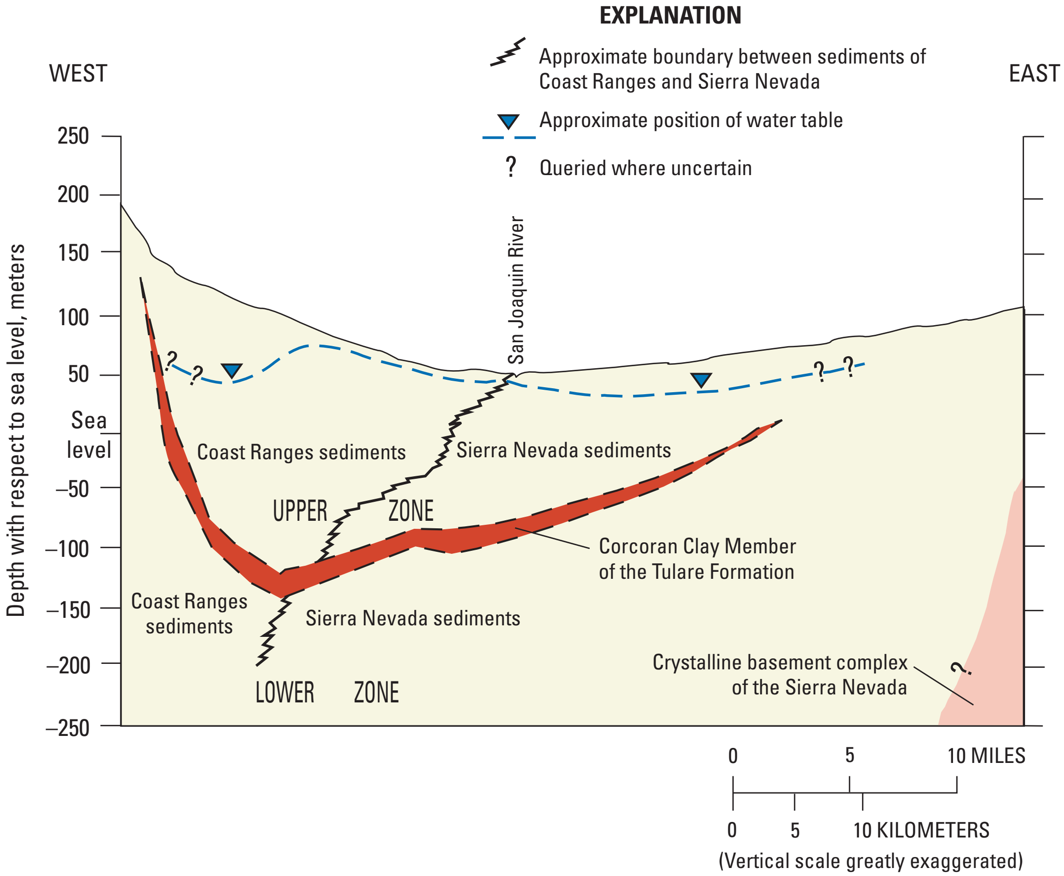
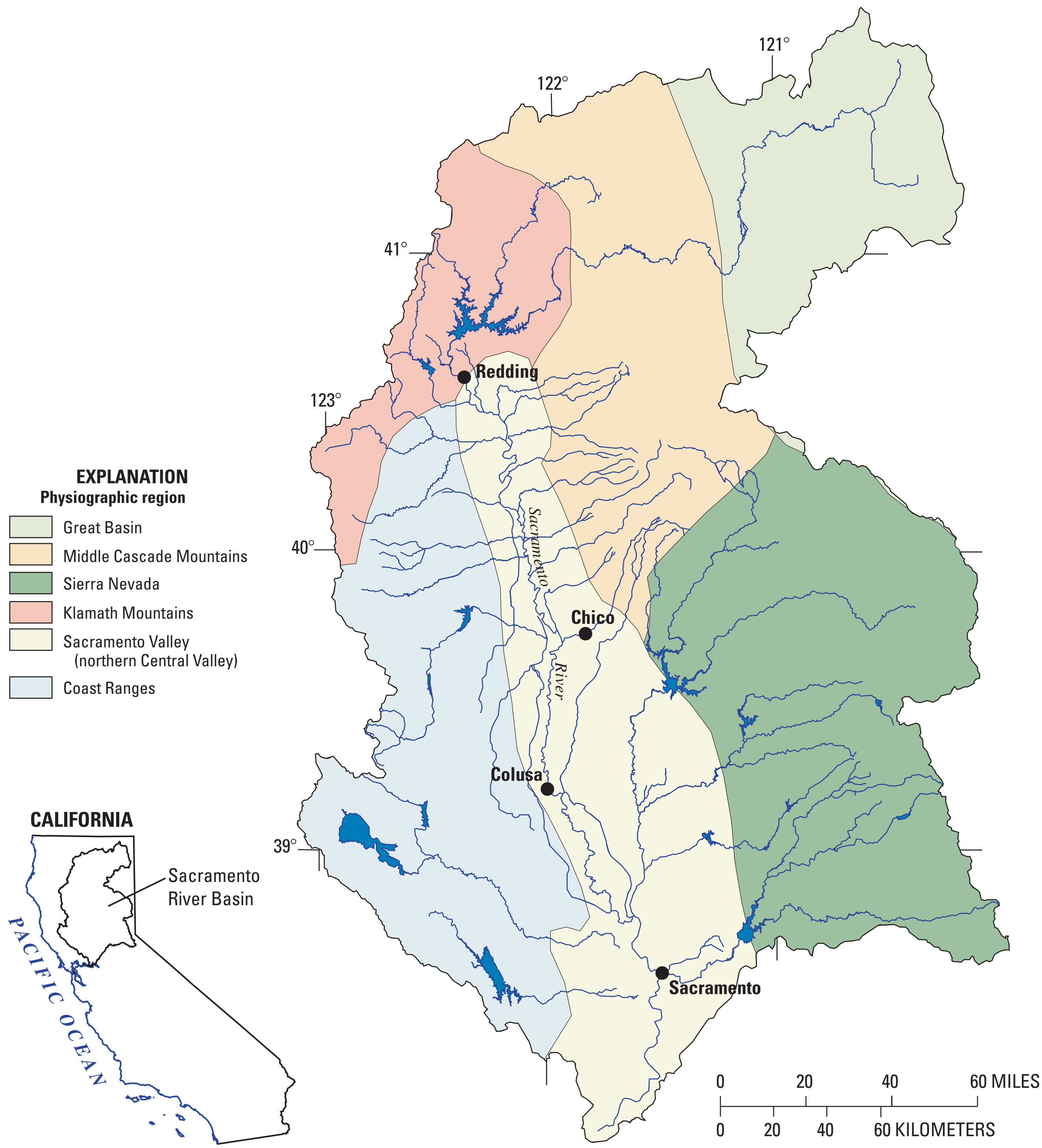


Figure 9. General geohydrologic cross section through the central part of the San Joaquin Valley, California, United States (modified slightly from Davis and others, 1959).

The San Joaquin Valley probably has the most diversified agricultural economy of the four regions included in this report. In 1987, about 10 percent of the total agricultural production in the United States came from California, of which 49 percent, or $6.82 billion (in United States dollars), was generated in the San Joaquin Valley (Gronberg and others, 1998). Major products are livestock and livestock products (35 percent), fruits and nuts (33 percent), cotton (13 percent), vegetables (6.5 percent), hay and grains (6 percent), and other crops (6.5 percent) (Gronberg and others, 1998).

Sacramento Valley

The Sacramento Valley is the low-lying part of the Sacramento River Basin (fig. 10). The Sacramento River Basin comprises six physiographic regions: the Great Basin, the Middle Cascade Mountains, the Klamath Mountains, the Coast Ranges, the Sierra Nevada, and the Sacramento Valley (fig. 10) (Domagalski and others, 1998). The Sacramento Valley is the primary region within the Sacramento River Basin where most of the ground-water use and potential effects on ground water occur. The Sacramento Valley is the northern one-third of the Central Valley. Page (1986) has described the geology of the Sacramento Valley as part of the northwestward-trending asymmetric-structural trough of the Central Valley that has been filled with sediment as much as 16 km in depth. The ages of the sedimentary rocks and deposits in the Sacramento Valley range from the Jurassic Period to the Quaternary Period (Holocene Epoch) and include marine and continental rocks and deposits. Much of the valley is classified as continental rocks and deposits that range from the Pliocene Epoch to Holocene Epoch, which are a heterogeneous mix of generally poorly sorted clay, silt, sand, and gravel. The valley also includes beds of claystone, siltstone, sandstone, and conglomerate. River and flood-basin deposits are also an important part of the valley's geology. The river deposits consist of gravel, sand, silt, and minor amounts of clays; the flood-basin deposits consist of clay, silt, and some sand deposited during flood stages of the rivers. The foothills of the Sierra Nevada and Cascade Mountains flank the eastern side of the valley. Those physiographic regions are composed of volcanic, marine, granitic, and continental rocks. The valley is flanked on the western side by rocks of the Coast Ranges, which are principally marine deposits. The Natural Resources Conservation Service (name changed from the "Soil Conservation Service" in



map data:
Fenneman and Johnson, 1946. U.S. Geological Survey, 1972; 1975a,b; 1976a,b,c,d; 1978b,c,d;
1979a,b,c; 1980; 1983a,b,d; 1984c,d,f,g,h. Steeves and Nebert, 1994

Figure 10. Physiographic regions of the Sacramento River Basin, California, United States (from Domagalski and others, 1998).

October 1994) has described the soils of the Sacramento Valley (Soil Conservation Service, 1993). Most of the soils are clay with very slow or moderately slow infiltration rates. Because of the regional extent of these clay soils, rice cultivation is a major agricultural practice in the Sacramento Valley. Fruits and nuts also are grown in the Sacramento Valley, but production is limited to regions with well-drained soils, primarily near river channels. Row crops, including corn and tomatoes, are also produced. Although clay soils are widespread throughout the Sacramento Valley, no major confining layers of clays, such as those that characterize parts of the San Joaquin Valley, occur in the Sacramento Valley. The aquifer of the Sacramento Valley resides under unconfined conditions in most of the valley (Page, 1986).

The average annual precipitation in the Sacramento River Basin is 914 mm/yr, with most of the precipitation in the form of rain or snow during November through March. The precipitation in the Sacramento Valley (fig. 10) is less than that of the overall basin, and the average annual precipitation measured in Sacramento is 472 mm/yr. Most of that precipitation falls also as rain during November through March. More rain falls in the mountainous regions, especially in the northern part of the basin.

Comparison of Study-Unit Characteristics

A comparison of geographic and hydrologic characteristics of the four study units is shown in table 1. The study units generally are in about the same range of latitude. The greatest differences are the variation in the amount of precipitation, the amount of irrigation water, and the density of population. The Delmarva Peninsula has the greatest amount of precipitation and, because a significant percentage of the annual precipitation falls during the growing season, there is less of a need for irrigation water. The Asian monsoon influences the weather of the Tangshan study unit, where most of the precipitation falls between June and September. Although Tangshan's precipitation coincides with its growing season, annual rainfall varies, and usually a significant amount of irrigation water is still needed. In contrast, little or no rain falls in the San Joaquin and Sacramento Valleys during the growing season, and as a result, successful agriculture in this region requires irrigation water.

DESIGN OF GROUND-WATER WELL NETWORKS FOR JOINT AGREEMENT

The overall design of the study was to characterize the regional ground-water quality in the Tangshan region of the People's Republic of China and to compare the water quality with that of similar areas in the United States. Unfortunately, it was not logistically possible or necessary to design the sampling strategy for the joint agreement such that all sampling would take place at the same general time. In fact, sampling for two of the study units of the United States—the Delmarva Peninsula and the San Joaquin Valley—took place prior to the actual design of the joint agreement for international study. Participants of the study determined that the basic concept of the NAWQA study-unit survey (Gilliom and others, 1995) would be the principal guidance for well selection and data analysis. The study unit survey relies primarily on the sampling of existing wells and, wherever possible, on the interpretation of existing data collected by other agencies or programs. Wells are selected using a grid-based random sampling approach (Scott, 1990; Alley, 1993). As mentioned, the ground-water well networks for study units in the United States were designed for specific studies, including but not limited to NAWQA, and had been sampled previously. The design for the joint agreement followed the criteria of these earlier studies as closely as possible. In all cases, the design of the ground-water networks was regional in scope. All well networks were designed to obtain water-quality data for a regional ground-water system in agricultural areas, and all study designs for these well networks included water-quality sampling for nitrate and other nutrient compounds. However, only the well networks of the San Joaquin Valley and the Tangshan aquifer system included samplings of a shallow well and a deep well in most chosen locations. Therefore, whereas comparisons can be made of the surficial aquifers in all four study units, comparisons of deeper aquifers can only be made for those in the San Joaquin Valley and the Tangshan study units.

The wells of the Delmarva Peninsula were sampled in 1989 and 1990, the wells of the San Joaquin Valley were sampled during 1985 through 1988, and those of the Sacramento Valley were sampled in 1996 and 1997. The wells of the Tangshan aquifer had two samplings for water quality. These were completed in May and September 1996 in order to obtain data prior to and following the rainy season, respectively. Much of the data analysis and interpretation for this study used the data from the May sampling, which included more comprehensive chemical analyses.

The design of the water-quality network for the Delmarva Peninsula is discussed in detail in Hamilton and others (1993). That study was part of the pilot program for the design of study-unit surveys for NAWQA. The Delmarva network consisted of two components: an aereal network and a transect network (fig. 7). The authors of this report decided that the two networks would be combined to provide better regional coverage of ground-water quality for this joint study.

Table 1. Comparison of geographic and hydrologic characteristics of the four study units in the People's Republic of China and the United States

[hm, hectometer; km, kilometer; m, meter; mm, millimeter; na, not available; yr, year; °C, degree Celsius]

Country:	People's Republic of China	United States		
Study unit:	**Tangshan (Hai He River Basin)**	**San Joaquin Valley (California)**	**Sacramento Valley (California)**	**Delmarva Peninsula (DE, MD, VA)[1]**
Geographic range:				
Latitude	39°03′–40°35′	35°–38°30′	38°–40°30′	37°–30°40′
Longitude	117°30′–119°18′	120°–120°30′	120°30′–122°20′	75°–76°20′
Area (km^2)	13,472	31,216	16,392	15,540
Precipitation[2] (mm/yr)	645	127–380	350–640	1,140
Evaporation (mm/yr)	1,585	1,245	1,245	na
Drought index (evaporation/ precipitation)	2.456	9.8–3.3	3.6–1.9	na
Air temperature, °C (mean, highest, lowest)	10, 39.6, –22.07	16.5, 43.9, –8.9	16, 45, –7.8	13.4, 38.5, –20
Aquifer characteristics (single or multilayer)	Multilayer	Multilayer	Single	Single
Thickness of the main aquifer (m)	10–50	730–2,740	730	30.5 for surficial aquifer
Depth of ground water (m)	7.5	6 or greater	6 or greater	6.1
Average annual recharge amounts of ground water (m^3/yr)	169,000	1,850,222,700 (combined for San Joaquin and Sacramento Valleys)		6,315,456,000
Ground-water use ($10^4 m^3/km^2$/yr)	14.1	25.8	20.1	1.5
Utilization coefficient of ground water (exploitation amount/ recharge amount)	Slightly greater than one	Greater than one	Less than one	Less than one
Area of farmland (km^2)	5,806	30,000	13,072	7,459
Proportion of farmland (farmland area/total land)	0.431	0.96	0.79	0.48
Irrigation water (m^3/hm^2)	44,275	4,540	5,080	na
Monitoring well amounts	111	178	59	103
Density of population (people/km^2)	512	87	134	45

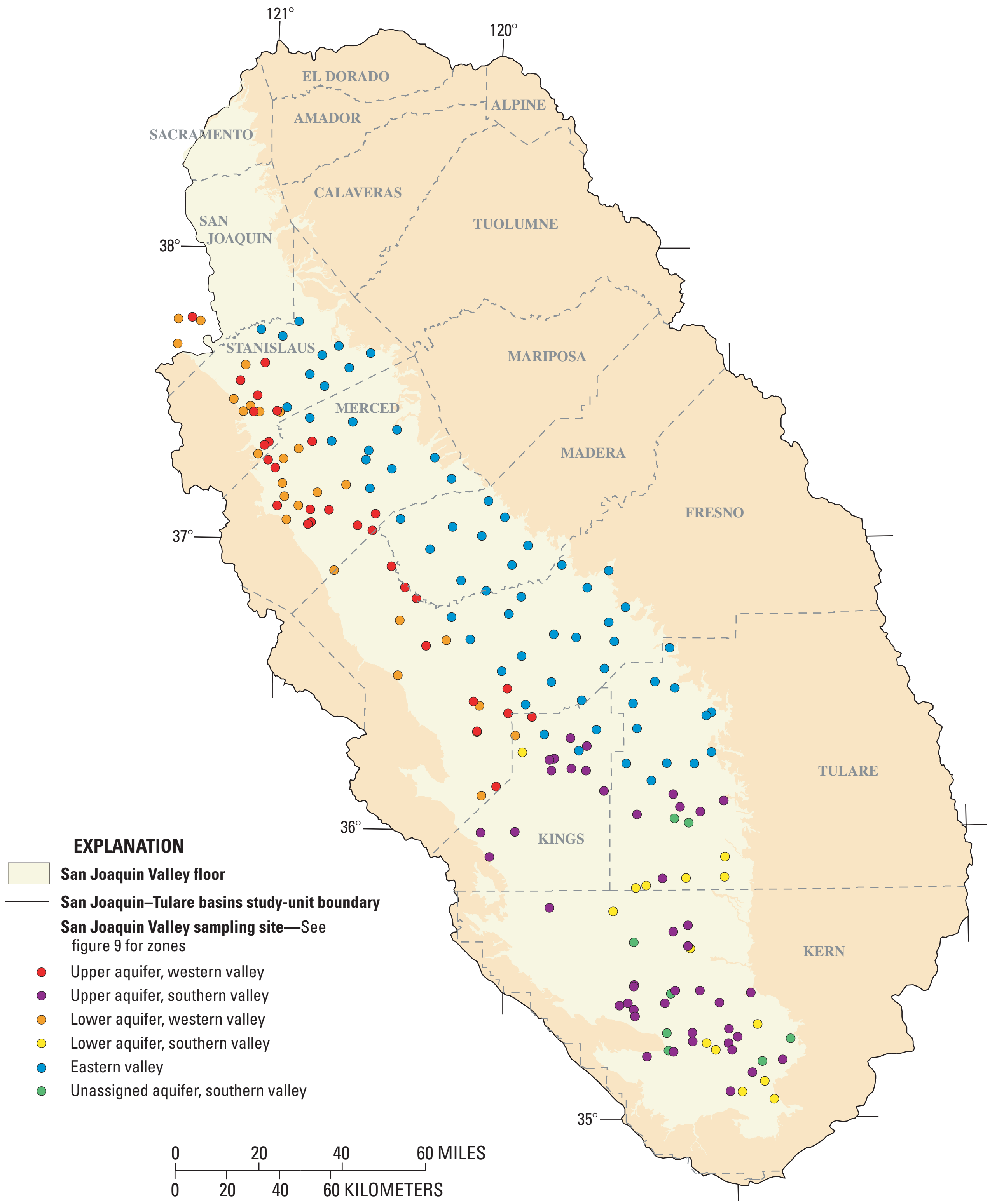
[1]DE, Delaware; MD, Maryland; VA, Virginia.

[2]Precipitation is shown as either the average or the range.

The design of the San Joaquin Valley network is described in Domagalski and Dubrovsky (1991). Those wells were sampled as part of the Regional Aquifer Systems Analysis (RASA) Program of the USGS. The basic design of the San Joaquin Valley RASA study was to sample a set of wells spaced randomly to evenly throughout the San Joaquin Valley, thereby approximating the general guidance for design of a NAWQA study-unit survey (fig. 11). The design of the San Joaquin Valley study most closely approximates that of the Tangshan study because shallow and deep wells were sampled through most of both study units.

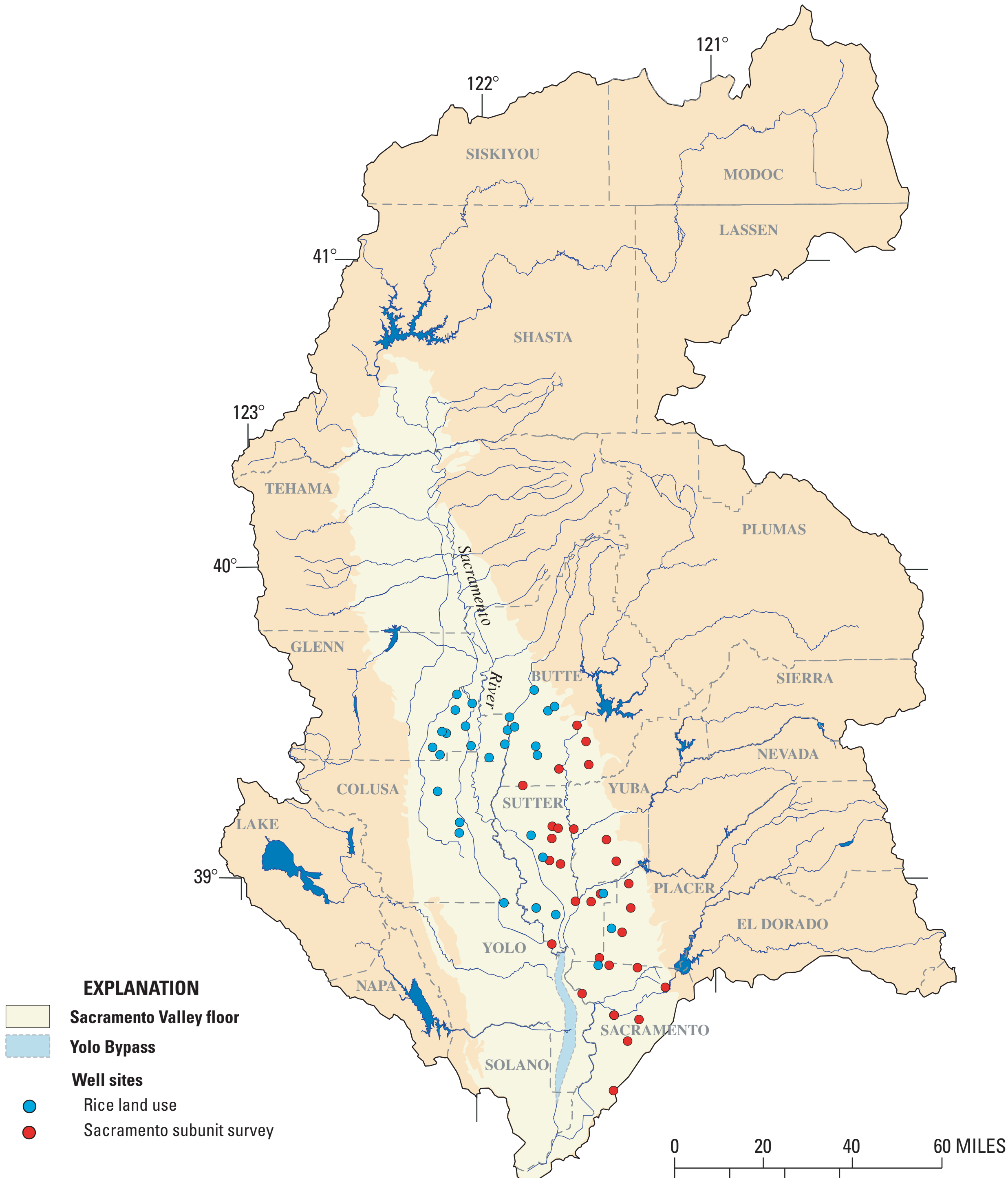
A general discussion of the design of the Sacramento Valley well network is given in Domagalski and others (1998). That well network included a study of a part of the Sacramento Valley (Sacramento subunit survey) and an agricultural (rice) land-use survey (fig. 12). The well network was based on the NAWQA guidance for well selection in a study unit. Because of the areally extensive nature of rice agriculture in the Sacramento Valley, the authors decided to combine two well networks for data interpretation to provide greater spatial coverage. However, the water-quality characteristics and interpretation of the water quality of the subunit survey and rice wells are discussed separately.

The well network for the Tangshan aquifer is shown in figure 4. A total of 111 wells, used for irrigation and domestic water, were sampled. Water-quality samples were also collected at three river sites—two on the Luan He River and one site on the Qinglong He



map data:
U.S. Geological Survey, 1978a. Charles Johnson, U.S. Bureau of Reclamation, unpub. data (county boundaries, scale 1:24,000), 1993

Figure 11. Locations of wells in the San Joaquin Valley, California, United States. Includes county boundaries.



map data:
U.S. Geological Survey, 1972; 1975a,b; 1976a,b,c,d; 1978b,c,d; 1979a,b,c; 1980; 1983a,b,d; 1984c,d,f,g,h.
Charles Johnson, U.S. Bureau of Reclamation, unpub. data (county boundaries, scale 1:24,000), 1993. Steeves and Nebert, 1994

Figure 12. Locations of wells in the Sacramento Valley, California, United States. Includes county boundaries.

River—to compare the chemistry of river water with that of ground water. The lower Luan He River was the only site sampled for major inorganic constituents, and all three sites were sampled for hydrogen and oxygen isotopes. At most locations, both a shallow and a deeper well were sampled. Four ground water transects were selected for detailed analysis by stable isotopes or dating analysis. Transects 1 and 2 (lines T1 and T2 shown in fig. 4) were sampled in June 1996, and the analyses included stable isotopes and dating. Water samples were also collected for the analysis of pesticides at select wells along those transects. Not all of the wells were sampled for all three types of dating methods because of logistics difficulties or because not all of the wells were suitable for this type of sampling. At the very least, samples for tritium (^3H) were collected. Transects 3 and 4 were sampled in September 1996 for stable isotopes to provide a better spatial resolution of the distribution of deuterium and oxygen isotopes in ground water. Water-quality technicians of the Hai He River Water Conservancy Commission or Tangshan Water Resources Bureau collected water-quality samples in May and September 1996. The May sampling occurred prior to the Asian monsoon season and the September sampling afterwards. In that way, the effects on water quality of very recently recharged water could be examined.

The well network for the Delmarva Peninsula (fig. 7) had a total of 103 wells sampled in 1989 and 1990. In the well network for the San Joaquin Valley (fig. 11), 178 wells were sampled. The wells of the western San Joaquin Valley were sampled in 1985, those of the southern part in 1986, and those of the eastern part in 1987. The 59 wells of the Sacramento Valley were sampled in 1996 and 1997. The well network of the Sacramento Valley is shown in figure 12.

METHODS AND SAMPLE ANALYSIS

The methodology chosen to collect water from ground-water wells for the study units of the United States conformed to established USGS procedures. Ground-water samples for the Delmarva study unit were collected according to the method in Hardy and others (1989), which called for the removal of standing water in the well by pumping at least three well-casing volumes of water and monitoring field-measured constituents such as temperature, pH, and specific conductance. After these field-measured constituents had stabilized, water samples were collected through non-contaminating equipment such as Teflon tubing. Water samples were filtered through 0.45 μm pore-size filters for dissolved constituents. Quality assurance and quality control practices for the Delmarva study were summarized in Jones (1987), Hardy and others (1989), and Koterba and others (1991). The purpose of the quality assurance and quality control practices was to ensure that accurate and representative water-quality data for each sampling network were acquired and to estimate the variability in selected water-quality constituents. These quality assurance and quality control practices included the cleaning of equipment used for sampling, collecting blank samples using the same procedures that are used for real water samples, and collecting replicate samples to determine variability caused by sampling or laboratory analysis.

A similar strategy was used for collecting water-quality samples from wells in the San Joaquin Valley, which is summarized in Dubrovsky and others (1991). Sampling for wells in the Sacramento Valley conformed to guidance provided by the NAWQA Program (Koterba and others, 1995). Most chemical analyses of water collected from all wells in the United States were conducted by the USGS's National Water Quality Laboratory in Arvada, Colorado, except for ^3H and $^3H/^3He$ analyses. Most of the analytical methods are described in Fishman and Friedman (1985). Some samples were analyzed for pesticides using the methods in Zaugg and others (1995).

Radiochemical analyses were completed on many samples, including some collected in the People's Republic of China. The dating methods were the ^3H, $^3H/^3He$, and CFC methods. Stable isotope analyses were limited to deuterium (^2H) to hydrogen (^1H) ratio and oxygen 18 (^{18}O) to oxygen 16 (^{16}O) ratios, both in water molecules; and to nitrogen (^{14}N to ^{15}N ratio) and oxygen (^{18}O to ^{16}O ratio) isotopes in nitrate.

Ground-water samples in the People's Republic of China were collected from existing domestic or irrigation wells. For wells that were not operational, standing water was removed prior to sampling. Water samples were collected for field-measured constituents (pH, dissolved oxygen, specific conductance, and alkalinity), major elements, nutrients, metals, and in some cases, coliform bacteria, according to standard methods for the collection of water samples established by the People's Republic of China. The samples were analyzed by the Hai He Basin Water Environmental Monitoring Center and the Tang-Qin Water Environmental Monitoring Center. A subset of samples collected in the People's Republic of China was analyzed by the National Water Quality Laboratory of the USGS for comparison. The results showed that the two laboratories obtained similar results for major constituents, nutrients, and metals.

NATURAL WATER CHEMISTRY

Ideally, natural water chemistry is defined on the basis of ground-water samples collected from aquifer zones that have been unaffected by agricultural or other anthropogenic activities. In practice, it is difficult to determine whether any ground water in a large agricultural region has been unimpacted by agricultural chemicals. Even water with no measurable nitrate may indeed have had a major flux of nitrate that subsequently degraded by bacterial action under anoxic conditions. In previous studies of the Delmarva Peninsula, such as Hamilton and others (1993), ground-water concentrations at or below 0.4 mg/L of nitrate as N were indicative of natural water unaffected by agricultural activities. Hamilton and others (1993) used the results from a sufficiently large population of wells in the Delmarva Peninsula to define this background. A study of ground water throughout the United States (Madison and Brunett, 1984) suggests that nitrate as N concentrations below 0.2 mg/L are indicative of natural ground water in the United States and that nitrate as N concentrations generally between 0.2 to 3.0 mg/L or in some cases, slightly higher, indicate water that is affected by agricultural activities. There are no corresponding studies from China that document levels of natural ground-water nitrate concentrations, but it is reasonable to assume that they are also low. A threshold value of 0.5 mg/L of nitrate as N has been chosen as the value below which ground water can be assumed to be relatively unaffected by agriculture, at least with respect to nitrate within the Tangshan region. The situation in the San Joaquin Valley, especially the western region of the valley, is more complicated because of localized areas of naturally occurring nitrate (Sullivan, 1978).

It is beyond the scope of the present study to determine the sources of nitrate measured in the wells of the western San Joaquin Valley. Therefore, it is possible that some of the nitrate concentrations that were measured were not the result of agricultural activities. However, the nitrate levels measured in the lower aquifer of the western San Joaquin Valley tend to have nitrate concentrations less than 0.5 mg/L (median = 0.4 mg/L). Given these caveats, natural ground-water chemistry is defined in this study as water with a low nitrate concentration. The composition of ground water with nitrate as N less than 0.5 mg/L and with nitrate as N less than 3 mg/L are used to compare ground water across these study units as likely having been unimpacted or minimally impacted by agricultural activities, respectively. This range of values is used for comparative purposes for all study units of this investigation, although some of the higher nitrate concentrations measured in the western San Joaquin Valley may have resulted from natural sources. Water with nitrate concentrations greater than 3 mg/L are therefore assumed as likely to have been affected by the use of nitrogen fertilizer.

The natural water chemistry of the Tangshan aquifer can be characterized as calcium–magnesium–carbonate water (fig. 13). The water of the Luan He River (fig. 14) is also a calcium–magnesium–carbonate type of water. The natural water chemistry of the ground water and the Luan He River is consistent with the mineralogy of the aquifer sediments, which include a mixture of igneous and carbonate rocks. Ground water of the Tangshan study unit tends to be close to saturation or supersaturated with respect to carbonate minerals. Natural sources of chloride and sulfate are not apparent in most of the aquifer system, except in the coastal zone where intrusion of salt water can lead to elevated concentrations of chloride and sulfate.

Hamilton and others (1993) have described the natural water chemistry of the surficial aquifer of the Delmarva Peninsula, noting that the water tends to be acidic and soft with low alkalinity, low sodium, and low specific conductance. The chemistry of the natural water tends to be primarily controlled by the chemical properties of rainfall and snowmelt, mineral dissolution, biological activity and its residence time in the soil zone and aquifer, and the nearby presence of saline water (Hamilton and others, 1993). Mineral dissolution may take place when the minerals of the soil and aquifer zones come in contact with water moving through the system, including meteoric water and irrigation water. The principle mineral of the aquifer is quartz with minor amounts of silicate minerals or clay minerals, as well as calcium carbonate from shells and shell fragments (Hamilton and others, 1993).

The major element chemistry of the natural ground water of the Delmarva Peninsula is displayed in a trilinear graph in figure 15. The chemistry of natural ground water, unaffected by agriculture, is displayed as white squares in figure 15. The cation and anion chemistry of natural ground water of the Delmarva Peninsula is variable (fig. 15). Much of the natural water is dominated by bicarbonate as the principal anion, but the water also includes a considerable amount of sulfate and chloride, which can be attributed to the proximity of the Atlantic Ocean. The cation chemistry shows that most of the natural ground water is dominated by sodium plus potassium, but several ground-water samples also have high amounts of calcium and magnesium. Most of the ground water of the Delmarva Peninsula is undersaturated with respect to carbonate minerals.

The chemistry of natural water in the San Joaquin and Sacramento Valleys of California is complicated because of the contrasting physiographic regions surrounding the valley and different types of sediment that make up the aquifer materials. The chemistry of the San Joaquin Valley ground water is not expected to be the same for each location because the chemical composition of the recharge water is different for each location.

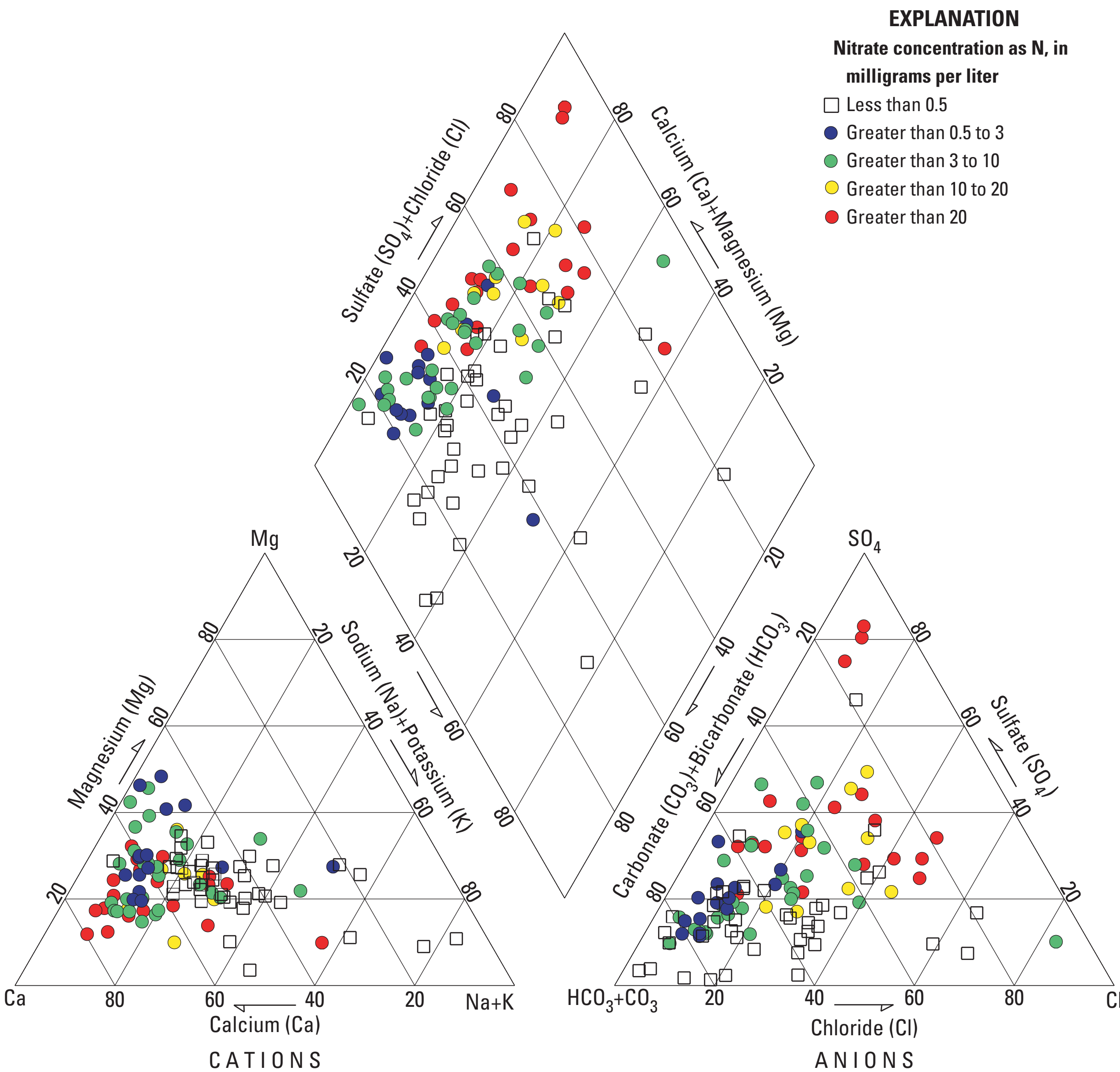


Figure 13. Trilinear graph displaying major element chemistry of Tangshan ground water, People's Republic of China. Each scale represents percentage of total milliequivalents per liter. N, nitrogen.

Trilinear graphs of ground water from wells sampled in the western, southern, and eastern parts of the valley are shown in figures 16 through 18. The western San Joaquin Valley is recharged principally by runoff from the Coast Ranges and from irrigation. The anion chemistry of the western San Joaquin Valley ground water is complex with all three types of waters present: bicarbonate, sulfate, and chloride dominated. The cation chemistry is mostly sodium with varying amounts of calcium and magnesium. Ground water of the southern San Joaquin Valley is recharged from a variety of sources, including the Coast Ranges, the Sierra Nevada, various streams, and irrigation. The anion chemistry is basically similar to that of the western San Joaquin Valley, but with a greater dominance of bicarbonate water. The cation chemistry of the natural ground water is generally similar to that of the western San Joaquin Valley. Ground water of the eastern San Joaquin Valley is recharged mainly from the Sierra Nevada runoff and from irrigation. The anion chemistry of the natural ground water is principally dominated by bicarbonate. The cation chemistry is different from that of the western and southern San Joaquin Valley in that calcium and magnesium tend to be the dominant ions. The ground water of the western San Joaquin Valley and much of the southern San Joaquin Valley tends to be close to saturation or supersaturated with respect to carbonate minerals, but the ground water of the eastern San Joaquin Valley tends to be undersaturated, reflecting the differences in chemistry of recharge water.

Hull (1984) recognized six hydrochemical facies throughout the Sacramento Valley. According to Hull

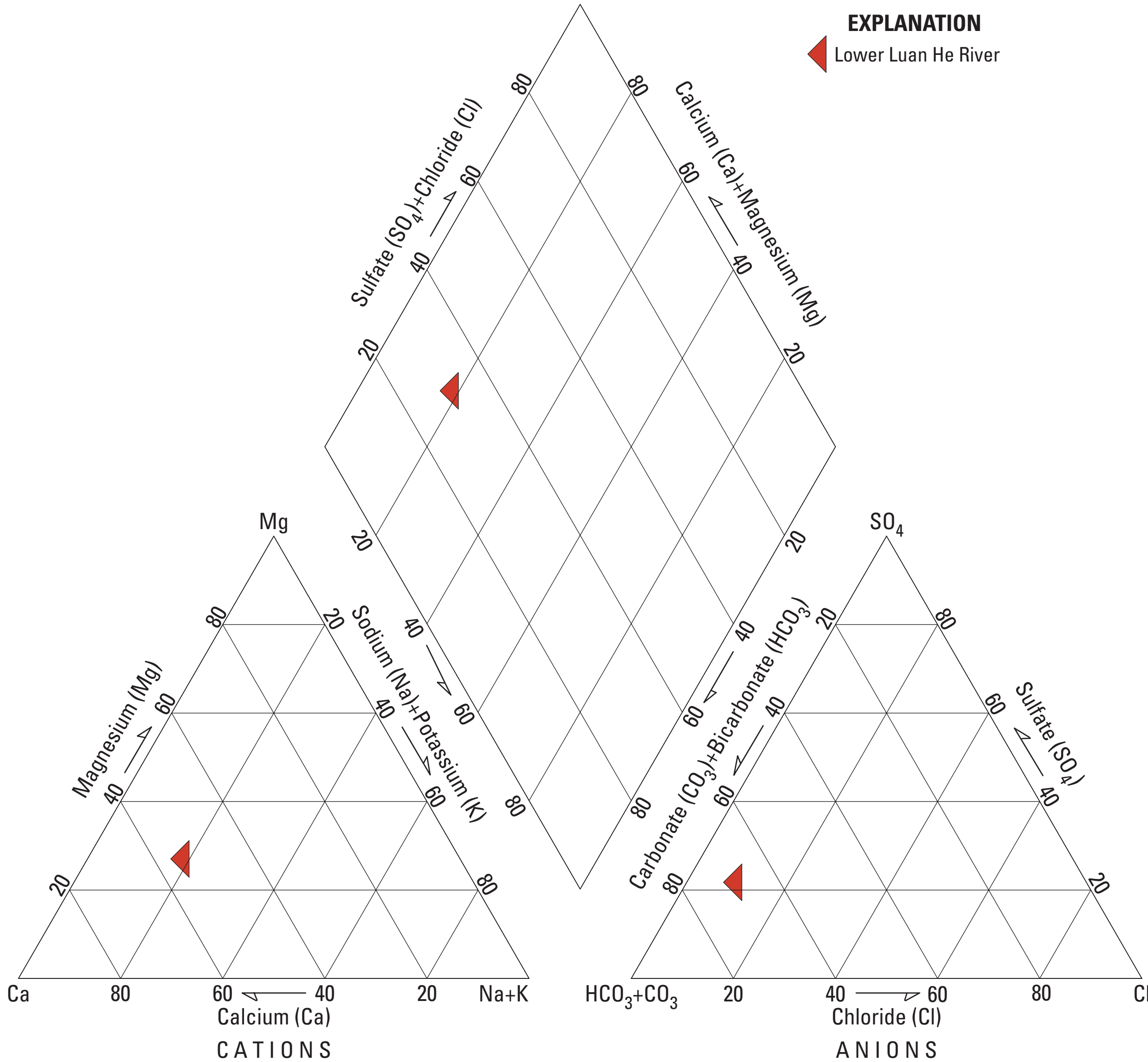


Figure 14. Trilinear graph displaying water chemistry of the Luan He River, People's Republic of China. Each scale represents percentage of total milliequivalents per liter.

(1984), the Sacramento subunit comprises two hydrochemical facies whereas the extent of the rice land-use study covers three hydrochemical facies. Under natural conditions, much of the recharge to the Sacramento subunit originates in the Sierra Nevada as dilute sodium or calcium bicarbonate water. Parts of the Sacramento subunit aquifer have areas with low dissolved oxygen and higher concentrations of chloride. The chemistry of the natural ground water of the Sacramento subunit is shown in figure 19. Bicarbonate is the dominant anion for most of the ground water sampled in the Sacramento Valley study with the exception of one well that has high chloride. The cation chemistry shows that the natural ground water is generally calcium and magnesium with varying amounts of sodium. The area of the Sacramento rice land-use study is on both sides of the Sacramento River and within three of the hydrochemical facies mentioned in Hull (1984). The area of the study unit to the west of the Sacramento River is likely to have higher concentrations of total dissolved solids, chloride, sulfate, and other constituents in ground water relative to the area east of the Sacramento River because of naturally occurring sources of these constituents in the Coast Ranges. The natural water chemistry of the ground water sampled for the Sacramento rice land-use study is shown in figure 20. More wells in the Sacramento rice study have higher sulfate and chloride composition than wells of the Sacramento subunit. The chemistry of the cations in the ground water of the Sacramento rice study is similar to that of the Sacramento subunit.

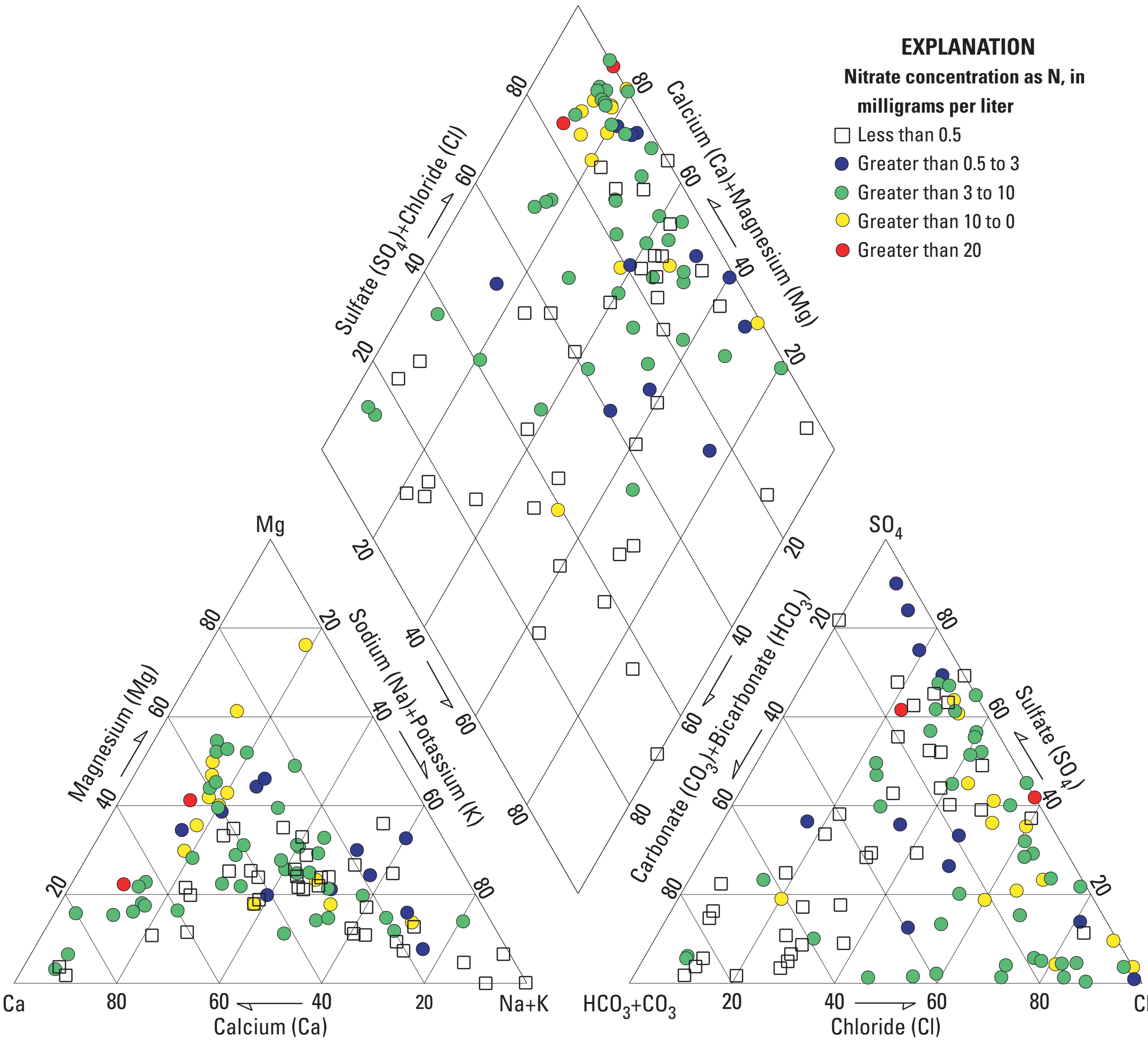


Figure 15. Trilinear graph displaying major element chemistry of ground water of the Delmarva Peninsula, United States. Each scale represents percentage of total milliequivalents per liter. N, nitrogen.

Boxplots of specific conductance for the wells of each study unit are shown in figure 21. The ground water with the lowest specific conductance is that of the Delmarva Peninsula with a median specific conductance of 203 µS/cm. The sampled ground water of the San Joaquin Valley has the highest specific conductance with a median value of 704 µS/cm. The specific conductance of sampled ground water of the Sacramento Valley is most similar to that of the Tangshan study unit, with median specific conductances of 612 and 625 µS/cm, respectively. Boxplots of specific conductance for wells of the three physiographic regions of Tangshan, including the upper and lower aquifer of the plain region, are shown in figure 22. The wells of the mountain region have the lowest median specific conductance, which is expected because most groundwater recharge is likely to occur under natural conditions in this region. The highest median specific conductance is shown for the wells of the upper aquifer of the plain region. That specific conductance is significantly higher than the specific conductance of the lower aquifer, which suggests that salts have been added to the water as a result of land use. The specific conductance of the wells of the coastal region are similar to that of the lower aquifer of the plain region. Whereas some of the ground water of the coastal region is known to have high salt content, the water in samples of this region are from parts of the aquifer that have not been affected by saltwater intrusion.

Boxplots of specific conductance for wells of the various regions of the San Joaquin Valley, including the upper and lower aquifers of the western and southern San Joaquin Valley, are shown in figure 23. The highest median specific conductance is about 1,500 µS/cm for the lower western San Joaquin Valley ground water. The western San Joaquin Valley ground water has the

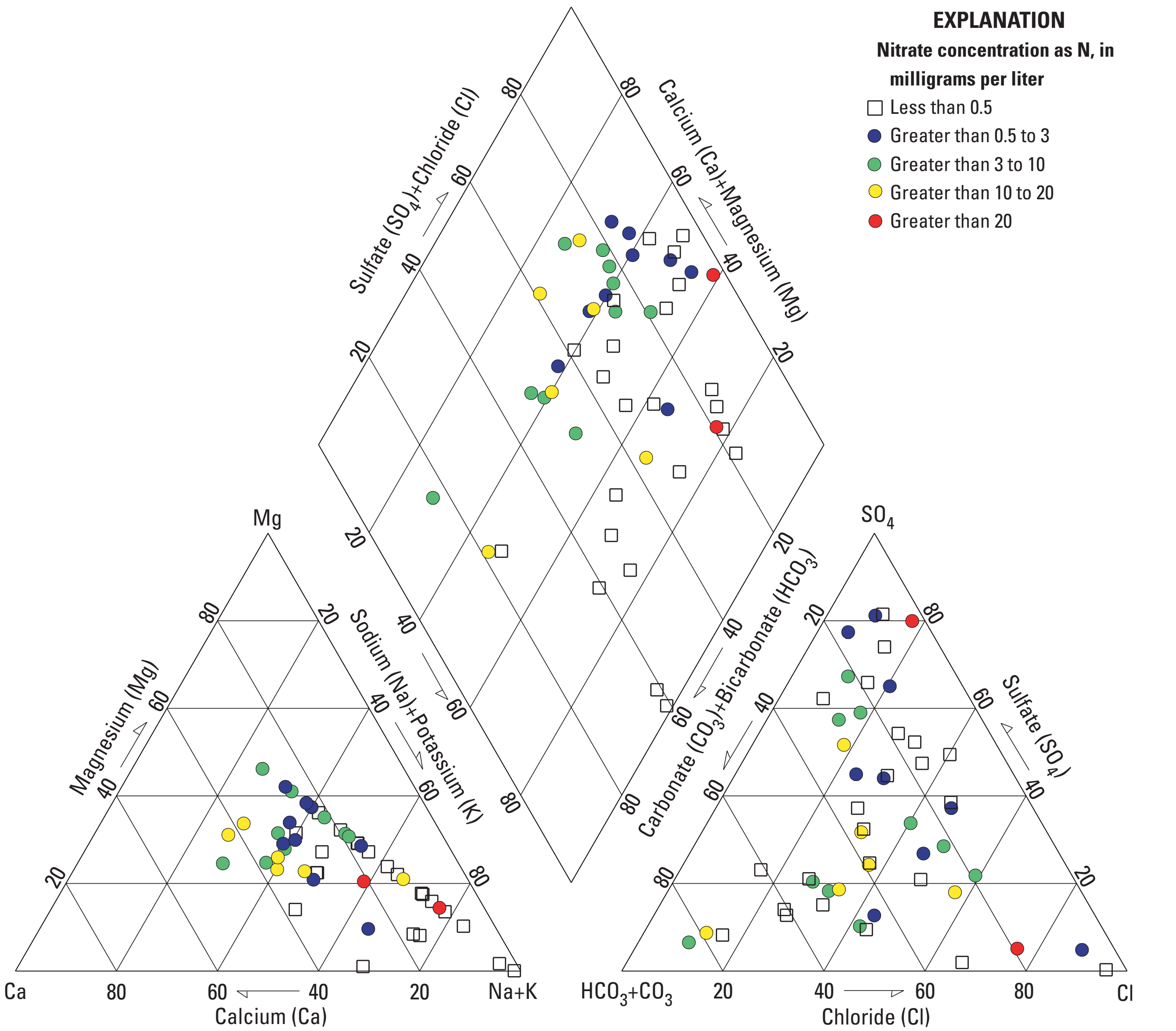


Figure 16. Trilinear graph of ground water of the western San Joaquin Valley, California, United States. Each scale represents percentage of total milliequivalents per liter. N, nitrogen.

highest specific conductance for several reasons. Some of the recharge to the aquifer originates within the Coast Ranges, and that recharge water is relatively high in total dissolved solids. Additionally, some parts of the western San Joaquin Valley have poor soil drainage. Irrigation over poorly drained soils in a semiarid environment can lead to high rates of evaporation, which leave behind salts. The median specific conductance for the other regions of the San Joaquin Valley are lower than those of the western San Joaquin Valley. Ground water of the eastern San Joaquin Valley tends to have the lowest specific conductance because the recharge originates from the Sierra Nevada, which has relatively low concentrations of total dissolved solids.

Boxplots of pH for the wells of each study unit are shown in figure 24. The lowest median pH (5.25) is for the Delmarva Peninsula. Because its aquifer mineralogy is dominated by quartz, a relatively insoluble mineral, the ground water pH is very similar to that expected for rain.

Concentrations of iron in ground water provide information on the state of oxidation or reduction of the ground water. Iron is insoluble when oxidized, but is much more soluble in the reduced state. Boxplots of iron for the various zones of study units or for an entire study unit are shown in figure 25. The greatest range in iron concentrations for the Tangshan study unit is for the upper aquifer of the plain zone. The median iron concentration for that part of the aquifer is 290 µg/L. Median iron concentrations are below 250 µg/L in the lower aquifer of the plain zone and also in the mountain zone. Median iron concentrations of the coastal zone of the Tangshan study unit are similar to those of the upper aquifer of the plain zone. The higher iron

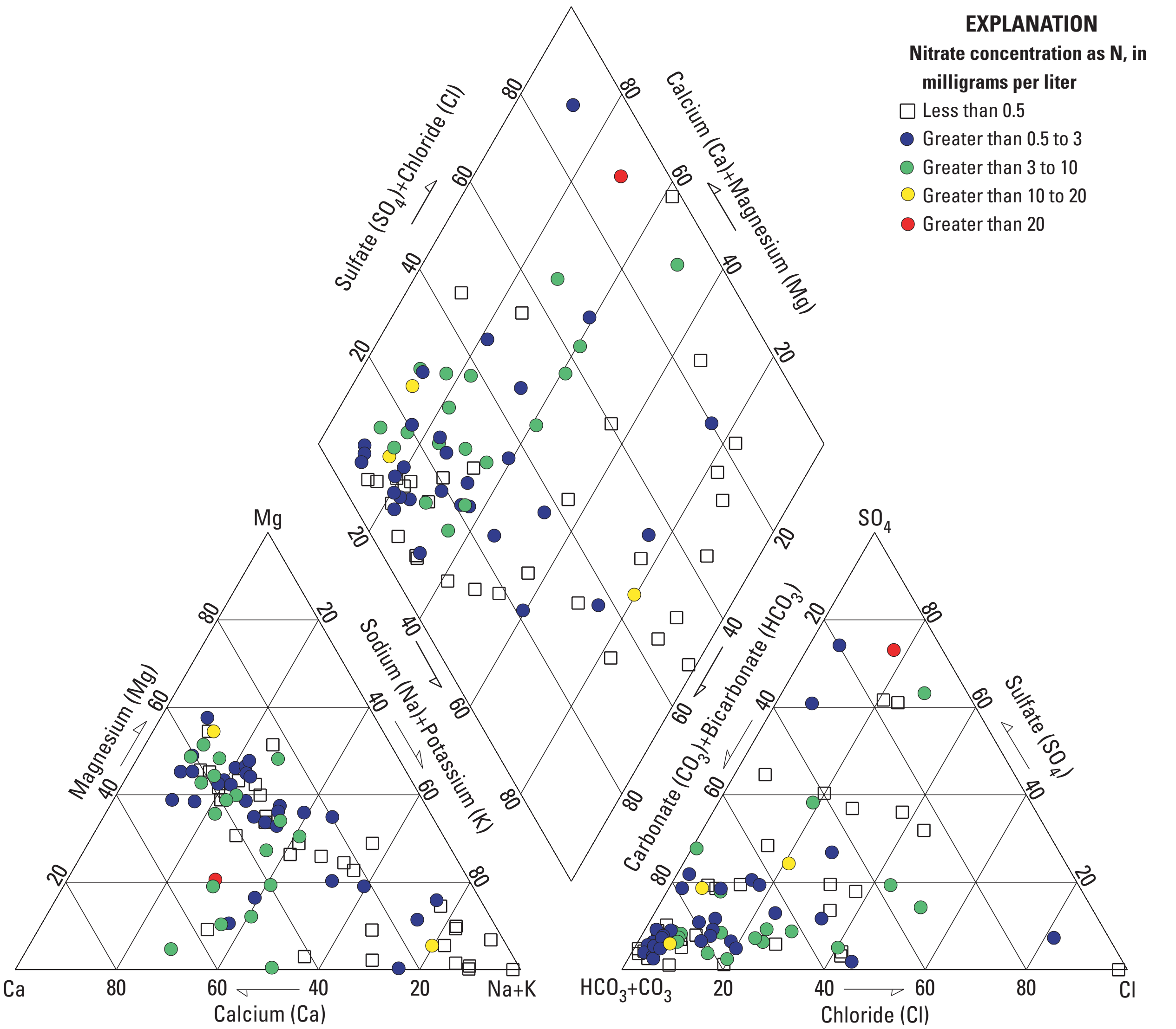


Figure 17. Trilinear graph of ground water of the southern San Joaquin Valley, California, United States. Each scale represents percentage of total milliequivalents per liter. N, nitrogen.

concentrations of the upper aquifer of the plain zone suggest that some processes are affecting the redox potential of the ground water, which is allowing the iron of the aquifer sediment to go into solution. Iron concentrations of the lower aquifer are expected to be highest because the deeper ground water is probably older and has had more time to undergo oxygen-depleting reactions. The wide range and higher concentrations of iron in the upper aquifer suggest that oxygen is being removed from the ground water by some process, which may be related to the use of manure on agricultural land or to the input of sewage waste over the land surface.

The ground water of the Delmarva Peninsula has a wide range of iron concentrations. The median concentration is only 24 µg/L, but the 90th percentile is close to 12,000 µg/L. Iron concentrations in the San Joaquin Valley tend to be lower than those measured in the Tangshan aquifer. The highest iron concentrations are in the western San Joaquin Valley and the lowest are in the eastern San Joaquin Valley. The aquifer of the eastern San Joaquin Valley is composed of coarser sediments relative to those of the western and southern San Joaquin Valley. Because of the coarser sediment, the aquifer is more open to the atmosphere, and hence the water has a greater amount of dissolved oxygen and less iron. Iron concentrations for the sampled wells of the Sacramento Valley are shown in figure 25. The median concentrations of iron in the ground water in the Sacramento subunit and the Sacramento rice zone (3.0 and 4.2 µg/L, respectively) are similar, but a larger range of concentrations is present in the wells of the rice land-use study. In summary, iron concentrations tend to be highest in the ground water of the Tangshan and

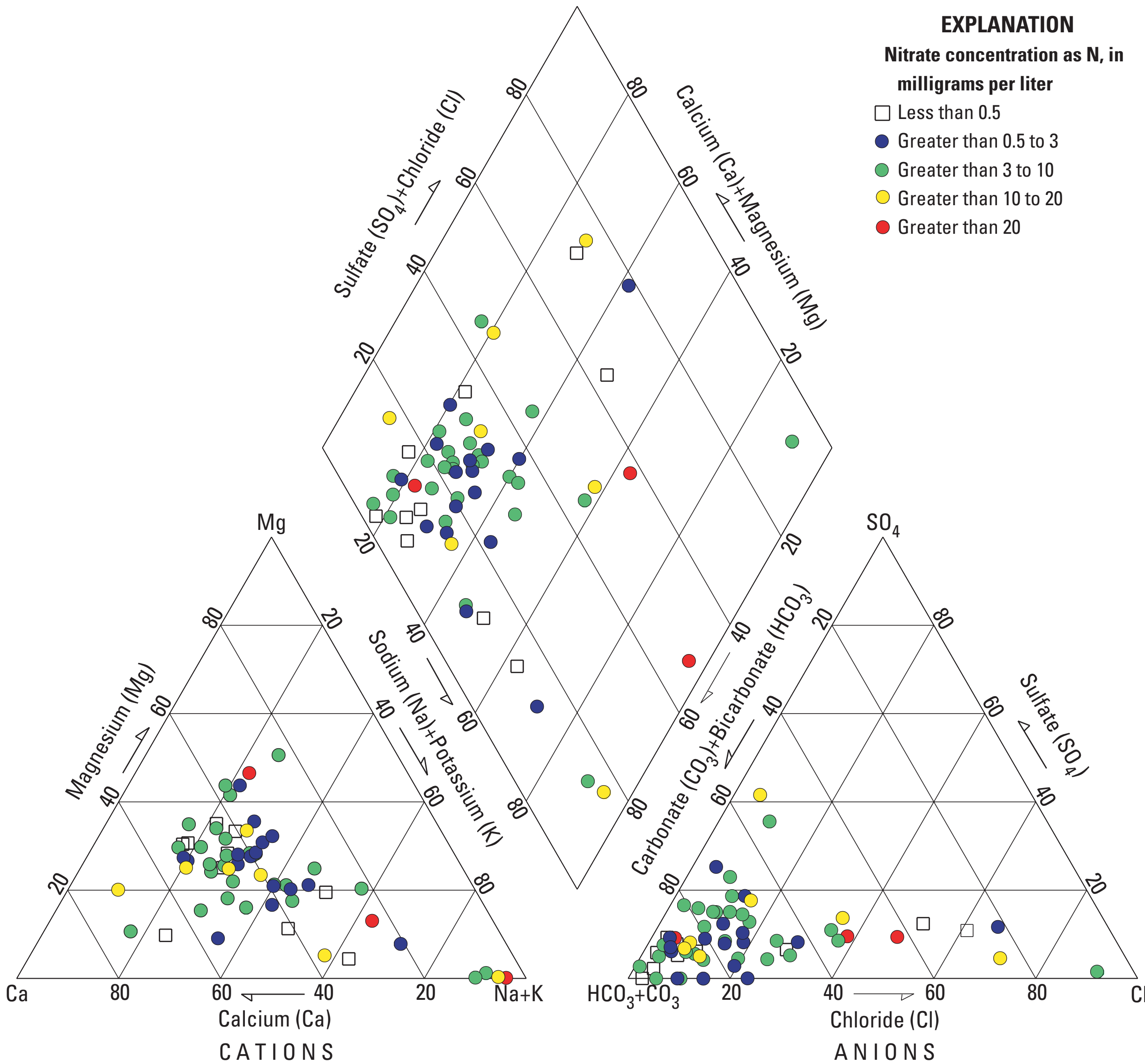


Figure 18. Trilinear graph of ground water of the eastern San Joaquin Valley, California, United States. Each scale represents percentage of total milliequivalents per liter. N, nitrogen.

Delmarva aquifers, relative to the ground water of the other aquifers of this study.

OXYGEN AND HYDROGEN ISOTOPES IN WATER

Variations in stable isotopes in water and dissolved constituents originate from the natural variation in atomic mass and from fractionation in the environment. Isotope fractionation is defined as the partitioning of isotopes by physical or chemical processes in a manner proportional to the differences in masses (Coplen, 1993). Stable isotopes in water molecules—hydrogen (^1H), deuterium (^2H), oxygen-16 (^{16}O), and oxygen-18 (^{18}O)—have long been used to help determine ground-water recharge or ground-water flow paths. The ratio of the isotopes is measured with a mass spectrometer. The ratios, expressed as δ notation, are given in parts per thousand (per mill). The principal fractionation mechanisms of stable isotopes are evaporation and precipitation. Lighter isotopes partition to water vapor, for example, leaving the heavier isotopes enriched in the remaining water. In contrast, rainwater is more enriched in heavier isotopes and becomes progressively lighter as clouds move over landmasses. Isotope ratios in rainwater can be measured and, thus, the pathways of ground-water recharge can be determined by measuring stable isotope ratios along ground-water flow paths. Stable isotope studies or analyses have been completed for wells of the San Joaquin Valley and Sacramento Valley study units from previous studies, but no stable isotope data are available for wells of the Delmarva Peninsula. This study reports on the first analyses of stable isotopes for the Tangshan study-unit ground water.

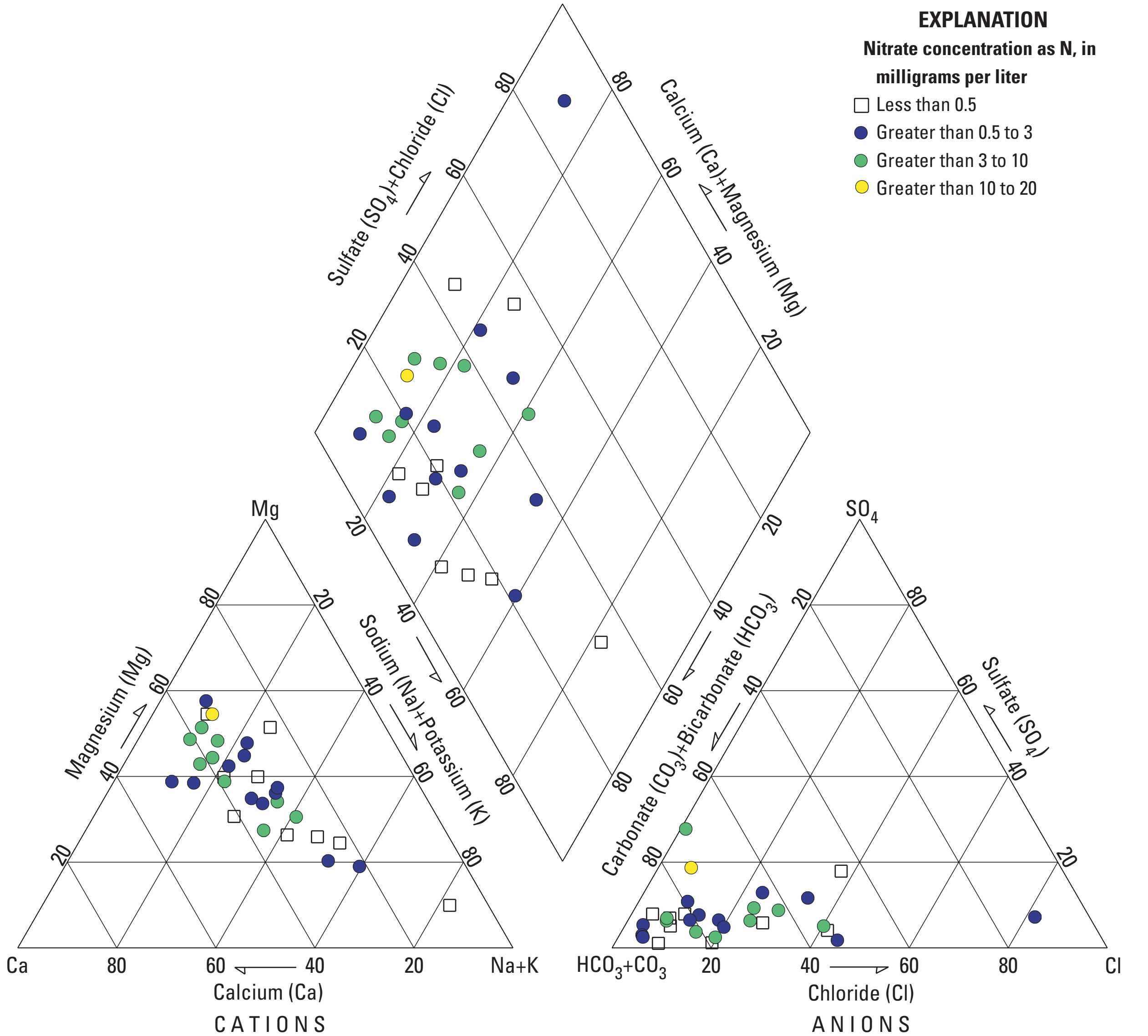


Figure 19. Trilinear graph of subunit ground water, Sacramento, California, United States. Note: Red circles are not shown here because ground water with nitrate greater than 20 milligrams per liter was not detected. Each scale represents percentage of total milliequivalents per liter. N, nitrogen.

The greatest variation in the distribution of stable isotopes is in the San Joaquin Valley ground water (fig. 26) where they vary for several reasons. Precipitation in that region generally results from winter storms that originate over the Pacific Ocean. Rain with heavier isotopes falls on the Coast Ranges, and rain that is relatively depleted in the heavier isotopes falls on the valley floor and the Sierra Nevada. The rain with the lightest isotopes falls on the Sierra Nevada. Ground-water recharge to the San Joaquin Valley aquifer originates from Coast Ranges runoff, precipitation on the valley floor, runoff from the Sierra Nevada, recharge from the San Joaquin River and its tributaries, and irrigation. Irrigation is currently the primary source of ground-water recharge to the aquifer of the San Joaquin Valley (Domagalski and Dubrovsky, 1991, 1992).

Irrigation water is provided by local rivers, water imported from northern California, and ground water. Irrigation also affects the stable isotope pattern in that partial evaporation of the irrigation water leads to enrichment in the heavier isotopes. The isotope ratio patterns for the eastern, western, and southern San Joaquin Valley generally overlap because of the complexity of recharge and other factors that affect the stable isotope patterns (fig. 26). Because of the wide variation in stable isotope ratios of ground water, the use of stable isotope data has aided in the interpretation of previous studies on contaminant chemistry of the San Joaquin Valley ground water (Deverel and Fujii, 1988) and has helped researchers to understand ground water–surface water relations (Phillips and others, 1991). In those cases, stable isotope data were useful

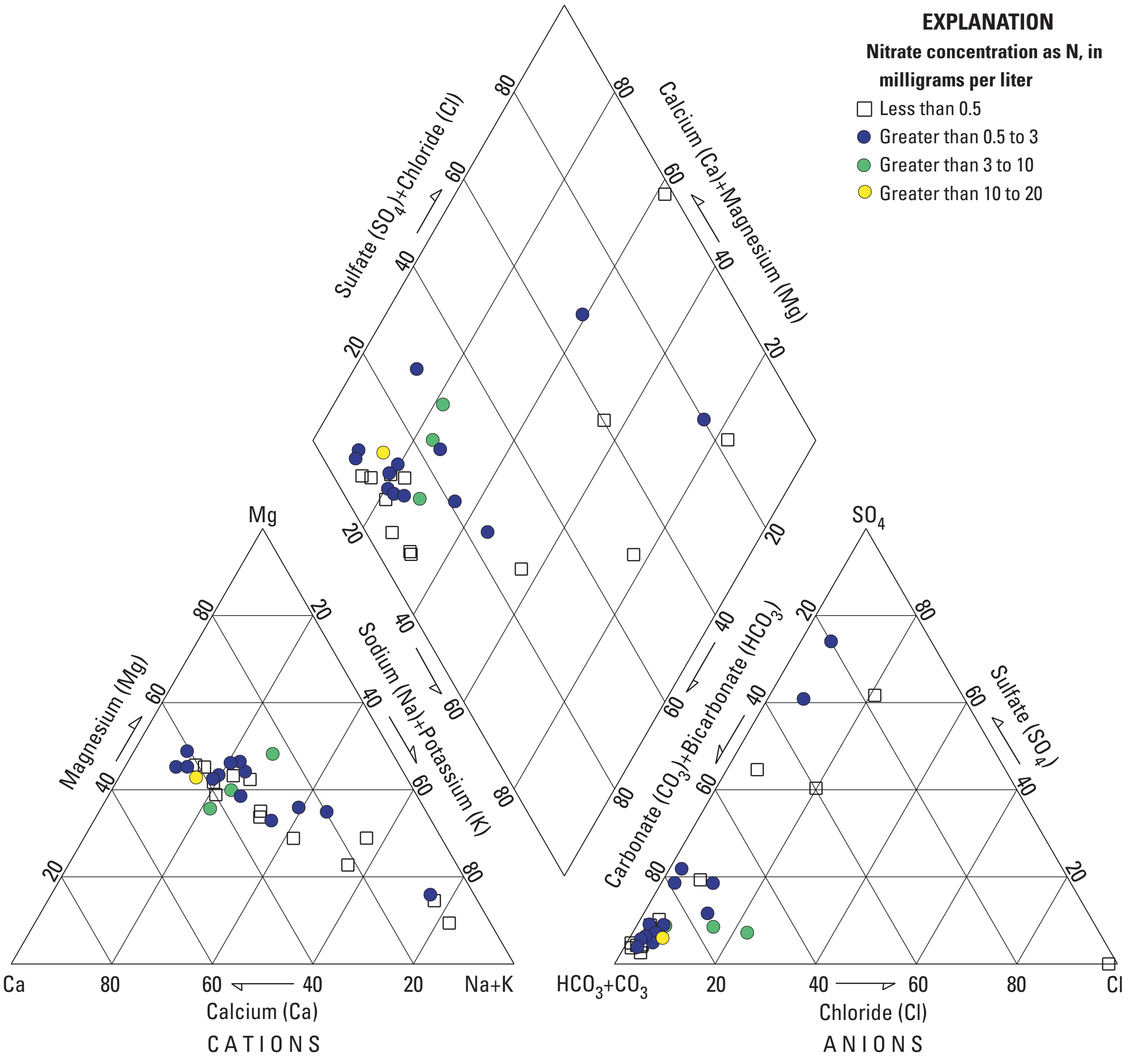


Figure 20. Trilinear graph of the rice land-use ground water, Sacramento, California, United States. Note: Red circles are not shown here because ground water with nitrate greater than 20 milligrams per liter was not detected. Each scale represents percentage of total milliequivalents per liter. N, nitrogen.

because waters originating from different sources, or geochemical processes related to natural phenomenon, such as evaporation, could clearly be distinguished because of the range in values of stable isotope ratios.

The same types of weather patterns described for the San Joaquin Valley also affect precipitation in the Sacramento Valley, and so the heaviest isotopes are found in runoff from the Coast Ranges and the lightest in rainfall from the Sierra Nevada and Cascade Mountains. The isotope ratio of the Sacramento River does not vary much because the flow is regulated by releases from large reservoirs that collect snowmelt runoff from high mountains, principally in the northern part of the basin and within the Sierra Nevada. The ratio of deuterium is close to –80 per mill and of ^{18}O is close to –11.5 per mill. These ratios of the San Joaquin River are similar because most of the flow of the San Joaquin River originates as runoff from the Sierra Nevada. Isotope patterns are more variable for streams that drain the Coast Ranges and tend to be heavier than those of the Sacramento and San Joaquin Rivers. Stable isotopes were used by Davisson and Criss (1993) to map recharge of irrigation water to municipal wells in a region west of Sacramento, California. Davisson and others (1993) were able to document the extent of ground-water recharge to the surficial aquifer of the lower Sacramento Valley from the large rivers (Sacramento and American Rivers) using stable isotope data. In these cases, the difference in isotope abundances was sufficiently great to allow mapping of isotope contours.

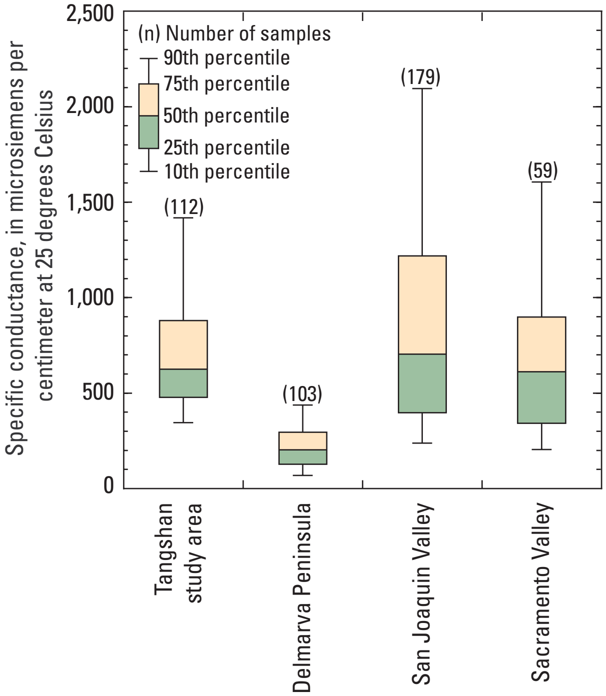


Figure 21. Boxplots of specific conductance for wells within each study unit in the People's Republic of China and the United States.

Agricultural practices may affect the isotope pattern of ground water underlying the rice fields of the Sacramento Valley (fig. 27). Because standing water is on the rice fields during the hottest part of the year, evaporation of water results in some fractionation. The isotope pattern for water underlying the rice fields tends to deviate from the global meteoric water line, a clear indication of the effect of evaporation.

Stable isotope samples were collected from ground water along four selected transects of the Tangshan study unit. Those transects were chosen to provide general information on the regional distribution of stable isotope ratios in this aquifer system. Transect 1 was closest to the Luan He River and was chosen to show how similar the stable isotopes of the ground water system are to those of the largest river. Transect 2 is located near ephemeral streams, such as the Qinglong He River, and was chosen to contrast the stable isotopes of that stream with those of nearby ground water. Transects 3 and 4 were chosen to obtain greater aerial coverage over the study unit. The stable isotope pattern of ground water in the Tangshan study unit (fig. 28 and table 2) varies less than that of the San Joaquin and Sacramento Valleys. This pattern is especially true in the mountain and plain regions where stable isotopes in ground water are very similar to those of the upper and lower Luan He River. Ground water of the coastal region has more variability, which is to be expected because seawater has infiltrated the ground water system. The ^{18}O ratio in the wells sampled in the mountain and plain regions, and that of the Luan He River, tend to be close to –8 to –8.5 per mill and the deuterium ratio is close to –60 per mill. One sampling site, near the Luan He River (location Lao6), was different. The shallow well (LaoQ6) was slightly enriched in the heavier isotopes, but the deeper well (LaoS6) was more depleted in the heavier isotopes. This was the closest sampling point to the Luan He River. The difference in isotope values may reflect changes in the isotopic chemistry of the Luan He River over time, especially prior to the construction of reservoirs. The stable isotopes of the Qinglong He River were relatively enriched in the heavier isotopes. This enrichment would be expected for an ephemeral stream owing to evaporation. The wells of the upper aquifer sampled closest to the Qinglong He River (sites Ben3 [wells BenQ3-1, BenQ3-2, and BenQ3-3] and Ben4) are slightly enriched in the heavier isotopes, suggesting that some recharge of partially evaporated stream water occurred.

The general uniformity of isotope ratios observed in most of the wells of the mountain and plain regions and the Luan He River probably results from the precipitation pattern. Rainfall originates over the

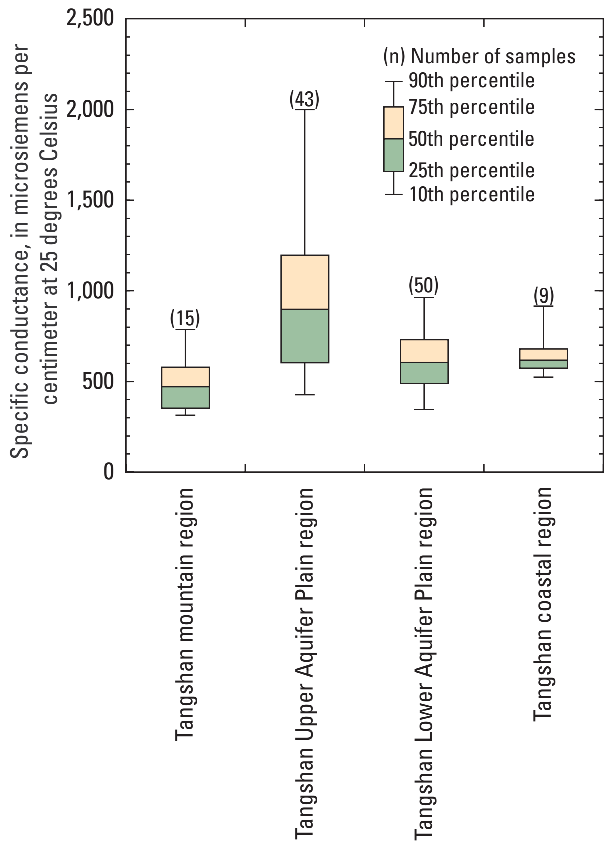


Figure 22. Boxplots of specific conductance for wells in various physiographic regions of the Tangshan study unit, People's Republic of China.

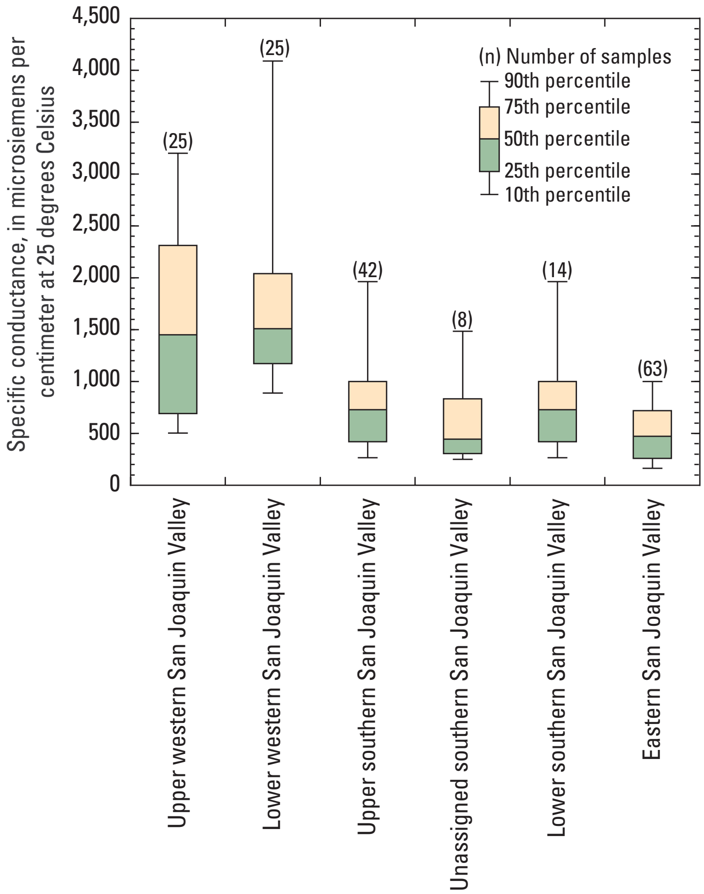


Figure 23. Boxplots of specific conductance for wells in various regions of the San Joaquin Valley, California, United States.

Pacific Ocean. Rain with a similar pattern of stable isotopes falls over the plain and mountain regions. Because most of the ground-water recharge comes from mountain runoff and meteoric input over the mountain and plain areas, the stable isotope pattern is very similar throughout. As a result, stable isotopes are not as useful a tool, on a regional pattern, to help determine ground-water flow paths for the mountain and plain regions of the Tangshan aquifer system. However, stable isotopes may be useful in local scale studies, such as near the ephemeral streams or within the coastal region in studies related to seawater intrusion, but that is beyond the scope of the present study.

DATING OF GROUND-WATER RECHARGE

Methods for dating ground-water recharge have been used extensively in the San Joaquin Valley, and more recently in the Sacramento Valley, to interpret the relative age of ground water with depth and to relate the detection frequency of various ground water contaminants to the age of ground water. For example, Domagalski and Dubrovsky (1991, 1992) showed that pesticide residues in ground water of the San Joaquin Valley were present only in relatively recent water (water with detectable ^{3}H). Older ground water (^{3}H below detection limit) had no detectable pesticide residues. Knowledge of the depth distribution of recent water in an aquifer provides a good understanding of which part of the aquifer may be susceptible to contamination from recent land-use practices. Ground water with detectable ^{3}H is defined for this study as having been recently recharged (from the 1950s to the present).

Prior to this study, there had been no measurements of ^{3}H or any attempts to establish the age of ground water in the Tangshan aquifer study unit. Results of dating analyses from this study are shown in table 3. The wells selected for these analyses are located along two transects shown in figure 4. The samples were collected in June 1996. ^{3}H or CFC can be detected to a well depth of 150 m. Ground water sampled from well depths of 212 and 230 m did not have measurable ^{3}H. Those two samples were collected from the coastal aquifer. The zone of ^{3}H-free water is probably at or below 150 m below land surface in this aquifer system. Ground water sampled in the lower aquifer of the plain region, at various depths, all had measurable ^{3}H or CFC, which suggests

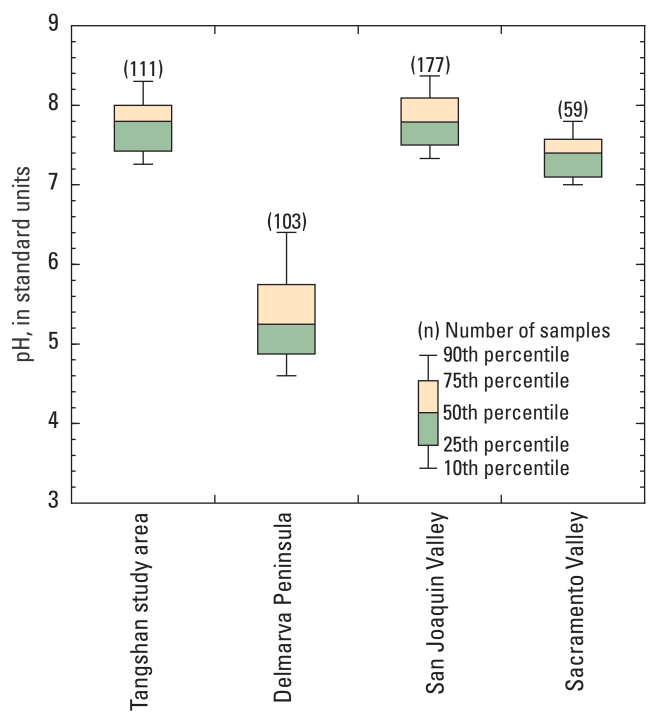


Figure 24. Boxplots of pH for wells within each study unit in the People's Republic of China and the United States.

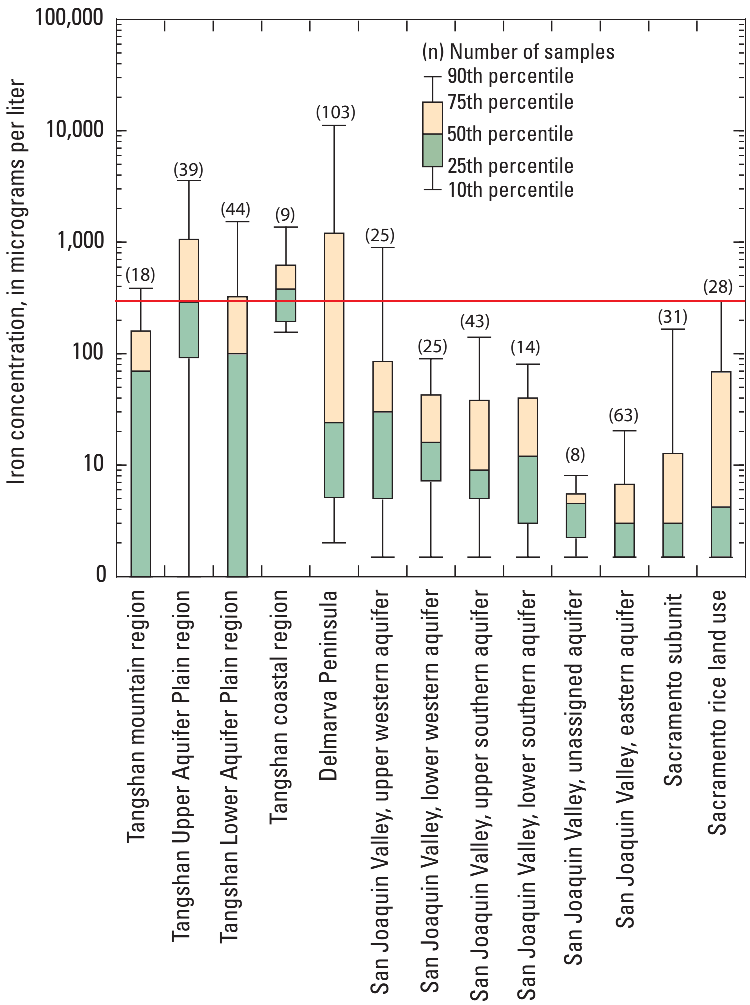


Figure 25. Boxplots of iron concentration for various zones within study units or for an entire study unit, People's Republic of China and the United States. The red line indicates drinking- water standard of China and secondary drinking-water standard of the U.S. Environmental Protection Agency.

that recently recharged water is present to a depth of at least 130 m and perhaps as deep as 150 m in the lower aquifer of the plain region.

Water with undetectable ^3H, such as that collected from wells Xian5 and Xian9, also could not be dated by the $^3H/^3He$ method. There was not close agreement of the ages obtained from the CFC and the $^3H/^3He$ methods, which might be expected because the methods do not work for all ground-water systems. In particular, the CFC method does not work for ground-water systems devoid of dissolved oxygen. Parts of the ground-water system of the Tangshan aquifer are devoid of dissolved oxygen as indicated by the high concentrations of dissolved iron measured at several wells. Therefore, the $^3H/^3He$ method provides a more reliable age for this ground water system.

The implication for the Tangshan aquifer system is that recent water is present in relatively deep parts of the aquifer, within approximately 150 m below land surface, which suggests that the ground water system is rapidly recharged either areally by meteoric water (during the Asian monsoon) or by infiltration from rivers, irrigation, or some combination. Water levels measured prior to and after the monsoon season in 1996 are shown in figure 29. Ground water levels were generally closer to land surface in September 1996 relative to May 1996 because the levels for September were measured just after the rainy season (fig. 29). Subsequent pumping of ground water helps to draw the recently recharged water to deeper levels. Soil contaminants, or contaminants present at shallow water levels, such as nitrate, can then be transported to deeper parts of the aquifer system.

ASSESSMENT OF WATER-QUALITY CONDITIONS

Water-quality conditions, with respect to the suitability of ground water as a source of drinking water for each study unit, were assessed on the basis of standards or methods used in the People's Republic of China and water-quality criteria specified in the Safe Drinking Water Act of the United States. In the United States, emphasis is given to meeting standards specified for each constituent that is regulated by the Safe Drinking

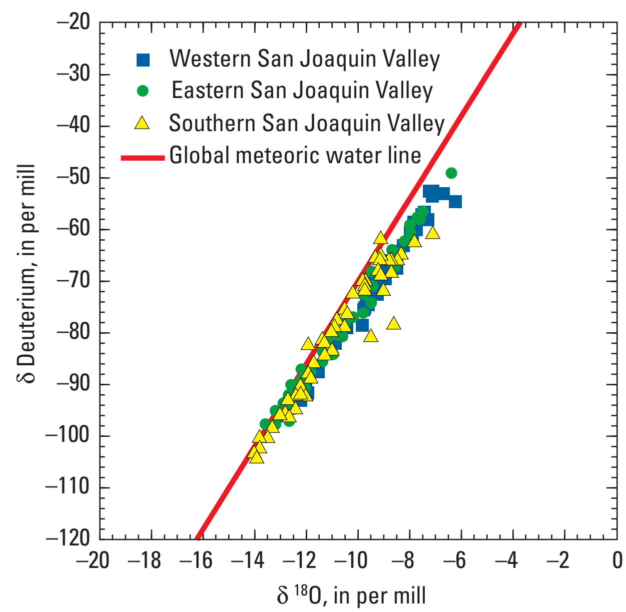


Figure 26. Stable isotopes δ deuterium (^2H) versus $\delta^{18}O$ of ground water in the San Joaquin Valley, California, United States. H, hydrogen; O, oxygen; δ, delta. Position of the global meteoric water line from Drever (1982).

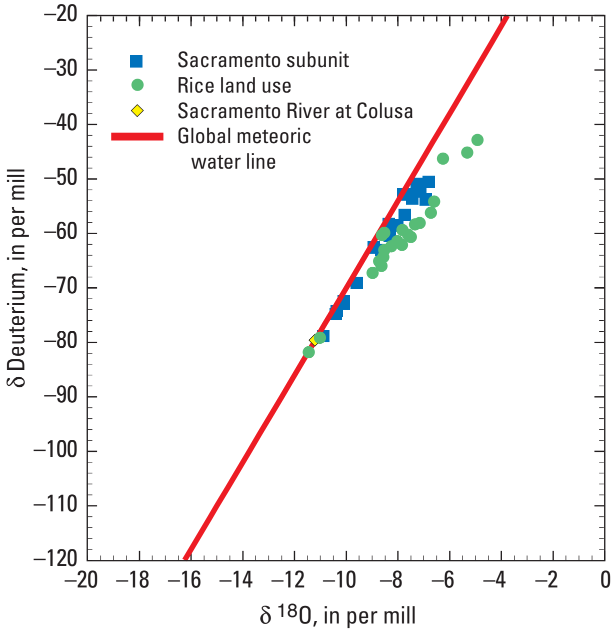


Figure 27. Stable isotopes δ deuterium (^2H) versus $\delta^{18}O$ of ground water in the Sacramento Valley and of the Sacramento River at Colusa, California, United States. H, hydrogen; O, oxygen; δ, delta. Position of the global meteoric water line from Drever (1982).

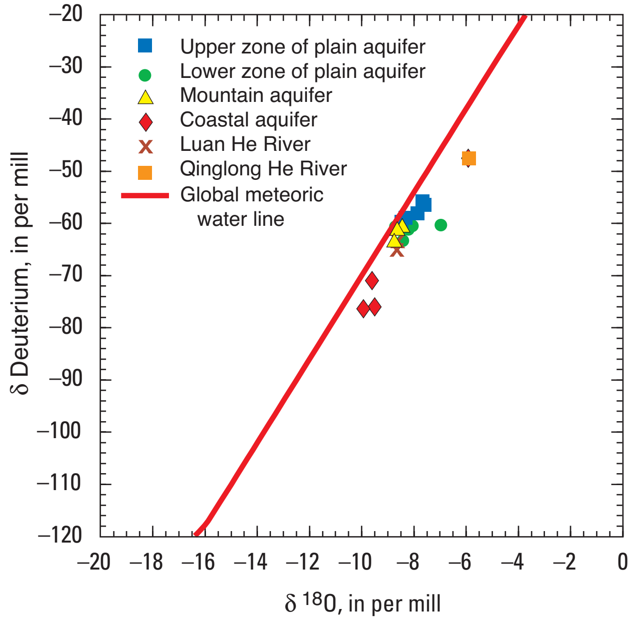


Figure 28. Stable isotopes δ deuterium (^2H) versus $\delta^{18}O$ of ground water in the Tangshan study unit and of the Qinglong and Luan He Rivers, People's Republic of China. H, hydrogen; O, oxygen; δ, delta. Position of the global meteoric water line from Drever (1982).

Water Act of the U.S. Environmental Protection Agency (EPA). When even a single standard is exceeded, there may be sufficient cause to stop the delivery of water supplied by a community well. For example, numerous wells in the San Joaquin Valley have been shut down because concentrations of the pesticide 1,2-dibromo-3-chloropropane (DBCP) exceeded the standard. Meeting individual standards is also important for the regulation of drinking water quality in the People's Republic of China. In addition, the suitability of ground water as a source of drinking water is assessed using a broader method of classification called the "gray pattern method." The results of the gray matrix calculations are presented to show the range of conditions in these aquifers.

Gray Pattern Method of Water-Quality Assessment

To classify the water with respect to a set of chosen water-quality constituents, the gray pattern method assesses the weights of contaminant concentrations, relative to both the National Standards of Groundwater Quality established by the People's Republic of China and to boundary values of various water classes. The assessment of overall water quality according to a set of standards allows water-quality managers in the People's Republic of China to prioritize decisions about the suitability of water for various uses. A set of 21 water-quality constituents regulated by National Standards of Groundwater Quality of the People's Republic of China was selected for this study. Scientists and water-quality specialists of the Hai He River Basin's Water Conservancy Commission, the Tangshan Water Resources Bureau, and the Ministry of Water Resources of the People's Republic of China determined that the 21 water-quality constituents listed in table 4 are the most important for the protection of ground-water quality in the Tangshan study unit. The boundary values of class 3 water, as shown in table 4, are the closest analogy to primary drinking water standards as understood in the United States. These are set for individual constituents. When applicable, the primary and secondary water standards of the EPA are also shown in table 4. Primary standards are enforceable standards that must be met by all public drinking water systems to which they apply. Secondary standards are nonenforceable, but are maintained to protect public welfare and to ensure a supply of pure, wholesome, and potable water. Some states require that all new wells or sources of drinking water meet the secondary standards.

The classes of water, according to the method in the People's Republic of China, represent a gradient of concentrations for each water-quality constituent, indicating suitability for drinking water to nonsuitability of the water. Class 1 water is of highest quality, whereas class 5 represents extremely poor water quality. The boundary values of class 3 (table 4) are most analogous to American drinking water primary standards. Note that the boundary value of class 3 for nitrate is set at

Table 2. Results of stable isotope analyses—δ deuterium and $\delta^{18}O$ in water—for wells of the Tangshan study unit, People's Republic of China

[na, not applicable; O, oxygen; per mill, parts per thousand; Q, shallow well; S, deep well; δ, delta]

Well name	Date sampled	Transect	Aquifer zone or river	δ deuterium (per mill)	$\delta^{18}O$ (per mill)
LuanQ5	23 June 1996	1	Plain upper	–60.2	–8.21
LuanS5	23 June 1996	1	Plain lower	–60.7	–8.75
LaoQ1	24 June 1996	1	Plain upper	–61.7	–8.41
LaoS1	24 June 1996	1	Plain lower	–61	–8.19
LaoQ6	24 June 1996	1	Plain upper	–58	–7.86
LaoS6	24 June 1996	1	Plain lower	–75	–9.61
Xian9	24 June 1996	1	Coastal	–76.2	–9.91
Xian9-1	24 June 1996	1	Coastal	–49.1	–5.93
Shan15	23 June 1996	2	Mountain	–61	–8.62
LuanS1	23 June 1996	2	Plain lower	–60.7	–8.51
BenQ3-1	23 June 1996	2	Plain upper	–56.4	–7.6
BenS3	22 June 1996	2	Plain lower	–60.3	–8.06
BenQ4	25 June 1996	2	Plain upper	–55.8	–7.68
BenS4	25 June 1996	2	Plain lower	–60	–8.3
Xian5	25 June 1996	2	Coastal	–75.8	–9.55
Shan9	23 June 1996	3	Mountain	–63.2	–8.72
Shan10	16 September 1996	3	Mountain	–60.3	–8.42
ShiS2	3 October 1996	3	Plain lower	–60.6	–8.37
NanQ2	3 October 1996	3	Plain upper	–59.7	–8.49
NanS2	3 October 1996	3	Plain lower	–58.2	–7.86
Xian3	4 October 1996	3	Coastal	–60.5	–8.07
RunS1	3 October 1996	4	Plain lower	–59.3	–8.22
RunQ2	24 September 1996	4	Plain upper	–59.9	–8.45
RunS2	16 September 1996	4	Plain lower	–63	–8.45
YuQ7	16 September 1996	4	Plain upper	–58.9	–8.33
YuS7	10 September 1996	4	Plain lower	–58.2	–8.01
RunS4	25 September 1996	4	Plain lower	–61.2	–8.45
Xian1	16 September 1996	4	Coastal	–71.1	–9.62
Upper Luan He River	23 June 1996	na	River	–63.4	–8.65
Lower Luan He River	24 June 1996	na	River	–65	–8.68
Qinglong He River	25 June 1996	na	River	–47.6	–5.91

20 mg/L. The primary (enforceable) American drinking water standard for nitrate is 10 mg/L as N.

The gray pattern method first calculates a pollution index for each constituent relative to the boundary value of the class 3 drinking-water standard. Water with water-quality constituent concentrations less than the boundary values of class 3 water shown in table 4 are ranked low, but as water quality greatly exceeds the boundary values, the ranks are correspondingly higher. Even a single "exceedance" (that is, a value that exceeds the standard) can result in water of overall class 5 if the measured concentrations are very high, that is, if they exceed class 5. A summation of the relative amounts of exceedances and the corresponding factor for each constituent are then calculated, and the matrix of calculations is referred to as the "gray dependency pattern." The output from the gray model is a comprehensive score. Water samples with class of 3 or higher indicate serious water-quality problems or that one or more standards have been exceeded. An examination of the detailed matrix then can provide information on which specific parameter or group of parameters contributed to the ranking.

The 21 constituents that were used to assess the quality of ground water according to the National Standards of the People's Republic of China were total dissolved solids, chloride, sulfate, total hardness, ammonia, nitrite, nitrate, chemical oxygen demand (permanganate index), cyanide, arsenic, phenol, chromium (VI), mercury, cadmium, lead, copper, iron, fluoride, manganese, zinc, and coliform bacteria. The coliform bacteria measurements were completed only

Table 3. Results of dating analyses for wells of the Tangshan study unit, People's Republic of China

[The $^3H/^3He$ results column shows samples tested for dating on the basis of years elapsed since recharge. CFC, chlorofluorocarbon; ^3H, tritium; $^3H/^3He$, tritium/helium-3; L, liter; m, meters; pCi, picocuries; Q, shallow wells; S, deep wells. —, sample not taken]

Well name	Well depth (m)	Aquifer zone	^3H (pCi/L)	$^3H/^3He$ results	CFC recharge date (period)
LuanQ5	27	Plain upper	34.2	—	—
LuanS5	48	Plain lower	46.46	—	Early 1970s
LaoQ1	21	Plain upper	34.7	6.08	Early 1960s or older
LaoS1	80	Plain lower	21.8	—	—
LaoS6	150	Plain lower	—	—	Mid-1940s
Xian9	212	Coastal	0	Old water[1]	—
Shan15	25	Mountain	98.79	7.36	Mid-1980s
LuanS1	130	Plain lower	38.75	20.71	—
BenQ3-1	13	Plain upper	97.6	—	—
BenS3	60	Plain lower	6.53	20.56	Mid-1960s
BenQ4	20	Plain upper	35.8	—	—
BenS4	120	Plain lower	10.2	—	—
Xian5	230	Coastal	0	Old water[1]	—

[1]Recharged before 1960.

for the wells of the upper aquifer (plain region) and only for the May 1996 sampling. The gray matrix summaries for the wells of the Tangshan study unit are shown in tables 5 through 13. The number of wells for each classification is shown in tables 5 through 13, and for each case, a median classification is presented. In each case, the median classification refers only to that individual grouping.

The highest median gray matrix results (table 5) were calculated for the upper aquifer (plain region) of the Tangshan study unit for the May 1996 sampling. May 1996 was the only time—and the wells selected during this time were the only wells—for which a complete set of coliform bacteria data was available. When the gray matrix is calculated without the coliform data, the result is a lower median gray matrix score (table 6). The median classification drops from 4.19 to 3.68, which indicates that coliform bacteria significantly degrades the water quality of the upper aquifer. The May 1996 score, without coliform data, is very similar to the median score calculated for the September 1996 sampling of the upper aquifer in the plain region. This similarity indicates that general water quality conditions did not change appreciably following the monsoon season. A total of 29 out of 39 wells of the upper aquifer (plain region) of the Tangshan study unit, sampled during May 1996, were scored in class 3 on the basis of this gray matrix classification. Exceedances of total dissolved solids, total hardness, ammonia, nitrate, and coliform bacteria contributed to these high scores. A total of 28 out of 39 wells of the upper aquifer (plain region) of the Tangshan study unit, sampled in September 1996, were scored in class 3 on the basis of this gray matrix classification. Therefore, even without the coliform analyses, most wells of the upper aquifer were in a relatively high classification, which indicates poor water-quality conditions. The median classification for each sampling of the upper aquifer was a value corresponding to class 3 or higher water.

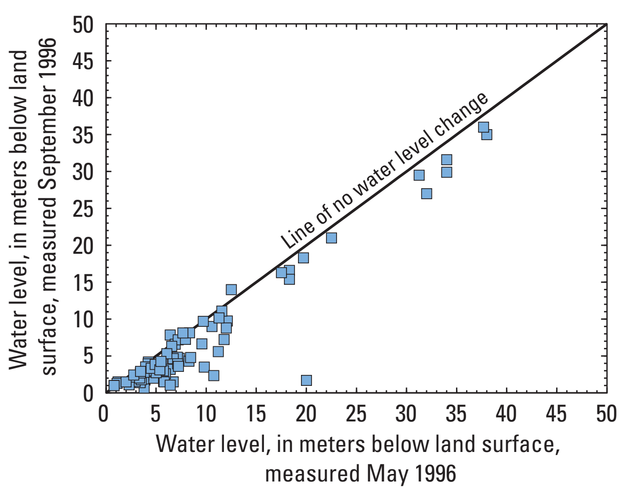


Figure 29. Water levels measured in May and September 1996, Tangshan study unit, People's Republic of China.

Water quality of the lower aquifer (plain region) of the Tangshan study unit is better because fewer ground-water samples were in the highest rating (poorest water quality). The median classification was slightly below that of an overall class 3 water. Although the gray matrix calculations suggest that the water of the lower aquifer is of higher general quality relative to that of the upper, some serious water-quality problems are still present. The constituents that contributed to the higher rankings were ammonia, nitrate, iron, manganese, and total hardness.

Table 4. Classification of representative values of National Standards of Groundwater Quality in the People's Republic of China, and of primary and secondary standards of the U.S. Environmental Protection Agency in the United States

[Values of constituents are in milligrams per liter, unless otherwise noted. Primary Standard: Enforceable standard that must be met for drinking water. Secondary Standard: Nonenforceable, but recommended for drinking water. Class 1 to 5: Classification of water according to a gradient of highly suitable (class 1) to highly unsuitable (class 5) with respect to the use of the water as a source of drinking water. Boundary values of class 3: Analogous to an enforceable standard of the EPA. $CaCO_3$, calcium carbonate; Cr, chromium; Cr^{+6}, chromate ion; EPA, U.S. Environmental Protection Agency; N , nitrogen; NH_3, ammonia. —, no available standard]

Water-quality constituent	People's Republic of China						United States	
	Class 1	Class 2	Class 3	Class 4	Class 5	Boundary values of Class 3	EPA primary standard	EPA secondary standard
Total dissolved solids	300	400	750	1,500	2,000	1,000	—	500
Chloride	50	100	200	300	350	250	—	250
Sulfate	50	100	200	300	350	250	—	250
Total hardness (as $CaCO_3$)	150	225	375	500	550	450	—	—
Ammonia (nitrogen as NH_3)	0.02	0.02	0.11	0.35	0.5	0.2	—	—
Nitrate (nitrogen as N)	2	3.5	12.5	25	30	20	10	—
Nitrite (nitrogen as N)	0.001	0.0055	0.015	0.06	0.1	0.02	1	—
Permanganate index	1	1.5	2.5	6.5	10	3	—	—
Cyanide	0.001	0.0055	0.03	0.075	0.1	0.05	0.2	—
Arsenic	0.005	0.0075	0.03	0.05	0.05	0.05	0.05	—
Phenol	0.001	0.001	0.0015	0.006	0.01	0.002	—	—
Chromium (as Cr^{+6})	0.005	0.0075	0.03	0.075	0.1	0.05	0.1 as total Cr	—
Mercury	0.00005	0.00028	0.00075	0.001	0.001	0.001	0.002	—
Cadmium	0.0001	0.00055	0.0055	0.01	0.01	0.01	0.005	—
Lead	0.005	0.0075	0.03	0.075	0.1	0.05	0.015	—
Copper	0.01	0.03	0.525	1.25	1.5	1	—	1
Iron	0.1	0.15	0.25	0.9	1.5	0.3	—	0.3
Fluoride	1	1	1	1.5	2	1	4.0	—
Manganese	0.05	0.05	0.075	0.55	1	0.1	—	0.05
Zinc	0.05	0.275	0.75	3	5	1	—	5
Coliforms	3	3	3	52	100	3	—	—

As indicated by the gray matrix scores, water quality of the mountain region was considerably better than that of the aquifer of the plain region. Relatively few samples had scores in the higher classes. The source of ground-water recharge to the plain region lies, at least in part, in the mountain region. Water quality may be better in this region because of less intensive agriculture. However, as will be shown later, nitrate may be a developing problem for ground water in that region.

Water-quality problems are also evident for the coastal region as indicated by a median gray score above or near that of class 3 water. The water-quality constituents most responsible for the loadings are ammonia and nitrite, but not nitrate, iron, and manganese.

The gray matrix summary of the Delmarva Peninsula ground water samples is shown in table 14. A total of 36 of 103 samples are of class 3 or higher. The presence of nitrate and iron contributed most to those higher water-quality class rankings. The median classification is that of class 2 water.

Gray matrix summaries for the San Joaquin Valley ground water are shown in tables 15 through 20. The upper and lower zones of the aquifer of the western San Joaquin Valley have relatively poor water quality as indicated by the gray matrix scores. Eighteen out of 25 wells of the upper aquifer are in class 3 or higher, and 14 out of 25 wells of the lower aquifer are in class 3 or higher. The water-quality constituents contributing to the higher gray matrix scores, for the upper and lower aquifer, are total dissolved solids, chloride, sulfate, total hardness, iron, and manganese. A total of 11 of 43 wells of the southern San Joaquin Valley, upper aquifer, had scores in class 3 or higher. The median score was lower than that of the western San Joaquin Valley. The lower aquifer of the southern San Joaquin Valley has much better water quality relative to that of the lower aquifer of the western San Joaquin Valley. Total dissolved solids, chloride, sulfate, and total hardness contribute to

Table 5. Gray matrix summary for upper aquifer (plain region) of the Tangshan study unit, People's Republic of China, May 1996 data

Range of classification	1.0 to 2.0	2.0 to 3.0	3.0 to 4.0	4.0 to 5.0
Number of wells (39 total)	0	10	8	21
Median classification	4.19			

Table 6. Gray matrix summary for upper aquifer (plain region) of the Tangshan study unit, People's Republic of China, May 1996 data, without coliform analysis

Range of classification	1.0 to 2.0	2.0 to 3.0	3.0 to 4.0	4.0 to 5.0
Number of wells (38 total)	2	11	10	15
Median classification	3.68			

Table 7. Gray matrix summary for upper aquifer (plain region) of the Tangshan study unit, People's Republic of China, September 1996 data

Range of classification	1.0 to 2.0	2.0 to 3.0	3.0 to 4.0	4.0 to 5.0
Number of wells (39 total)	1	10	15	13
Median classification	3.65			

Table 8. Gray matrix summary for lower aquifer (plain region) of the Tangshan study unit, People's Republic of China, May 1996 data

Range of classification	1.0 to 2.0	2.0 to 3.0	3.0 to 4.0	4.0 to 5.0
Number of wells (45 total)	10	15	14	6
Median classification	2.71			

Table 9. Gray matrix summary for lower aquifer (plain region) of the Tangshan study unit, People's Republic of China, September 1996 data

Range of classification	1.0 to 2.0	2.0 to 3.0	3.0 to 4.0	4.0 to 5.0
Number of wells (45 total)	6	20	17	2
Median classification	2.8			

Table 10. Gray matrix summary for aquifer of the mountain region of the Tangshan study unit, People's Republic of China, May 1996 data

Range of classification	1.0 to 2.0	2.0 to 3.0	3.0 to 4.0	4.0 to 5.0
Number of wells (18 total)	6	9	2	1
Median classification	2.085			

Table 11. Gray matrix summary for aquifer of the mountain region of the Tangshan study unit, People's Republic of China, September 1996 data

Range of classification	1.0 to 2.0	2.0 to 3.0	3.0 to 4.0	4.0 to 5.0
Number of wells (18 total)	4	10	4	0
Median classification	2.17			

Table 12. Gray matrix summary for aquifer of the coastal region of the Tangshan study unit, People's Republic of China, May 1996 data

Range of classification	1.0 to 2.0	2.0 to 3.0	3.0 to 4.0	4.0 to 5.0
Number of wells (9 total)	0	2	7	0
Median classification	3.4			

Table 13. Gray matrix summary for aquifer of the coastal region of the Tangshan study unit, People's Republic of China, September 1996 data

Range of classification	1.0 to 2.0	2.0 to 3.0	3.0 to 4.0	4.0 to 5.0
Number of wells (9 total)	0	5	4	0
Median classification	2.98			

Table 14. Gray matrix summary for aquifer of the Delmarva Peninsula study unit, United States

Range of classification	1.0 to 2.0	2.0 to 3.0	3.0 to 4.0	4.0 to 5.0
Number of wells (103 total)	38	29	5	31
Median classification	2.22			

Table 15. Gray matrix summary for upper aquifer of the western region of the San Joaquin Valley study unit, California, United States

Range of classification	1.0 to 2.0	2.0 to 3.0	3.0 to 4.0	4.0 to 5.0
Number of wells (25 total)	4	3	9	9
Median classification	3.65			

Table 16. Gray matrix summary for lower aquifer of the western region of the San Joaquin Valley study unit, California, United States

Range of classification	1.0 to 2.0	2.0 to 3.0	3.0 to 4.0	4.0 to 5.0
Number of wells (25 total)	1	8	12	4
Median classification	3.37			

Table 17. Gray matrix summary for upper aquifer of the southern region of the San Joaquin Valley study unit, California, United States

Range of classification	1.0 to 2.0	2.0 to 3.0	3.0 to 4.0	4.0 to 5.0
Number of wells (43 total)	16	16	6	5
Median classification	2.14			

Table 18. Gray matrix summary for lower aquifer of the southern region of the San Joaquin Valley study unit, California, United States

Range of classification	1.0 to 2.0	2.0 to 3.0	3.0 to 4.0	4.0 to 5.0
Number of wells (14 total)	8	5	0	1
Median classification	1.875			

Table 19. Gray matrix summary for the unassigned aquifer of the southern region of the San Joaquin Valley study unit, California, United States

Range of classification	1.0 to 2.0	2.0 to 3.0	3.0 to 4.0	4.0 to 5.0
Number of wells (8 total)	4	2	2	0
Median classification	1.675			

Table 20. Gray matrix summary for the eastern aquifer of the San Joaquin Valley study unit, California, United States

Range of classification	1.0 to 2.0	2.0 to 3.0	3.0 to 4.0	4.0 to 5.0
Number of wells (63 total)	39	16	8	0
Median classification	1.91			

the higher scores (class 3 or higher) of the 16 wells of the lower aquifer in the western San Joaquin Valley. Water quality of the unassigned aquifer of the southern San Joaquin Valley is similar to that of the lower aquifer of the southern San Joaquin Valley. A total of 8 out of 63 wells of the eastern San Joaquin Valley were in class 3 or higher (table 20). Water-quality constituents contributing to the class 3 scores are varied, but include total dissolved solids, nitrate, chloride, and sulfate. Total dissolved solids of the eastern San Joaquin Valley aquifer are lower than those of the western San Joaquin Valley; therefore, the gray matrix scores are correspondingly lower.

Gray matrix summaries of the Sacramento Valley show a marked difference between the subunit survey and the rice land-use survey (tables 21 and 22). The wells of the southeastern Sacramento Valley generally have good water quality. Only 3 wells out of 31 were in class 3 or higher. In contrast, 13 out of 28 wells of the rice land-use survey were in class 3 or higher. The water-quality constituents that contribute to the higher scores of the wells of the rice land-use survey are total dissolved solids, chloride, sulfate, total hardness, nitrite (in three wells), iron, and manganese. Nitrate is not a problem for the ground water of the rice land-use region.

Table 21. Gray matrix summary for aquifer of the Sacramento subunit area of the Sacramento Valley study unit, California, United States

Range of classification	1.0 to 2.0	2.0 to 3.0	3.0 to 4.0	4.0 to 5.0
Number of wells (31 total)	21	7	1	2
Median classification	1.72			

Table 22. Gray matrix summary for the aquifer of the rice land-use study area of the Sacramento Valley study unit, California, United States

Range of classification	1.0 to 2.0	2.0 to 3.0	3.0to 4.0	4.0 to 5.0
Number of wells (28 total)	3	12	7	6
Median classification	2.72			

Boxplots showing the results of the gray matrix rankings for all study units are shown in figure 30. The highest median ranking is for the wells of the upper aquifer of the plain region of the Tangshan study unit. The median is slightly less when recalculated without the coliform data. Coliform data were available only for the upper aquifer of the plain region of the Tangshan study unit and were not available for any other subunit, including those of the United States. The gray matrix rankings of the upper aquifer of the Tangshan plain region are similar to those of the western part of the San Joaquin Valley with respect to the median ranking and range of ranking, which suggests some similar or common water-quality problems, such as total dissolved solids and the oxidation potential of the water (elevated concentrations of iron and manganese). The wells of the eastern San Joaquin Valley have a much lower ranking because of the dilute nature of that water. The ground water of the eastern San Joaquin Valley is of better quality with respect to total dissolved solids, but its water quality has been degraded because of pesticides, especially DBCP (Domagalski and Dubrovsky, 1991, 1992).

The wells of the Delmarva Peninsula have the greatest range in gray scores. The median gray ranking is below those of the plain and coastal regions of the Tangshan study unit and also below that of the western San Joaquin Valley. Low total dissolved solids contribute to lower gray rankings for the Delmarva Peninsula whereas nitrate, iron, and manganese contribute to higher gray rankings. The wells of the Sacramento subunit survey provide a good representation of the quality of ground water actually used for consumption in that part of the Sacramento Valley. The gray matrix ranking for the Sacramento subunit indicates a very good water quality, and tests for pesticides and volatile organic chemicals showed that organic chemicals are either absent from the water or present only in extremely low concentrations. In contrast, the wells of the Sacramento rice land-use study rank much higher in the gray ranking because of higher concentrations of total dissolved solids and concentrations of iron and manganese, related to the oxidation–reduction potential of the water. This ranking suggests that the rice land use is

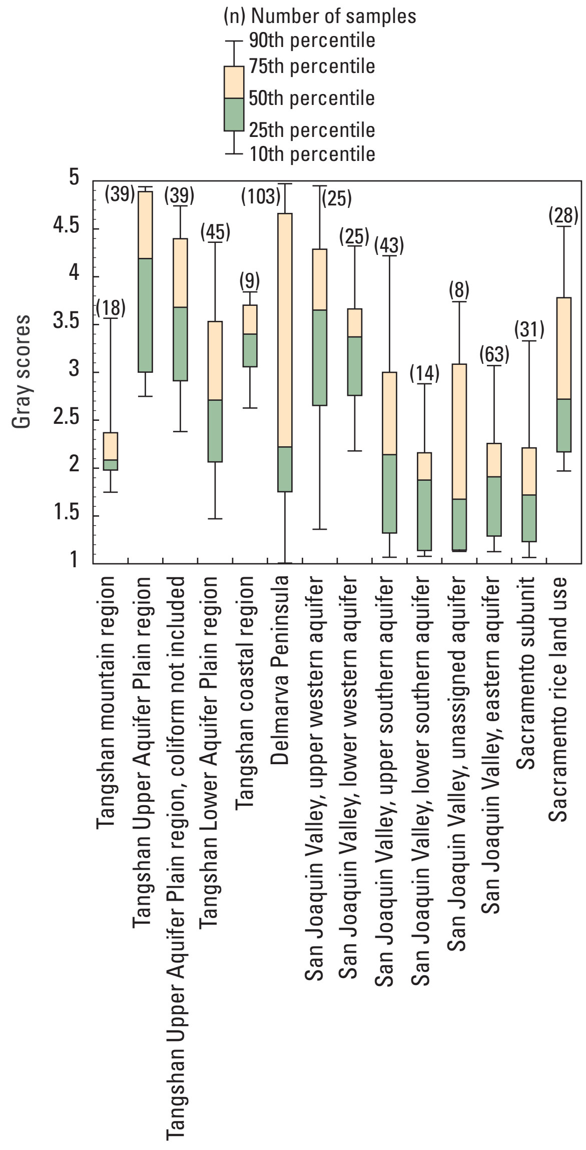


Figure 30. Boxplots of gray scores (gray matrix calculations) for study-unit wells in the People's Republic of China and the United States.

affecting the quality of the shallow ground-water resource.

Boxplots of nitrate concentrations for ground water in all study units are shown in figure 31. The boxplot representing the upper aquifer wells in the Tangshan plain region has the greatest range in nitrate concentrations and the highest concentration of all regions of the Tangshan study unit and all study units of the United States, but it does not have the highest median concentration. In fact, the median concentration of the Tangshan upper plain region is less than that of the mountain aquifer and the lower plain zone region. Over 25 percent of the wells sampled in the upper plain zone exceeded the Chinese standard for nitrate. Over 10 percent of the wells of the mountain region (mountain aquifer) and the lower aquifer (lower plain region) exceeded this standard. Only the wells of the coastal zone of the Tangshan study unit (coastal aquifer) have low nitrate concentrations. The wells sampled in the study units of the United States generally have a lower range of nitrate concentrations than wells in the plain region of the People's Republic of China. Ten percent of the wells of the lower aquifer in the southern San Joaquin Valley exceed the Chinese standard.

Figure 31 shows that nearly 25 percent of the wells of the Delmarva Peninsula and nearly 25 percent of the upper aquifer wells in the western San Joaquin Valley are close to or exceed the American standard (U.S. Environmental Protection Agency) for nitrate. Close to 25 percent of the samples collected in the eastern San Joaquin Valley also exceed the American nitrate standard. Relatively few samples of the ground water collected in the United States, from these studies, exceed the Chinese drinking-water standard for nitrate.

As indicated by the gray matrix rankings, total dissolved solids is a problem for ground water in the People's Republic of China and for some parts of the study units in the United States. Boxplots of total dissolved solids data in ground water for all of the study units are shown in figure 32. At least 25 percent of the wells sampled in the Tangshan upper plain region exceed the Chinese standard for total dissolved solids and about 50 percent of these same wells exceed the secondary standard of the EPA. The higher median concentrations of the upper aquifer relative to those of the lower aquifer, mountain aquifer, and coastal aquifer of the Tangshan study unit suggest that agricultural and other land-use activities have contributed to the total dissolved solids content of ground water. Because the aquifer mineralogy is the same for the upper and lower zones, the higher total dissolved solids concentrations cannot be explained on the basis of natural water–rock interactions.

Ground water of the western San Joaquin Valley also has high total dissolved solids. Although some of the high dissolved solids can be attributed to natural processes, such as higher total dissolved solids content of the recharge water, some can also be attributed to agricultural activities, which have greatly affected the total dissolved solids content of the ground water in the western San Joaquin Valley. The western San Joaquin Valley has a long history of irrigation. Irrigation is required for successful agriculture in the San Joaquin Valley because little or no rain falls during the growing season. The soils of the western San Joaquin Valley tend to be poorly drained. Irrigation of crops and poor drainage in a semiarid environment lead to a high rate of evaporation of the irrigation water. Subsequent recharge can increase the salt loading to the aquifer and thereby increase the degradation of water quality with respect to total dissolved solids. In contrast, irrigation is not used as much in the Delmarva Peninsula, and rain or infiltration of stream water provides more recharge to the aquifers. As mentioned previously, the median concentration of total dissolved solids in the water samples of the Sacramento rice land-use study exceeds that

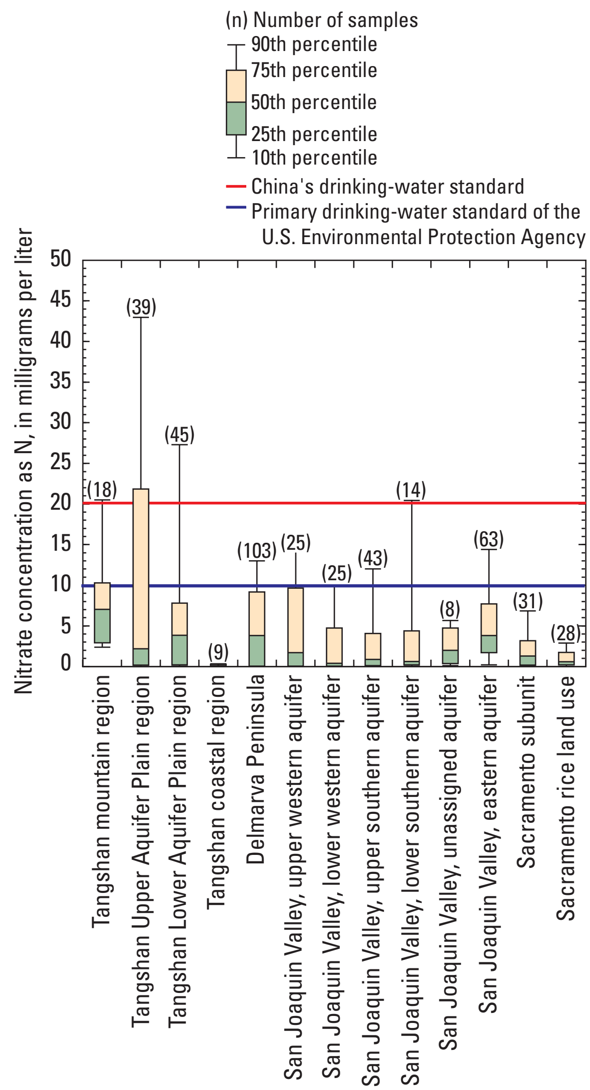


Figure 31. Boxplots of nitrate concentrations in ground water for various zones within study units or for an entire study unit in the People's Republic of China and the United States. N, nitrogen.

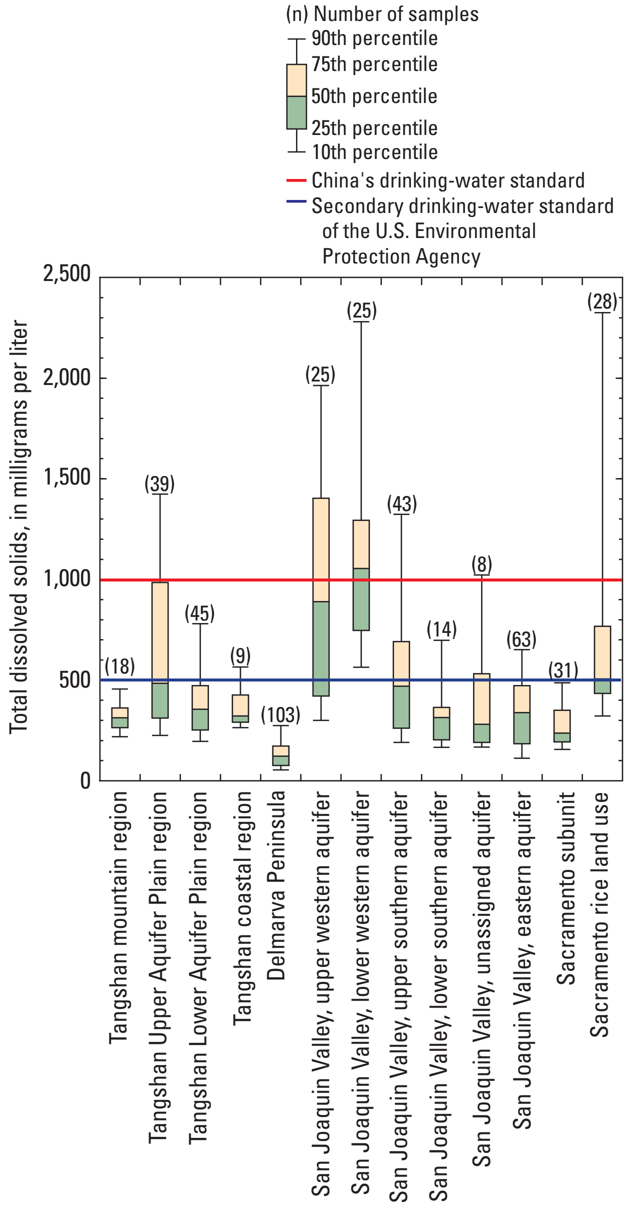


Figure 32. Boxplots of total dissolved solids concentrations in ground water for various zones within study units or for an entire study unit in the People's Republic of China and the United States.

of the total dissolved solids of water samples collected in the Sacramento subunit survey. At least 50 percent of the samples of the rice land-use study exceed the secondary standard for total dissolved solids of the EPA. The high total dissolved solids of the Tangshan aquifer cannot be explained by evaporative concentration of irrigation water because of a different climate. It also cannot be explained on the basis of water–rock interactions because the aquifer mineralogy does not contain salt deposits. The higher total dissolved solids may be attributed to a longer history of agricultural production in the Tangshan region relative to the San Joaquin Valley and other study units of the United States, or to the greater amount of animal and sewage wastes disposed on land within the Tangshan study unit.

Results of the gray matrix rankings indicate that iron concentrations are a water quality problem for some study units. Boxplots of iron concentrations for all study units are shown in figure 25. Iron concentrations that exceed the Chinese standard (0.3 mg/L) are present throughout the Tangshan study unit. The mountain region has the lowest relative iron concentration. Apparently, iron dissolves throughout the upper and lower parts of the plain and coastal aquifers in response to decreasing concentrations of dissolved oxygen. The only study unit in the United States with comparable iron concentrations is the Delmarva Peninsula.

Chemical Signatures of Ground Water Affected by Agriculture

The water quality of the aquifers in the Tangshan study unit has been affected by agricultural activities, which have resulted in a redistribution of major ions, in addition to elevated nitrate concentrations, for the agriculturally affected waters relative to natural ground water (fig. 13). The trilinear graph shows that the water becomes more enriched in calcium and sulfate as nitrate concentrations increase. This enrichment can probably be attributed to the application of other chemicals in the applied fertilizers. Agricultural chemicals (fig. 15) also affected the natural ion chemistry of the Delmarva Peninsula as indicated by association with higher nitrate concentrations. Hamilton showed that the ground water that is affected by agricultural activities in the Delmarva Peninsula has significantly higher levels of calcium, magnesium, potassium, and chloride, in addition to nitrate (Hamilton and others, 1993). Because of the evaporative concentration of irrigation water prior to recharge, agriculture signatures of the western and southern San Joaquin Valley ground water, when arranged according to ranges in nitrate concentration, are not as evident as the signatures of Tangshan and the Delmarva Peninsula. There is no clear distinction of signatures for anions, but there appear to be slightly greater proportions of calcium and magnesium in agriculturally affected ground water (figs. 16 and 17). The agricultural signature of ground water of the eastern San Joaquin Valley is represented by slightly elevated chloride and sulfate (fig. 18). As mentioned previously, one signature of agriculturally affected ground water in the Sacramento Valley is elevated total dissolved solids. The increase in total dissolved solids is caused mainly by evaporative concentration, especially during the rice-growing season, as evidenced in the trilinear plot for the wells of the Sacramento rice land-use study (fig. 20). The cation chemistry tends to shift from a calcium–magnesium water to a water with sodium as the most abundant cation. The shift probably results from precipitation of carbonate minerals such as calcite or aragonite.

The effects of agricultural land-use on major element chemistry can be further assessed by comparing the range in concentrations of individual water-quality constituents in ground water that have low nitrate concentrations with those that have high nitrate concentrations. Boxplots of calcium and sulfate concentrations in Tangshan study unit ground water with low nitrate (less than 0.5 mg/L as N) and high nitrate in ground water are shown in figures 33 and 34. The median calcium and sulfate concentrations in low nitrate wells are lower than those in high nitrate wells. The difference in medians for calcium was statistically significant at $p = 0.0032$ whereas the difference for sulfate was significant at $p = 0.0013$ using the nonparametric Mann–Whitney test. Evidence of geochemical processes that affect nitrate concentration can be seen by comparing the pH of ground water in samples from low and high nitrate wells (fig. 35). The difference in medians is statistically significant ($p = 0.0004$) by the Mann–Whitney test. It would be expected that iron concentrations might be higher in wells with low nitrate because of the oxidation state of the water. That is the case for the wells of the Tangshan study unit (fig. 36). The difference in medians is significant ($p = 0.003$) by

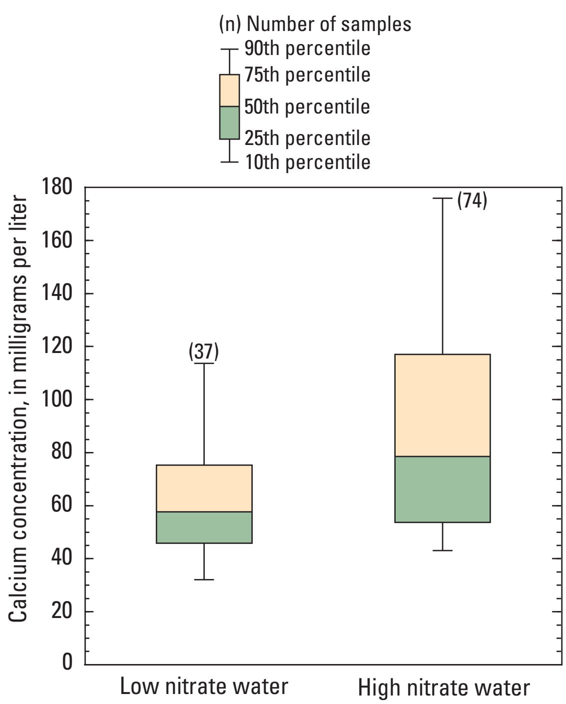


Figure 33. Boxplots of calcium concentrations in wells with low and high nitrate in the Tangshan study unit, People's Republic of China.

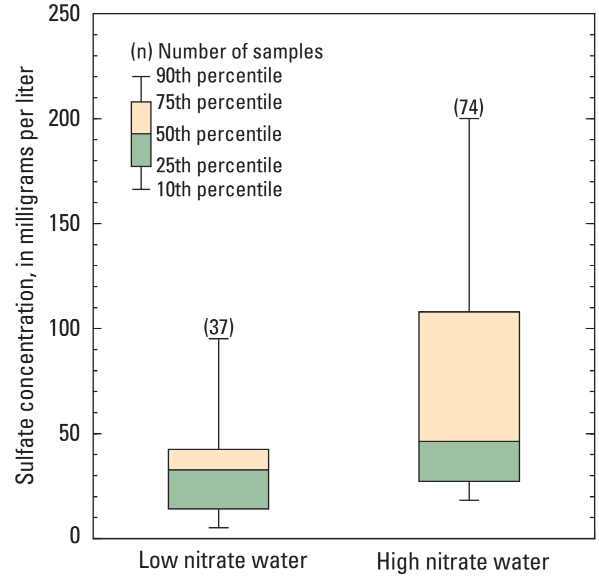


Figure 34. Boxplots of sulfate concentrations in wells with low and high nitrate in the Tangshan study unit, People's Republic of China.

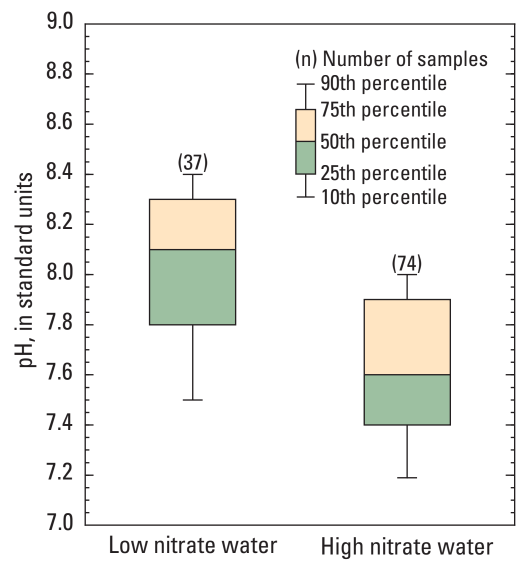


Figure 35. Boxplots of pH in wells with low and high nitrate in the Tangshan study unit, People's Republic of China.

the Mann–Whitney test (fig. 36). It is possible that iron dissolution and nitrate reduction may be partially linked by geochemical processes in the Tangshan aquifer. No other water-quality constituents, such as chloride, sodium, potassium, and magnesium, had statistically different concentrations in ground water of high or low nitrate in the Tangshan study unit.

Agriculture is most likely to affect the major element chemistry of ground water when concentrations of the major elements in natural ground water are very low, as in the case of the Delmarva Peninsula. Hamilton

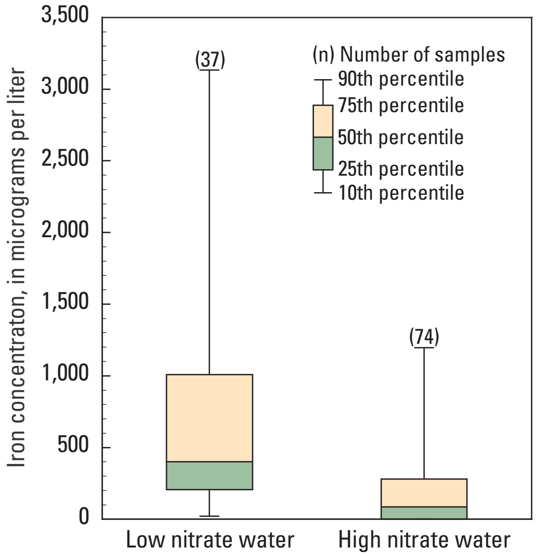


Figure 36. Boxplots of iron concentrations in wells with low and high nitrate in the Tangshan study unit, People's Republic of China.

and others (1993) found that the concentrations of calcium, magnesium, potassium, and chloride were higher in waters affected by nitrate contamination relative to natural ground water. Those authors attributed the changes to the application of various fertilizers. Evaporative processes that occur after irrigation and prior to recharge affect the ground water of the Central Valley of California. Furthermore, it is more difficult to see changes in the major element chemistry of ground water in that region that can be attributed to fertilizer application.

Principal Component Analysis

Principal component analysis is a statistical technique that can help explain variation in large data sets of multiple components, such as the water chemistry of the study units. Principal component analysis will allow for the grouping of variables that may help to explain a process that is controlling the particular grouping observed. The following constituents were selected to represent the variables for principal component analysis for this study: total dissolved solids, sodium, potassium, calcium, magnesium, chloride, sulfate, fluoride, bicarbonate, nitrate, and iron. These constituents were measured in the ground water of all study units. Principal component analysis may provide reasons for the variation observed for these constituents. Principal component analysis requires a normally distributed data set. The water chemistry data from these study units are generally not normally distributed. Therefore, a log transform was applied to all data to approximate normality. Results of principal component analysis for the various study units are shown in tables 23 through 28. The first two principal components are shown for each study unit because subsequent ones could not be attributed to any geochemical or anthropogenic process. The first two principal components explain between just under 60 percent to close to 70 percent of the variation with this set of water-quality data.

The first principal component is probably a general indication of the water chemistry that is attributed to recharge processes. The sign of the loadings is the same (tables 23 to 28) and of generally similar magnitude for major constituents of the ground water, such as total dissolved solids, magnesium, calcium, potassium, chloride, and sulfate. Two important points in interpreting the results of principal component analysis are the absolute values of the loadings and the positive or negative value of the results relative to one another. For example, all of the results for principal component 1 of the Tangshan study unit have the same sign, indicating that those water-quality constituents are affected by a similar process such as dissolution of minerals, which provides magnesium, calcium, sodium, chloride, and sulfate to the ground water. The second principal component shows that nitrate and iron concentrations are related but in opposite ways because of the change in sign, which is an indication of redox processes. As nitrate concentrations increase, iron concentrations tend to decrease, and as iron concentrations tend to increase, nitrate concentrations decrease.

Principal component analysis can be obtained for each well under investigation. The individual variable range for the principal component 2 of the Tangshan study unit is shown on the geomorphology map in figure 37. The figure shows where the state of ground water is mainly under reducing or oxidizing conditions. The range of principal component 2 values is also shown for the Delmarva Peninsula in figure 38. Like the map of the Tangshan study unit, this map shows the locations where the state of ground water is under reducing conditions and where nitrate reduction may be removing some of the nitrate from the ground water.

The eastern San Joaquin Valley was the only location for this study that does not show an indication of iron dissolution or nitrate reduction. The lack of these two types of redox processes indicates that the ground water in this region is oxidizing, the iron concentrations are low, and the nitrate reduction is not an important process because nitrate reduction to nitrogen gas does not occur to a large extent. In the eastern San Joaquin Valley, the oxidizing condition is consistent with the sandy or coarse-grained texture of the aquifer materials, which allows for greater diffusion of oxygen to the ground water.

Table 23. Results of principal component analyses of chemical data from the Tangshan study unit, People's Republic of China

[N, nitrogen; —, loadings have absolute values of less than 0.30]

Water quality constituent	Principal component 1	Principal component 2
Total dissolved solids	–0.424	—
Magnesium	–0.368	—
Calcium	–0.361	—
Sodium	–0.325	—
Potassium	—	—
Chloride	–0.36	—
Sulfate	–0.351	—
Fluoride	—	–0.494
Nitrate as N	—	0.581
Bicarbonate	—	–0.305
Iron	—	–0.36
Percent variation explained	47.5	20.4
Cumulative percent variation explained	47.5	67.9

Table 24. Results of principal component analyses of chemical data from the Delmarva Peninsula study unit, United States

[N, nitrogen; —, loadings have absolute values of less than 0.30]

Water quality constituent	Principal component 1	Principal component 2
Total dissolved solids	0.421	—
Magnesium	0.387	—
Calcium	0.382	—
Sodium	—	–0.341
Potassium	0.365	—
Chloride	0.405	—
Sulfate	0.303	—
Fluoride	—	—
Nitrate as N	—	0.488
Bicarbonate	—	–0.401
Iron	—	–0.516
Percent variation explained	39.9	23.7
Cumulative percent variation explained	39.9	63.6

Table 25. Results of principal component analyses of chemical data from the western region of the San Joaquin Valley study unit, California, United States

[N, nitrogen; —, loadings have absolute values of less than 0.30]

Water quality constituent	Principal component 1	Principal component 2
Total dissolved solids	–0.429	—
Magnesium	–0.4	—
Calcium	–0.425	—
Sodium	–0.334	–0.456
Potassium	—	—
Chloride	–0.383	—
Sulfate	—	—
Fluoride	—	—
Nitrate as N	—	0.424
Bicarbonate	—	—
Iron	—	–0.528
Percent variation explained	42.0	15.8
Cumulative percent variation explained	42.0	57.8

Table 26. Results of principal component analyses of chemical data from the southern region of the San Joaquin Valley study unit, California, United States

[N, nitrogen; —, loadings have absolute values of less than 0.30]

Water quality constituent	Principal component 1	Principal component 2
Total dissolved solids	0.42	—
Magnesium	0.356	—
Calcium	0.383	—
Sodium	0.302	0.456
Potassium	0.348	—
Chloride	0.325	—
Sulfate	0.375	—
Fluoride	—	0.359
Nitrate as N	—	–0.353
Bicarbonate	—	—
Iron	—	0.42
Percent variation explained	42.5	21.5
Cumulative percent variation explained	42.5	64.0

Table 27. Results of principal component analyses of chemical data from the eastern region of the San Joaquin Valley study unit, California, United States

[N, nitrogen; —, loadings have absolute values of less than 0.30]

Water quality constituent	Principal component 1	Principal component 2
Total dissolved solids	–0.431	—
Magnesium	–0.308	–0.417
Calcium	–0.397	—
Sodium	–0.324	0.399
Potassium	—	–0.343
Chloride	–0.342	—
Sulfate	–0.371	—
Fluoride	—	0.584
Nitrate as N	—	—
Bicarbonate	–0.352	—
Iron	—	—
Percent variation explained	44.5	17.3
Cumulative percent variation explained	44.5	61.8

Table 28. Results of principal component analyses of chemical data from the Sacramento Valley study unit, California, United States

[N, nitrogen; —, loadings have absolute values of less than 0.30]

Water quality constituent	Principal component 1	Principal component 2
Total dissolved solids	0.427	—
Magnesium	0.376	—
Calcium	0.36	—
Sodium	0.368	—
Potassium	—	—
Chloride	0.264	—
Sulfate	0.402	—
Fluoride	0.154	—
Nitrate as N	—	–0.682
Bicarbonate	0.359	—
Iron	—	0.566
Percent variation explained	48.2	14.1
Cumulative percent variation explained	48.2	62.3

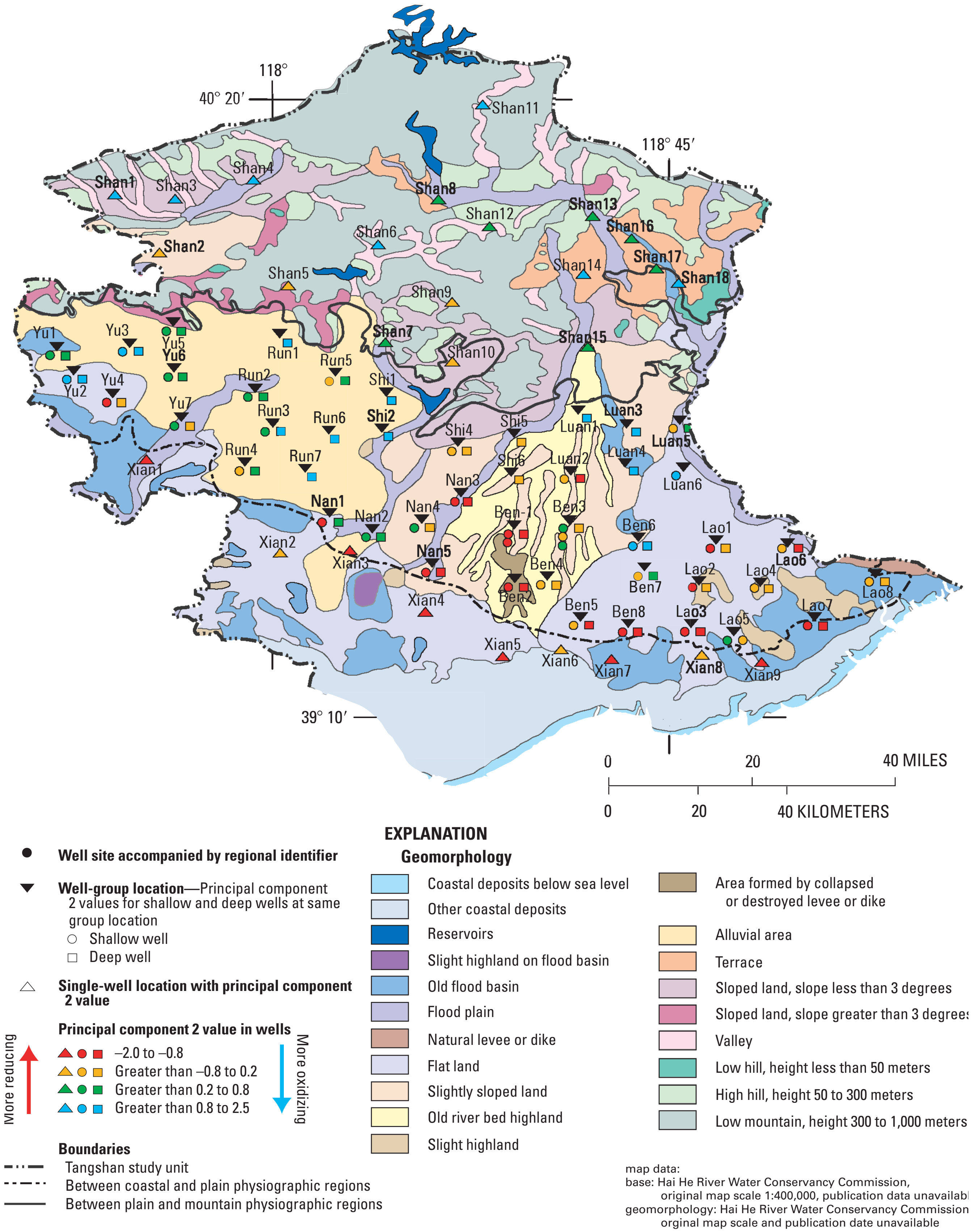
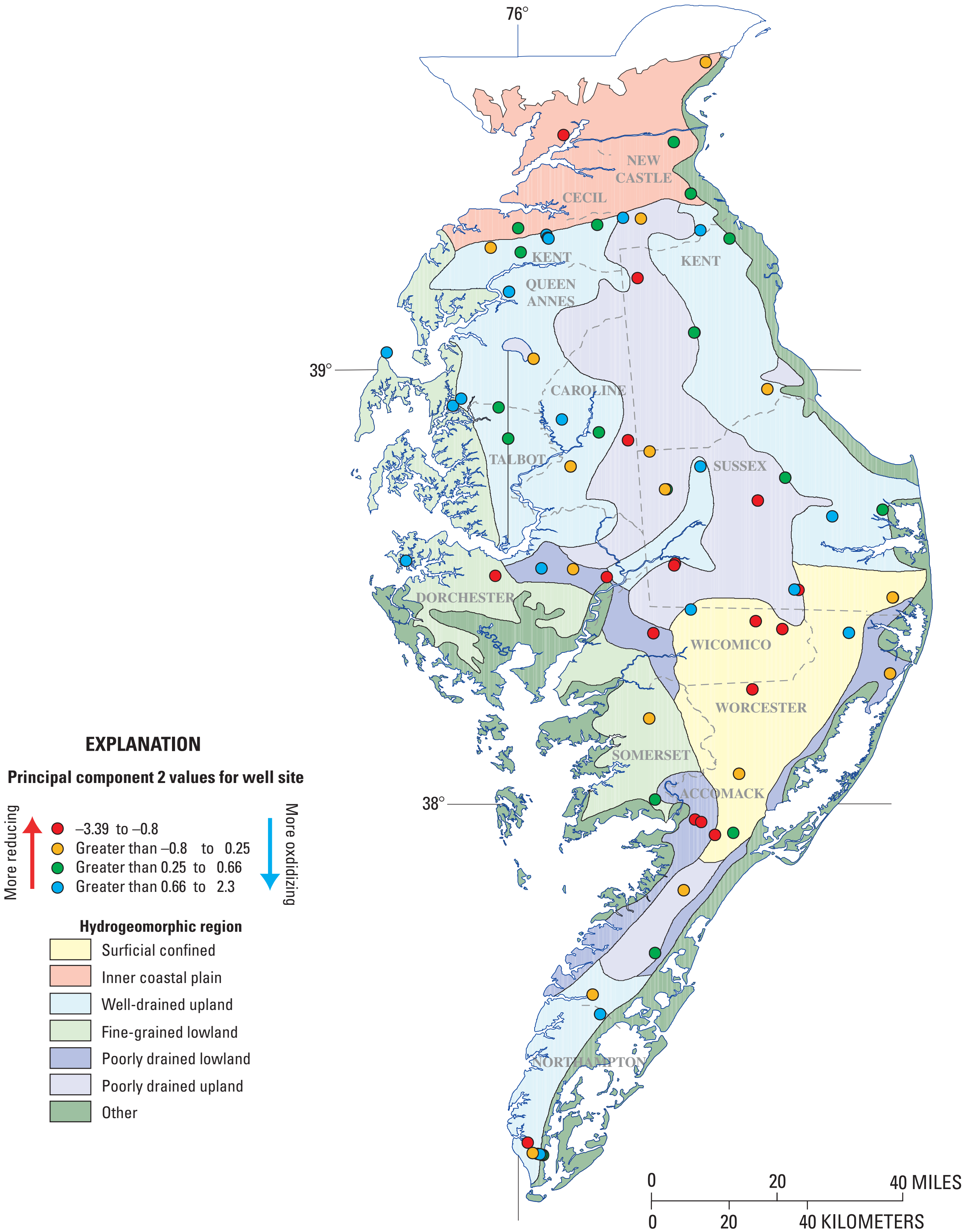


Figure 37. Geomorphology and range of principal component 2 values for wells of the Tangshan study unit, People's Republic of China.



map data: Hamilton and others, 1993.
U.S. Geological Survey, 1981a,b; 1983c,e,f,g; 1984a,b,e,i; 1999

Figure 38. Range of principal component 2 values for wells of the Delmarva Peninsula study unit, United States.

NITRATE AND DETECTION FREQUENCY OF PESTICIDES IN GROUND WATER

Comparison of Nitrate Use in Study Units

Nitrogen use data for each county in the study units were available for comparison of application amounts per given area. In each case, the most recent year of available nitrogen use data was used where a complete set of data was available.

A comparison of nitrate usage for counties within the four study units is shown in table 29. Data for study units of the United States were obtained from Battaglin and Goolsby (1995). Their data are based on documented sales, in each county, of fertilizers that are used primarily for agriculture. Therefore, the authors of this report assumed that all of the fertilizer that was purchased was used. The Hai He River Water Conservancy Commission obtained data for the Tangshan study unit through a similar process. On table 29, we see that nitrogen applications for some counties of the Central Valley of California are higher than those for the Delmarva Peninsula, but overall, the use is similar per unit area for the study units of the United States. The nitrogen usage in the counties of the Tangshan study unit is considerably higher than that of the study units of the United States by as much as a factor of 10, in some cases. Therefore, higher use of nitrogen fertilizer in this agricultural region of the People's Republic of China is one possible explanation for the higher nitrate concentrations and for other agricultural contaminants found in the ground water of the Tangshan study unit.

In contrast to nitrogen fertilizer, counties in the United States have a higher use or generation of manure than counties in the People's Republic of China. The usage or generation of manure within the study units is shown in table 30. Data for the study units of the United States were obtained from Puckett and others (1998). Puckett and others (1998) based their estimates on the animal census of each county. Through a similar process, the Hai He River Basin's Water Conservancy Commission obtained data for the counties of the Tangshan study unit. This generation of manure can be attributed to larger animal production facilities in the United States, especially cattle production. Manure is not necessarily used as an agricultural additive in the United States, but the generation of manure at animal operation centers represents a potential point source of nitrogen and other contaminants to ground water.

The amount of nitrogen in manure varies depending on the animal source. The nitrogen contents assumed for calculating possible nitrate effects from various animals are shown in table 31. The principal elements in manure are carbon, oxygen, and hydrogen. In all cases, nitrogen is a minor component of manure. The highest N content, 0.11 percent, is for broiler or other meat-type chickens, and the lowest, 0.028 percent, is for hogs, pigs, horses, and ponies. Although the N content in manure is relatively low, nitrate formed from the oxidation of manure can migrate to ground water. Six wells in the People's Republic of China were sampled for nitrogen isotopes and oxygen isotopes in nitrate. Two of the wells (Shan15 and BenS3) had a clear signature of nitrogen from fertilizer because the values for $\delta^{15}N$ were close to 5 per mill (fig. 39). Two wells showed a mixed source of the nitrate because the

Table 29. Comparison of nitrate use in counties within study units in the People's Republic of China and the United States

[km^2, square kilometer; Mg, megagram]

Tangshan study-unit counties	Nitrogen use, 1996 (Mg/km^2)	Delmarva study-unit counties	Nitrogen use, 1991 (Mg/km^2)	Sacramento Valley study-unit counties	Nitrogen use, 1987 (Mg/km^2)	San Joaquin Valley study-unit counties	Nitrogen use, 1987 (Mg/km^2)
Laoting	59.1	Kent	5.3	Butte	2.4	Fresno	4.0
Zunhua	48.4	New Castle	3.0	Colusa	4.1	Kern	2.3
Fengnan	50.4	Sussex	3.1	Glenn	3.1	Kings	6.3
Fengrun	44.1	Caroline	4.9	Placer	0.2	Madera	2.4
TangHai	56.5	Cecil	2.7	Sacramento	2.5	Merced	4.8
Luannan	49.3	Dorchester	2.4	Solano	2.6	San Joaquin	7.4
Yutian	33.1	Kent	5.8	Sutter	7.9	Stanislaus	4.6
Qianxi	40.5	Queen Annes	5.2	Tehama	0.4	Tulare	2.9
Tangshan	36.0	Somerset	2.0	Yolo	4.8		
Luan Xian	28.5	Talbot	4.9	Yuba	2.2		
Qian'an	23.7	Wicomico	2.2				
		Worcester	2.0				
		Accomack	1.7				
		Northampton	2.9				

Table 30. Usage or generation of manure in counties within study units in the People's Republic of China and the United States

[km², square kilometer; Mg, megagram]

Tangshan study-unit counties	Total manure, 1996 (Mg/km²)	Delmarva study-unit counties	Total manure, 1992 (Mg/km²)	Sacramento Valley study-unit counties	Total manure, 1992 (Mg/km²)	San Joaquin Valley study-unit counties	Total manure, 1992 (Mg/km²)
Laoting	1,225.8	Kent	1,604.1	Butte	801.6	Fresno	3,575.8
Zunhua	1,831.1	New Castle	540.6	Colusa	495.2	Kern	1,266.7
Fengnan	1,623.7	Sussex	8,973.5	Glenn	2,905.6	Kings	7,990.9
Fengrun	3,133.5	Caroline	5,052.0	Placer	626.3	Madera	2,837.5
TangHai	158.5	Cecil	2,141.1	Sacramento	5,399.1	Merced	10,601.4
Luannan	1,753.0	Dorchester	2,023.7	Solano	2,498.6	San Joaquin	8,727.9
Yutian	1,165.1	Kent	2,873.8	Shasta	596.5	Stanislaus	13,824.5
Qianxi	1,806.1	Queen Annes	2,123.9	Sutter	992.4	Tulare	7,434.1
Tangshan	4,461.0	Somerset	6,212.5	Tehama	1,430.9		
Luan Xian	4,240.2	Talbot	1,741.1	Yolo	1,163.6		
Qian'an	3,066.1	Wicomico	8,042.8	Yuba	3,375.4		
		Worchester	5,922.9				
		Accomack	1,437.8				
		Northampton	18.5				

Table 31. Nitrogen content of manure from various animals (Puckett and others, 1998)

[kg, kilogram; N, nitrogen; Mg, megagram]

Animal	(N content of manure in kg of N)/(Mg of manure)
Beef cows	0.315
Milk cows	0.4
Heifers and calves	0.31
Steers	0.315
Hogs and pigs	0.28
Sheep and lambs	0.45
Horses and ponies	0.28
Chickens (more than 3 months old)	0.83
Chickens (less than 3 months old)	0.62
Broilers and other meat-type chickens	1.1
Turkeys	0.74

$\delta^{15}N$ values were close to 10. Finally, two wells had relatively high enrichment in $\delta^{15}N$, which is assumed to be from manure or sewage. Although an isotropic signature from two of the sampled wells indicated a source of nitrate from animal waste, this signature could also have come from sources of nitrate from human wastes or sewage. In the People's Republic of China, sewage inputs to ground water are a possibility because not all rural areas have adequate wastewater treatment.

Physical and Chemical Factors Related to the Detection Frequency of Nitrate

Nitrate concentrations versus well depths for the Tangshan study unit are shown in figure 40. These results are consistent with the isotope dating results; nitrate concentrations also are above those expected for natural ground water are present to a depth of 130 to 140 m. Below that depth, nitrate concentrations tend to be below detection limits. Nitrate concentrations in older water, therefore, range from low to undetectable, and the higher concentrations are a result of a

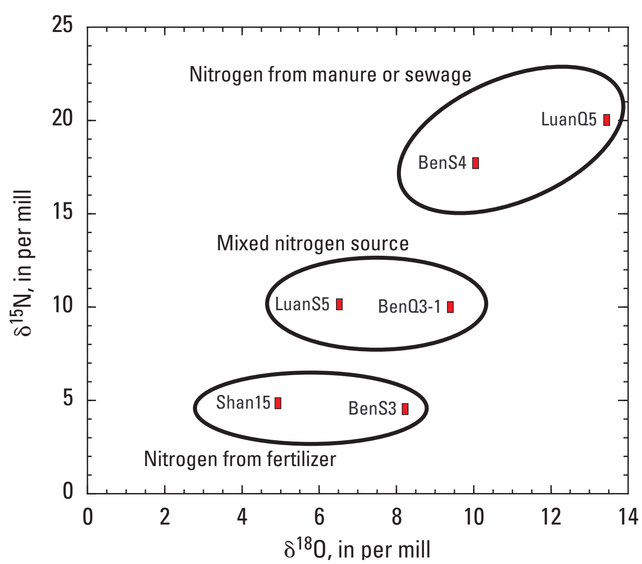


Figure 39. $\delta^{15}N$ and $\delta^{18}O$ in nitrate for select wells of the Tangshan study unit, People's Republic of China. N, nitrogen; O, oxygen; δ, delta.

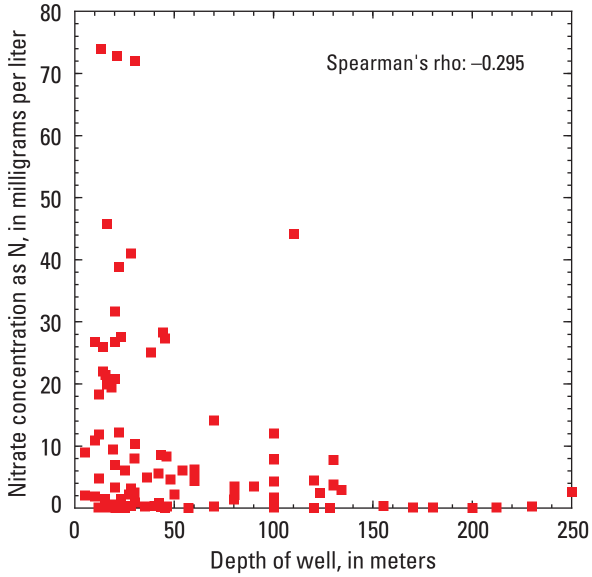


Figure 40. Nitrate concentration versus well depth for wells of the Tangshan study unit, People's Republic of China. N, nitrogen.

combination of land use practices, hydrology, and geochemical processes. No linear relation of nitrate and well depth is apparent (fig. 40). The Spearman's rho (ρ) or Spearman's rank correlation, a nonparametric test, was used to determine whether a consistently decreasing trend of nitrate concentration correlated with well depth. A nonparametric test was required because the data were not normally distributed. Spearman's rho is a test of the correlation between ranks of two variables, in this case nitrate concentrations and well depths. Values of ρ will be between –1 and 1. A negative value implies an inverse relation whereas a positive value indicates a positive relation. A value near zero indicates no correlation between the two variables. An absolute value of 1 implies a strong monotonic relation for the two variables. The value of ρ for the two variables (well depth and nitrate concentration) was –0.295, indicating a weak relation between well depth and nitrate concentration. Nitrate concentrations versus depth to water are shown in figure 41. The value of ρ for this pair of variables is 0.05, which indicates no relation between depth to water and nitrate concentration. It was not possible to plot nitrate concentration against the depth to the top of the screened intervals of individual wells because location of well screens is not known for the wells of the Tangshan study unit. The absence of a strong relation between nitrate concentrations and well depth is not unusual. The value of ρ for nitrate and well depth of the Delmarva Peninsula is –0.152, and the value for the wells of the San Joaquin Valley is –0.302. Similar results were obtained in an analysis of the eastern San Joaquin Valley by Burow and others (1998). Burow's team suggested that factors other than well depth, such as soil and sediment texture, may be more important in the distribution of nitrate in ground water of the eastern San Joaquin Valley.

Nitrate concentrations versus iron concentrations for the wells of the Tangshan study unit are shown in figure 42. As expected, most of the wells with higher nitrate concentrations also have low iron concentrations, but some have relatively high iron concentrations. In those wells, nitrate reduction is apparently not sufficient to reduce nitrate to relatively low levels. Those wells may be affected by a combination of nitrogen from fertilizer and sewage or manure. The value of ρ for the combination of nitrate and iron concentrations in the Tangshan study unit is –0.382, which suggests a weak monotonic relation between the two variables.

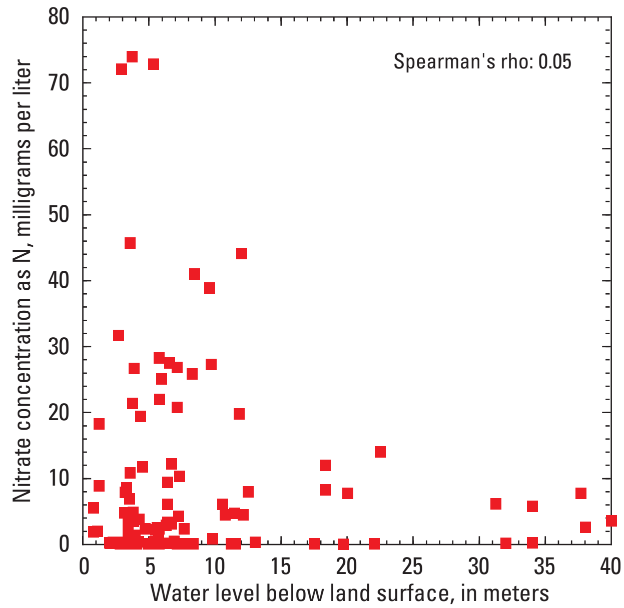


Figure 41. Nitrate concentration versus water level below land surface for wells of the Tangshan study unit, People's Republic of China. N, nitrogen.

Nitrate concentrations versus total dissolved solids are plotted in figure 43. The calculation of ρ for this set of two variables is 0.317, which suggests a weak positive monotonic relation between the ranks of the two variables. Although nitrate seems to be weakly related to total dissolved solids, the relation is not statistically significant when compared with other tests. The median of total dissolved solids was tested in wells of low nitrate (less than 0.5 mg/L as N) and in wells of higher nitrate (greater than 0.5 mg/L as N) concentrations. The medians were assessed to be statistically similar ($p = 0.27$) when tested with the nonparametric Mann–Whitney test of medians. The p value associated

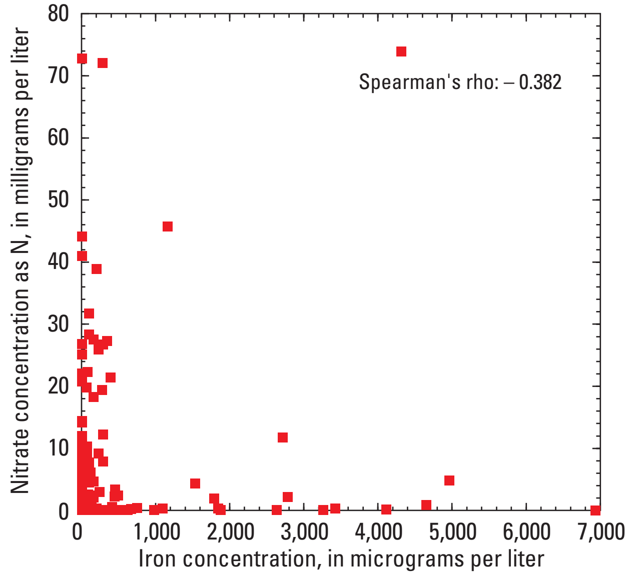


Figure 42. Nitrate concentration versus iron concentration for wells of the Tangshan study unit, People's Republic of China. N, nitrogen.

with an observed value of a test statistic is the smallest level of significance that would have allowed the null hypothesis to be rejected. A value of p less than 0.05 suggests that medians are different. Therefore, the relatively high p value of 0.27 suggests that the medians are statistically the same. Although nitrate and total dissolved solids are not strongly correlated, the total dissolved solids of the ground water in the plain region of the Tangshan study unit seem to have been affected by agricultural or other land-use practices. As mentioned previously, total dissolved solids (fig. 32) of the upper aquifer of the plain region are higher relative to other

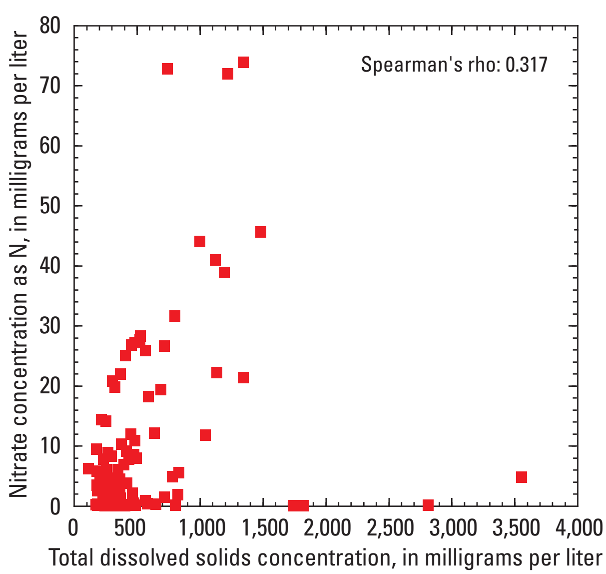


Figure 43. Nitrate concentration versus total dissolved solids concentration for wells of the Tangshan study unit, People's Republic of China. N, nitrogen.

locations of the Tangshan study unit. This difference cannot be explained by water–rock interactions because of similar mineralogy; also, the deeper ground water would be expected to have a higher total dissolved solids content because of the longer time for mineral dissolution and equilibrium to occur.

As part of this project, a collaborative laboratory and field study of ammonia and nitrate transport has been completed by the Hai He River Water Conservancy Commission and Tsinghua University (Xianbi Lue, written commun., 1998). Soil samples from Luannan County were collected for a laboratory scale simulation and a field experiment. The soil type in that part of Luannan County is fine sand with less than 0.02 percent clay content. The results of those studies indicated that, while ammonia nitrogen is strongly adsorbed to soil particles, it is also rapidly oxidized to nitrate and then easily transported to deeper soil horizons. The collaborative team also showed that the use of nitrogen from manure results in a lower amount of nitrate transport. The experimental design also compared different water management scenarios. Nitrate transport was greatest during the rainy or monsoon season, and irrigation during the monsoon season resulted in the highest transport of nitrogen to deeper subsurface horizons.

The locations of wells with corresponding levels of nitrate concentrations for the Tangshan study unit are shown in figure 44. Boxplots of nitrate concentrations of well by name designation in the Tangshan study unit are shown in figure 45. The wells of the Tangshan study unit have a name designation, which indicates a regional location, such as the Shan (mountain), or Xian (coastal) wells, or named as part of governmental entity, such as the Ben, Lao, Luan, Nan, Run, Shi, or Yu designations. The location that tends to have the most dense distribution of wells with high nitrate is in the western part of the study unit, where wells are labeled "Yu," with decreasing concentrations of nitrate extending eastward to the locations where wells are labeled "Run." A few locations in the mountain (Shan) region had samples that exceeded 10 mg/L of nitrate as N and, in some instances, even 20 mg/L. In contrast, wells of the Xian designation always tend to have low nitrate. Another cluster of wells with higher relative nitrate concentrations is the location where wells are labeled as "Luan" or "Ben." The location of the Ben wells is where the variation in concentration is greatest. The median concentration of the Ben wells is relatively low, compared with the Yu wells. This great variation in the nitrate concentrations of the Ben wells, along with the relatively low median concentration in that area, suggests that land-use practices around individual wells may be most responsible for the outlying concentrations. The higher median concentrations of the Yu wells suggest that a combination of land use and hydrologic

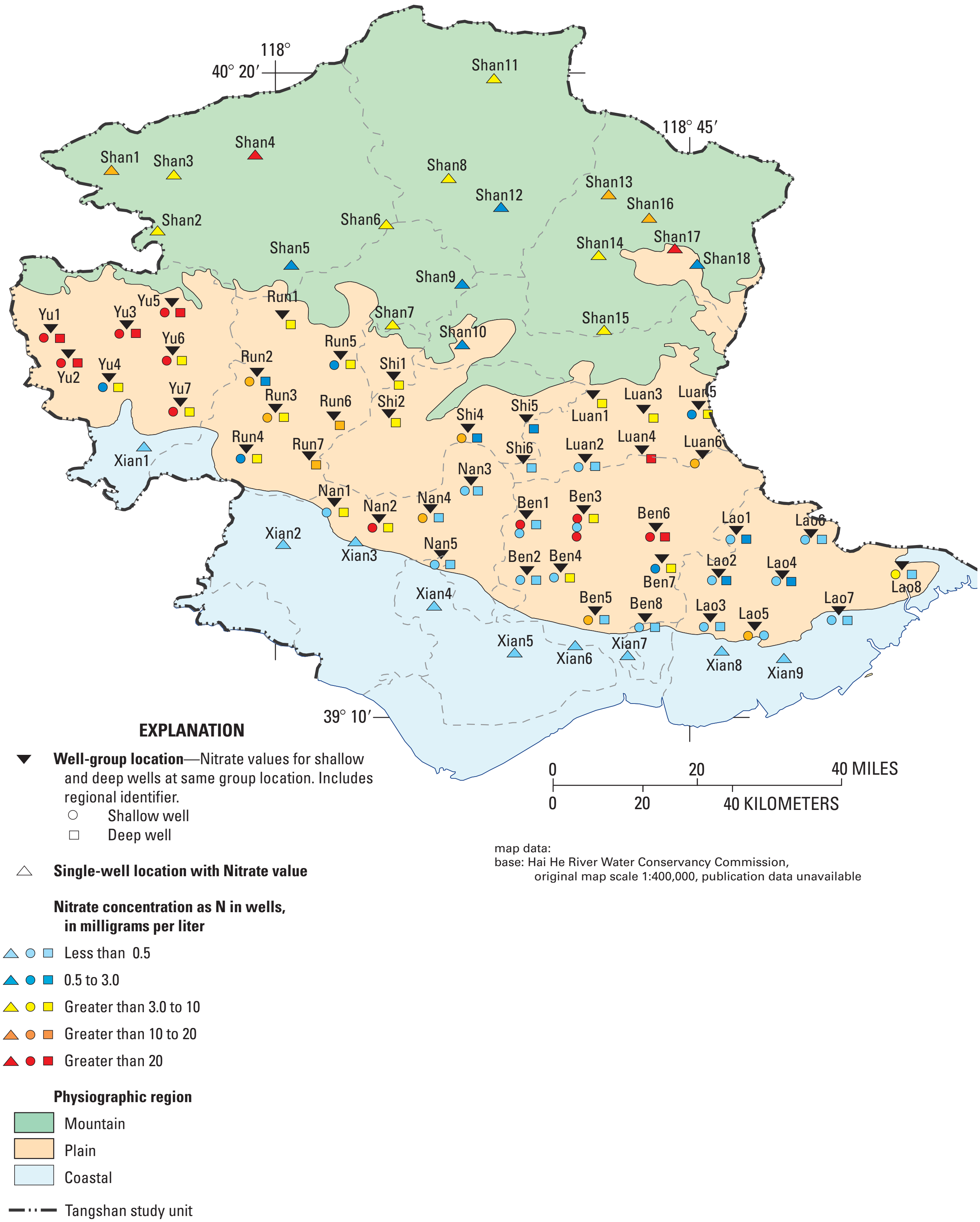


Figure 44. Locations of wells and corresponding levels of nitrate concentrations for the Tangshan study unit, People's Republic of China. Well location Ben3 has three shallow wells (Q1, Q2, and Q3); Ben1 has two shallow wells (Q1 and Q2); all others have either one shallow well or no shallow well. N, nitrogen

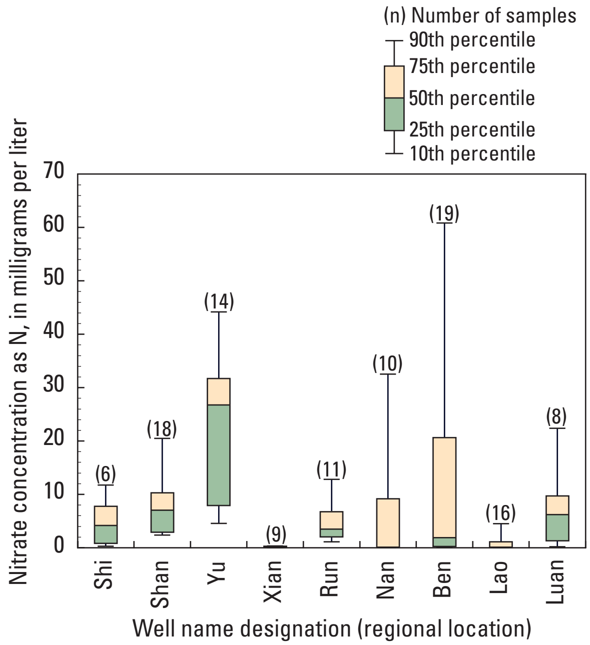


Figure 45. Boxplots of nitrate concentrations by Chinese name designation for wells of the Tangshan study unit, People's Republic of China. N, nitrogen.

factors may be responsible for the high nitrate concentrations of wells in that region. It has already been shown that the ground water in that region has low iron and probably contains dissolved oxygen. Those factors would tend to inhibit the reduction of nitrate.

The distribution of nitrate in ground water may also be due to other important factors, such as well construction techniques, the texture of the unsaturated zone, climate, and ground-water pumpage. Some wells in the Tangshan study unit are perforated from near, or at, ground level, which allows water with high amounts of nitrate that is derived from the soil zone to directly infiltrate the well. Extremely high amounts of ground-water pumpage can result in the drawdown of water levels and the transfer of contaminants to deeper subsurface zones. The ratio of ground-water recharge to ground water use in the People's Republic of China is near 1 or less than 1 depending on the strength of the Asian monsoon. The ratio of the Delmarva Peninsula is not known, but that region does not rely as heavily on irrigation water as do the Tangshan and California study units. In fact, rainfall is normally sufficient in the Delmarva Peninsula to support agriculture. The San Joaquin Valley is highly dependent on irrigation water, and its areas have serious ground-water overdraft problems (Gronberg and others, 1998). Although ground water is used for irrigation in the Sacramento Valley in some areas, irrigation water is normally provided from the Sacramento River. As previously mentioned, some regions of the Tangshan study unit, such as the Yu region, have several ground-water problems, including elevated nitrate, total dissolved solids, and coliform bacteria. These problems indicate either well construction problems or a highly vulnerable aquifer setting, or some combination of factors that is seriously degrading ground-water quality. Because a more detailed description of agricultural land-use management for the Tangshan study unit is beyond the scope of the current study, not all causative factors can be completely addressed here. Dating of the ground water in shallow and deeper zones and more thorough land-use analyses might be addressed in future studies.

Pesticides

Pesticides have been detected in the ground water of all three study units of the United States. Koterba and others (1993) reported on pesticides in the shallow ground water of the Delmarva Peninsula. The most commonly detected pesticides were organonitrogen and other herbicides, which are applied directly to the soil. These herbicides included atrazine, cyanazine, simazine, alachlor, metolachlor, and dicamba. These herbicides were generally present in concentrations below drinking-water standards. The detection frequency of these herbicides was most strongly correlated with corn, soybean, and small grains (winter wheat, barley, hay) grown in well-drained soils. Pesticides in ground water have affected the suitability of the ground water resource in parts of the San Joaquin Valley (Domagalski and Dubrovsky, 1991, 1992; Domagalski, 1997). The types of pesticides that are most frequently detected in the Central Valley of California and the Delmarva Peninsula are herbicides and soil fumigants; insecticides are only rarely detected. Herbicides and soil fumigants have a greater frequency of detection because they are applied directly to the soil and can migrate to ground water after rainfall or irrigation application, unless degradation reactions occur in the soil. Although herbicides or fumigants are frequently detected in ground water, only rarely are their concentrations above drinking-water standards. One exception is for the soil fumigant DBCP. Soil fumigants tend to be used more in the Central Valley of California relative to other agricultural regions of the United States because of the higher amount of fruit production in California. DBCP was used heavily in parts of the eastern San Joaquin Valley where orchards and vineyards are the principal land use (the use of DBCP was stopped in 1977). The EPA drinking-water standard for DBCP is set at 0.2 μg/L.

DBCP was detected in 1,419 of 4,507 wells sampled between 1971 and 1988 with a median concentration near 2.0 μg/L or a factor of 10 greater than the drinking-water standard (Domagalski, 1997). Other factors that contributed to the multiple detections of DBCP were high water solubility, high use in areas with coarse-grained soil texture, and a long environmental half-life.

Few ground-water samples in the Tangshan study unit had been studied previously for the presence of pesticides. As a result, the collaborative team decided to sample wells of transects 1 and 2 (fig. 4) for pesticides. Samples were extracted in the People's Republic of China, and the extracts were returned to the United States for analysis by mass spectrometry. Ground-water extracts were indistinguishable from blank extracts, indicating that pesticides were not present. However, samples were not available for wells of the Yu region, where high nitrate was found. Therefore, although no pesticides have been detected in one part of the study unit, sampling should be completed in other regions. Pesticide applications may not be as high in the People's Republic of China as in the United States. That may be one explanation for the lack of pesticide detections in the ground water of the Tangshan study unit. Another possible explanation is that pesticides are present in the soil horizons, but have not yet been transported to the water table.

SUMMARY AND CONCLUSIONS

A regional assessment of ground-water quality in one region of the People's Republic of China, the Tangshan region, showed that nitrate, total dissolved solids, iron, and other contaminants are affecting the recently recharged ground water. When compared with the ground water in similar agricultural regions of the United States, median nitrate concentrations tended to be similar, but the data from the Tangshan study unit showed a much greater range in concentrations. In the People's Republic of China, the nitrate drinking water standard is set at 20 mg/L as N, whereas in the United States, the nitrate drinking water standard is set at 10 mg/L as N. Many wells in the regions under investigation in the United States exceeded the American (EPA) standard, but only a few wells in the United States exceeded the Chinese standard. The high values of nitrate concentrations in the Tangshan ground water were attributed to larger nitrate applications, to the application of animal wastes and sewage to agricultural land and to land near ground-water wells, to regional hydrology such as soil texture and oxidation–reduction processes, and possibly to well construction techniques. The use of dating techniques, especially the $^3H/^3He$ method, indicated that recently recharged water could be detected to depths as much as 150 m in the Tangshan study unit. The implication for that study unit is that agricultural contaminants could also be detected to those depths and that the drilling of deeper wells may be necessary, in some locations, to provide water of suitable quality. The western part of the San Joaquin Valley was shown to have some similar water quality problems, especially with respect to total dissolved solids. Total dissolved solids of the San Joaquin Valley are elevated mainly because of the evaporation of irrigation water in a semiarid environment. The climate of the Tangshan study unit is less arid than that of the San Joaquin Valley, and so the higher total dissolved solids content may be attributed less to evaporation and more to the longer period that the land has been in agricultural production, and to the greater amounts of land disposal of manure and animal wastes. Pesticides do not seem to be a current problem for this region of the ground-water system in the People's Republic of China, but not all areas were sampled adequately to provide a full assessment.

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