

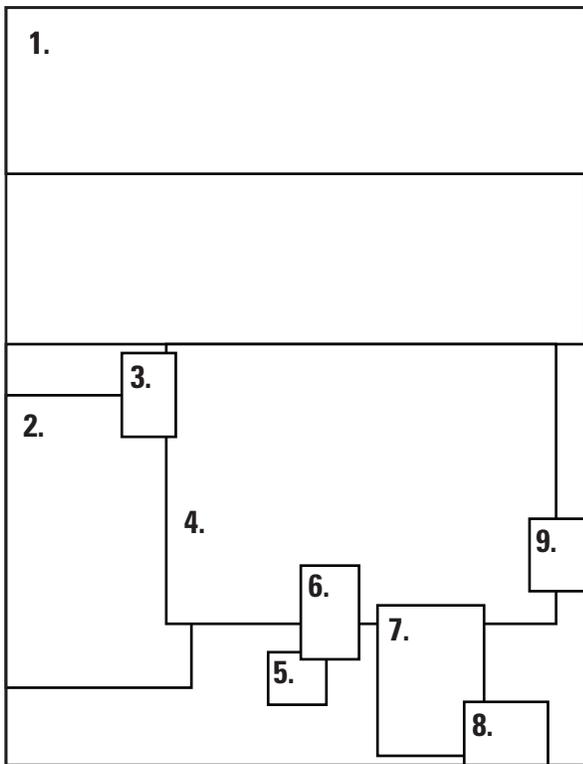


Ground-Water Quality in the Santa Ana Watershed, California: Overview and Data Summary

Water Resources Investigations Report 02-4243

NATIONAL WATER-QUALITY ASSESSMENT PROGRAM

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By Scott N. Hamlin, Kenneth Belitz, Sarah Kraja, *and* Barbara Dawson

U.S. GEOLOGICAL SURVEY

Water-Resources Investigations Report 02-4243

NATIONAL WATER-QUALITY ASSESSMENT PROGRAM

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U.S. DEPARTMENT OF THE INTERIOR

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U.S. GEOLOGICAL SURVEY

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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. (<http://www.usgs.gov/>). 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.

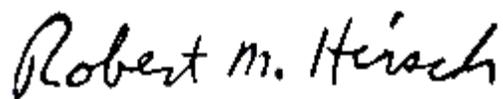
The USGS implemented the National Water-Quality Assessment (NAWQA) Program to support national, regional, and local information needs and decisions related to water-quality management and policy. (<http://water.usgs.gov/nawqa>). Shaped by and coordinated with ongoing efforts of other Federal, State, 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 and priorities. 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. (<http://water.usgs.gov/nawqa/nawqamap.html>). 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. (<http://water.usgs.gov/nawqa/natsyn.html>).

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
Associate Director for Water

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CONVERSION FACTORS, VERTICAL DATUM, AND ABBREVIATIONS AND ACRONYMS

CONVERSION FACTORS

	Multiply	By	To obtain
acre-foot (acre-ft)		1,233	cubic meter
acre-foot per year (acre-ft/yr)		1,233	cubic meter per year
mile (mi)		1.609	kilometer
square mile (mi ²)		2.590	square kilometer
picocurie per liter (pCi/L)		0.037	becquerel per liter

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

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

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

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

VERTICAL DATUM

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.

Altitude, as used in this report, refers to distance above or below sea level.

***Transmissivity:** The standard unit for transmissivity is cubic foot per day per square foot times foot of aquifer thickness [(ft³/d)/ft²]ft. In this report, the mathematically reduced form, foot squared per day (ft²/d), is used for convenience.

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

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

NOTE TO USGS USERS: Use of hectare (ha) as an alternative name for square hectometer (hm²) is restricted to the measurement of small land or water areas. Use of liter (L) as a special name for cubic decimeter (dm³) is restricted to the measurement of liquids and gases. No prefix other than milli should be used with liter. Metric ton (t) as a name for megagram (Mg) should be restricted to commercial usage, and no prefixes should be used with it.

Abbreviations and Acronyms

acre-ft/yr	acre foot per year
dD	delta deuterium
d ¹⁸ O	delta oxygen-18
L	liter
mi	mile
mi ²	square mile
mg/L	milligrams per liter

mL	milliliter
mm	millimeter
pCi/L	picocurie per liter
per mil	parts per thousand
ppm	parts per thousand
µg/g	micrograms per gram
µg/L	micrograms per liter
1,1-DCE	1,1-dichloroethene
1,2-DCE	1,2- dichloroethene
CAS	California Aquifer Susceptibility study
CFC-11	trichlorofluoromethane
CFC-113	1,1,2-trichloro-1,2,2-trifluoroethane
COFPS	Coastal flow-path study
COLUS	Coastal urban land-use study
COSUS	Coastal subunit survey
DBCP	dibromochloropropane
DHS	California Department of Health Services
DOC	dissolved organic carbon
DWR	California Department of Water Resources
EMWD	Eastern Municipal Water District
EPA	Environmental Protection Agency
FPS	flow-path study
ID	identifier
IEUA	Inland Empire Utilities Agency
INFPS	Inland flow-path study
INSUS	Inland subunit survey
LC	laboratory code
LLNL	Lawrence Livermore National Laboratory
LRL	laboratory reporting limit
LT-MDL	long-term method detection level
LUS	land-use study
MCL	maximum contaminant level
MMM	multimedia mitigation
MRSD	mean relative standard deviation
MTBE	methyl tert-butyl ether
NAWQA	National Water-Quality Assessment Program
NWQL	USGS National Water-Quality Laboratory
OCCAS	Orange County California Aquifer Susceptibility (study)
OCWD	Orange County Water District
PCE	tetrachloroethylene
PVC	polyvinyl chloride
QC	quality-control sample
SANA	Santa Ana NAWQA (study unit)
SANCAS	San Jacinto California Aquifer Susceptibility (study)
SANSUS	San Jacinto subunit survey
SAWPA	Santa Ana Watershed Project Authority
SMOW	Standard Mean Ocean Water
SUS	subunit survey
SWRCB	California State Water Resources Control Board
TCA	1,1,1-trichloroethane
TCE	trichloroethylene
TDS	total dissolved solids
ULUS	urban land-use study
USGS	U.S. Geological Survey
VOC	volatile organic compound

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EXECUTIVE SUMMARY

Water-quality samples were collected from 207 wells in the Santa Ana Basin in the Coastal Range Province of southern California to assess the occurrence and distribution of dissolved constituents in ground water as part of the U.S. Geological Survey's National Water-Quality Assessment (NAWQA) program. These wells were sampled during eight studies from 1999 to 2001 that were designed to sample the used water resource at different scales: (1) three subunit surveys (SUS) characterized water quality at a regional scale, (2) two flow-path studies (FPS) focused on spatial and temporal variations in water quality along a flow path, (3) an urban land-use study (LUS) focused on evaluation of water quality in shallow ground water, and (4) two California Aquifer Susceptibility studies (CAS) assessed aquifer susceptibility to contamination.

The Santa Ana Basin is divided into three subbasins; the Coastal Basin, the Inland Basin, and the San Jacinto Basin. In the Coastal Basin, four studies were done; the Coastal Subunit Survey, Coastal Land-Use Study, Coastal Flow-Path Study, and Orange County California Aquifer Susceptibility assessments. The urban land-use study sampled shallow monitoring wells not used for public supply; samples for the other three studies were primarily from deep production wells. In the Inland Basin, there were two studies: the Inland Subunit Survey, which sampled deep production wells and the Inland Flow-Path Study, which sampled deep monitoring and production wells. In the San Jacinto Basin, production wells

were sampled for two studies: the San Jacinto Subunit Survey and the San Jacinto California Aquifer Susceptibility study.

The Coastal Basin includes a relatively small unconfined recharge area and a relatively large confined area where ground-water pumping is the primary source of discharge. Land use is almost entirely urban. The Inland Basin is predominantly unconfined and land use is urban and agricultural. The San Jacinto Basin is largely unconfined and land use is mostly agricultural.

Major-ion composition of ground water is similar in the subbasins, except for shallow ground water in the Coastal Basin sampled for the urban land-use study, ranging between calcium-bicarbonate and sodium-sulfate/chloride water types. Many of these monitoring wells are located in a historical marsh area and water quality reflects the influence of seawater.

Water-quality data discussed in this report are compared with U.S. Environmental Protection Agency (EPA) drinking-water standards, both primary and secondary. The EPA secondary maximum contaminant level (MCL) for dissolved-solids concentration is 500 mg/L. This standard was exceeded in 39 percent of the deep production wells sampled in all three subbasins, and in 92 percent of the urban land-use monitoring wells; one shallow monitoring well had a dissolved-solids concentration of 25,500 mg/L (milligrams per liter). Many of these shallow monitoring wells tap nonpotable ground water; water quality generally reflects the historical saltwater marsh environment in much of the area and the effects of landscape maintenance at many of the sites.

The secondary MCLs for chloride and sulfate are each 250 mg/L. The chloride standard was exceeded in several production wells not used for public supply; one well in the Coastal Basin and in two wells in the San Jacinto Basin. Water from about 40 percent of the coastal urban land-use monitoring wells exceeded the secondary MCL for chloride; the highest concentration was 9,430 mg/L. The sulfate standard was exceeded in five production wells used for irrigation distributed among the three basins. However, 80 percent of the samples from the urban land-use monitoring wells exceeded the secondary MCL for sulfate; the highest concentration was 5,270 mg/L. A potential source of high chloride and sulfate concentrations is residual saltwater from the historical marsh environment.

The MCL for nitrate (as nitrogen) is 10 mg/L. The San Jacinto Basin had the greatest percentage of exceedances for nitrate; water from 22 percent of the production wells sampled for the subunit survey exceeded the MCL. The highest nitrate concentration from these samples was 16.6 mg/L. In the Inland Basin, nitrate concentrations exceeded the MCL in water from 14 percent of the production wells sampled; the highest nitrate concentration was 20.1 mg/L. In the confined Coastal Basin, all municipal-supply wells sampled produced water having nitrate concentrations below 10 mg/L. However, water from 19 percent of the shallow monitoring wells sampled for the urban land-use study had nitrate concentrations exceeding the MCL.

Water-quality samples were analyzed for 22 trace elements. Water from some wells exceeded secondary MCLs for manganese (50 µg/L [micrograms per liter]) and iron (300 µg/L) and (or) proposed MCLs for arsenic (10 µg/L) and

uranium (30 µg/L). Of the 94 production wells sampled for trace elements, 3 irrigation wells in the Coastal Basin produced water that exceeded the secondary MCL for manganese. Water samples from all other production wells were in compliance with EPA standards for all other trace elements, including the proposed MCL for arsenic. However, existing secondary MCLs and proposed MCLs were exceeded in water from some monitoring wells. In the urban land-use assessment, secondary MCLs for iron and manganese were exceeded in water samples from 11 and 20 wells, respectively. Also in the urban land-use assessment, proposed MCLs for arsenic and uranium were exceeded in water from 5 and 12 wells, respectively. In the Inland flow-path study, secondary MCLs for iron and manganese were exceeded in samples from two and seven monitoring wells, respectively.

Radon is a radioactive decay product of radium, which in turn is a decay product of uranium. The EPA has developed a proposed MCL of 300 pCi/L (picocuries per liter) and an alternative MCL of 4,000 pCi/L for radon in drinking water. The proposed MCL applies to areas that do not have multimedia mitigation programs in place that satisfy the requirements of the alternative MCL for indoor air. Water from production wells sampled in all three subbasins exceeded the proposed MCL, including about 95 percent of the wells sampled for the coastal subunit survey. About 75 percent of the sites sampled for the urban land-use study had radon concentrations exceeding the proposed MCL. The alternative MCL for radon was exceeded in a sample from a single public-supply well in the Inland Basin (4,560 pCi/L).

Two U.S. Geological Survey (USGS) laboratory schedules were used for pesticide analyses; schedule 2001 (133 wells sampled) and laboratory code 9060 (92 wells sampled). Pesticides were detected above the laboratory reporting limit (LRL) in 50 percent of the production and monitoring wells sampled in the Santa Ana Basin. Deethylatrazine, simazine, atrazine, tebutiuron, and prometon were the five most commonly detected pesticides in the current USGS studies. All pesticide concentrations detected in these studies were below MCLs established by the EPA. Pesticide detections were most frequent in the unconfined Inland Basin aquifers (83 percent) and least frequent in the confined Coastal Basin aquifers (about 34 percent). Pesticides were detected less frequently in the deep production wells of the Coastal Basin (25 percent) than in the intermediate-depth production wells (43 percent).

The 85 volatile organic compounds (VOCs) analyzed for include solvents, refrigerants, fumigants, disinfection by-products, and gasoline compounds; 38 compounds were detected above the LRL in the wells sampled. VOCs were detected in 115 wells (56 percent) of the 207 wells sampled. Of the 38 VOCs detected, only 13 were detected in more than five wells. The most commonly detected VOCs, in order of detection frequency, were chloroform; trichloroethylene, TCE; 1,1,1-trichloroethane, TCA; trichlorofluoromethane, CFC 11; 1,1,2-trichloro-1,2,2-trifluoroethane, CFC 113; tetrachloroethylene, PCE; bromodichloromethane; methyl tert-butyl ether, MTBE; 1,1-dichloroethene, 1,1-DCE; and 1,2-dichloroethene, 1,2-DCE. VOCs were detected most frequently in production wells in the unconfined Inland Basin (66 percent) and least

frequently in the confined Coastal Basin (48 percent). In the Coastal Basin, VOC detection frequency was not clearly a function of aquifer depth. The only exceedances of EPA MCLs for VOCs occurred in six irrigation wells sampled for the Inland Subunit Survey, and in two deep monitoring wells sampled for the Inland Flow-Path Study.

ABSTRACT

Water-quality samples were collected from 207 wells in the Santa Ana Basin in the Coastal Range Province of southern California to assess the occurrence and distribution of dissolved constituents in ground water as part of the U.S. Geological Survey's National Water-Quality Assessment (NAWQA) program. These wells were sampled during eight studies from 1999 to 2001 that were designed to sample the used water resource at different scales: (1) three studies characterized water quality at a regional scale; (2) two studies focused on spatial and temporal variations in water quality along flow paths; (3) a land-use study focused on evaluation of water quality in shallow ground water; and (4) two studies assessed aquifer susceptibility to contamination.

The Santa Ana Basin is divided into the Coastal Basin, the Inland Basin, and the San Jacinto Basin. The Coastal Basin includes a relatively small unconfined recharge area and a relatively large confined area where ground-water pumping is the primary source of discharge. Land use is almost entirely urban. The Inland Basin is predominantly unconfined and land use is urban and agricultural. The San Jacinto Basin is largely unconfined and land use is mostly agricultural.

Water-quality data discussed in this report are compared with U.S. Environmental Protection Agency (EPA) drinking-water standards, both primary and secondary. Most exceedances of maximum contaminant levels (MCLs) occurred in the shallow, coastal monitoring wells that tap ground water not used for water supply. Water from several irrigation wells in the Inland and San Jacinto basins exceeded the 10 mg/L (milligrams per liter) MCL for nitrate. Water from some wells exceeded secondary MCLs for manganese (50 µg/L [micrograms per liter]) and iron (300 µg/L) and (or) proposed MCLs for arsenic (10 µg/L) and uranium (30 µg/L). Of the 94 production wells sampled for trace elements, 3 irrigation wells in the Coastal Basin produced water that exceeded the secondary MCL for manganese. Water from production wells sampled in all three subbasins exceeded the proposed MCL for radon (300 pCi/L [picocuries per liter]).

Pesticides were detected above the laboratory reporting limit (LRL) in 50 percent of the production and monitoring wells sampled in the Santa Ana Basin. Deethylatrazine, simazine, atrazine, tebuthiuron, and prometon were the five most commonly detected pesticides in the current USGS studies. All pesticide concentrations detected in these studies were below MCLs established by the EPA.

Volatile organic compounds (VOCs) were detected in 115 wells (56 percent) of the 207 wells sampled. Of the 38 VOCs detected, only 13 were detected in more than five wells. The most commonly detected VOCs, in order of detection frequency, were chloroform; trichloroethylene, TCE; 1,1,1-trichloroethane, TCA; trichlorofluoromethane, CFC 11; 1,1,2-trichloro-1,2,2-trifluoroethane, CFC 113; tetrachloroethylene, PCE; bromodichloromethane; methyl tert-butyl ether, MTBE; 1,1-dichloroethene, 1-1-DCE; and 1,2-dichloroethene, 1,2-DCE. The only exceedances of EPA MCLs for

VOCs occurred in six irrigation wells and in two deep monitoring wells sampled in the Inland Basin.

INTRODUCTION

The Santa Ana NAWQA (SANA) study unit is located in the Coastal Range Province of southern California ([fig. 1](#)). The Santa Ana River is the largest stream system in southern California, beginning in the San Bernardino Mountains (which reach altitudes exceeding 10,000 ft) and flowing more than 100 mi to the Pacific Ocean near Huntington Beach. The climate is mediterranean having hot, dry summers and cool, wet winters. Average annual rainfall ranges from 12 in. in the coastal plain, and 18 in. in the inland valley, to 40 in. in the San Bernardino Mountains.

Major water-quality issues in the SANA study unit are total dissolved solids (TDS), nutrient loading (nitrate), and VOCs. In general, the quality of surface and ground water becomes progressively poorer as water moves along hydraulic flow paths. The highest quality water is typically associated with tributaries flowing from surrounding mountains and with ground water recharged by these streams. Water quality is altered by high-salinity water imported from the Colorado River, wastewater discharge, urban runoff, dairy operations (360,000 cows in an area less than 50 mi² upstream from Prado Reservoir), point sources of VOCs, and artificial recharge (Hamlin and others, 1999).

The 2,700-mi² watershed is home to over 4 million people, and the population is expected to increase by more than 50 percent by the year 2020. During the same period, water demand is expected to increase by somewhat less than 50 percent (Santa Ana Watershed Project Authority, 1998).

Ground water is the main source of supply in the watershed, providing about two-thirds of the total water demand (about 1.2 million acre-ft/yr). Imported water from northern California and the Colorado River accounts for about one-quarter of the total consumptive demand. Local surface water provides the remaining supply. Urban water use (63 percent) exceeds agricultural water use (28 percent of total use) in the study area (Hamlin and others, 1999).

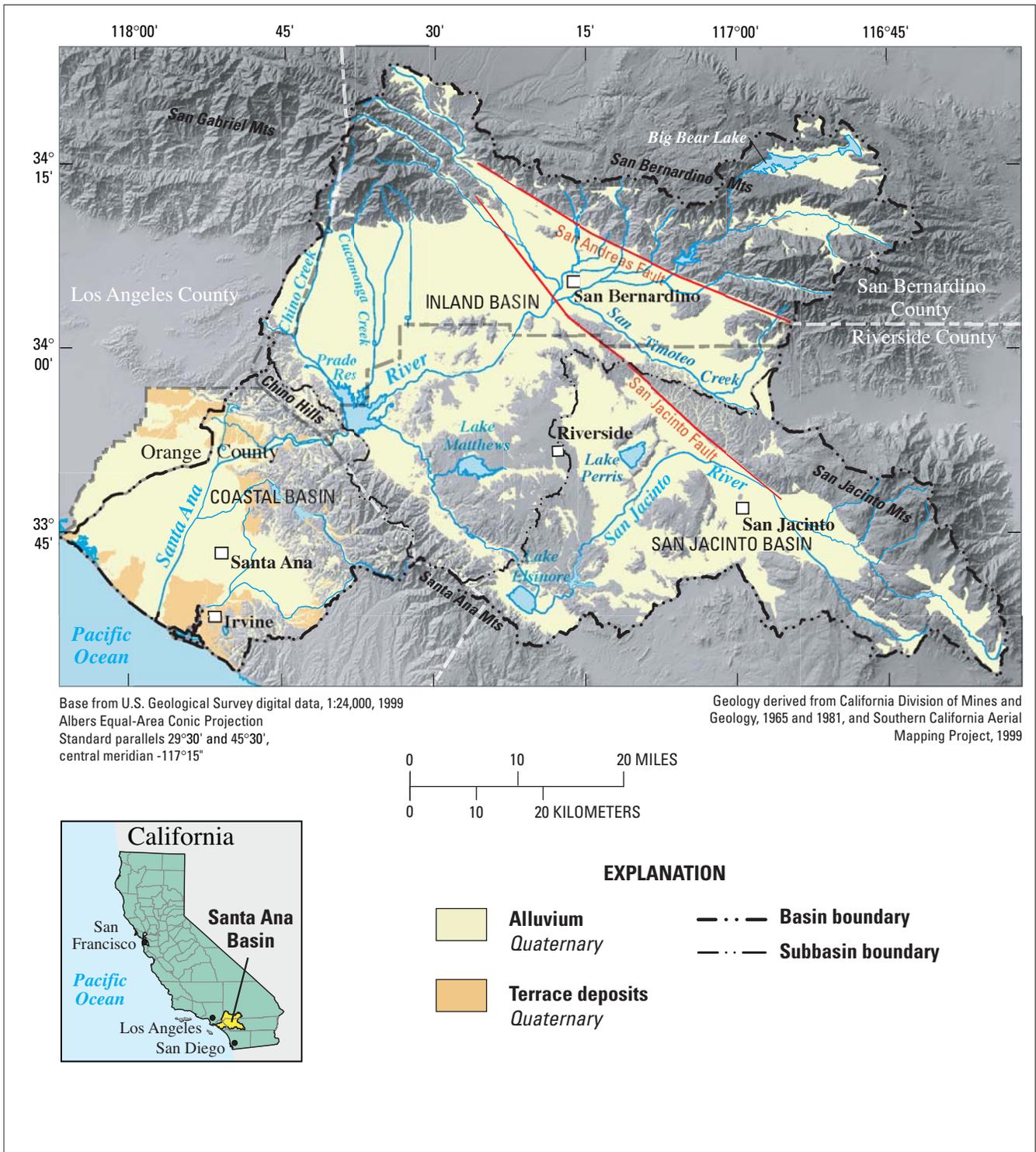


Figure 1. Location of the Santa Ana study unit, subunit study areas, and distribution of alluvial deposits.

The Santa Ana study unit can be subdivided into three primary subunits; the Coastal Basin, the Inland Basin, and the San Jacinto Basin (fig.1). Water-bearing deposits in the alluvium-filled basins are bounded by relatively impervious uplands. Urban and agricultural land uses occur primarily in the alluvium-filled valleys and coastal plain. Land use in the watershed is about 35-percent urban; 10-percent agricultural; and 55-percent open space, primarily steep mountain slopes.

The Coastal Basin occupies the southern third of the approximately 800-mi² coastal Los Angeles Basin. Within this basin, the freshwater-bearing deposits are as great as 4,000 ft thick (Herndon and others, 1997). The Orange County Water District (OCWD) monitors ground-water pumpage (about 300,000 acre-ft/yr) and manages artificial recharge (200,000 to 250,000 acre-ft/yr) to ameliorate historical ground-water overdraft.

The Coastal Basin has been subdivided into the Main Basin and the Irvine subbasin (Herndon and others, 1997). The Main Basin has been divided into forebay (recharge) and pressure (confined) areas on the basis of relative abundance of shallow clay layers (California Department of Public Works, 1934). The forebay area occupies about 50 mi² along, and adjacent, to the Santa Ana River after it leaves the Santa Ana Mountains and is located north and east of the Interstate-5 freeway (fig. 2). The forebay consists of unconsolidated sands and gravels with occasional lenses of clay and silt (Herndon and others, 1997). The clay and silt lenses do not generally impede vertical ground-water flow (Herndon and others, 1997). Spreading basins in the forebay area, operated by the OCWD, provide the primary source of recharge to the ground-water basin. The sources of recharged water are the Santa Ana River and water imported from northern California and the Colorado River. Production from the aquifer system occurs primarily in the confined (pressure) areas of the basin. The main production zones are generally between 300 and 1,500 ft below land surface, with most of the pumpage from the interval between 500 and 1,000 ft. The main production zone is overlain by 300 to 500 ft of deposits which consist primarily of silt and clay, which typically impede vertical ground-water flow (Herndon and others, 1997). Seawater has intruded alluvial aquifers in some coastal areas (Herndon and others, 1997).

Injection-well barriers that utilize freshwater have been installed to prevent further intrusion of seawater into major production zones. Pumpage is the major component of ground-water discharge in the Coastal Basin (Herndon and others, 1997).

The Irvine subbasin is in the southeastern part of the Coastal Basin. The deposits in this subbasin are thinner (typically 200 to 1,000 ft) and substantially finer grained (primarily clay and silt) than those in the Main Basin. The aquifers in the Irvine subbasin are relatively thin, composed of silty sand with lesser amounts of gravel (Herndon and others, 1997). Water quality in the Irvine subbasin is suitable for irrigation but generally not for municipal supply (Nira Yamachika, OCWD, oral commun., 2002). Although less transmissive, deposits in the Irvine subbasin are hydraulically continuous with the aquifers in the Main basin (Herndon and others, 1997).

The Inland Basin is filled with alluvial deposits eroded from the surrounding mountains. The thickness of these deposits ranges from less than 200 to more than 1,000 ft (Wildermuth Environmental, Inc., 2000). Recharge to the basin varies seasonally and is largely from infiltration of runoff from the San Gabriel and San Bernardino Mountains. Much of the runoff is diverted into storm-detention basins, which also operate as ground-water recharge facilities (fig. 3). Surface water imported from northern California and the Colorado River is also used to recharge the ground-water basin. Depth to water ranges from hundreds of feet near the flanks of mountains to near land surface along rivers and in wetland areas. Ground-water discharge occurs primarily by ground-water withdrawal for public supply.

Faults play an important role in the ground-water flow system of the Inland Basin. The San Andreas Fault, which lies along the base of the San Bernardino Mountains, and other faults, which lie along the base of the San Gabriel Mountains and Chino Hills, bound the Inland Basin flow system on three sides. Other faults, such as the San Jacinto Fault, divide the basin into several subbasins. These interior faults locally restrict ground-water flow and control the location of ground-water discharge (Izbicki and others, 1998; Woolfenden and Kadhim, 1997).

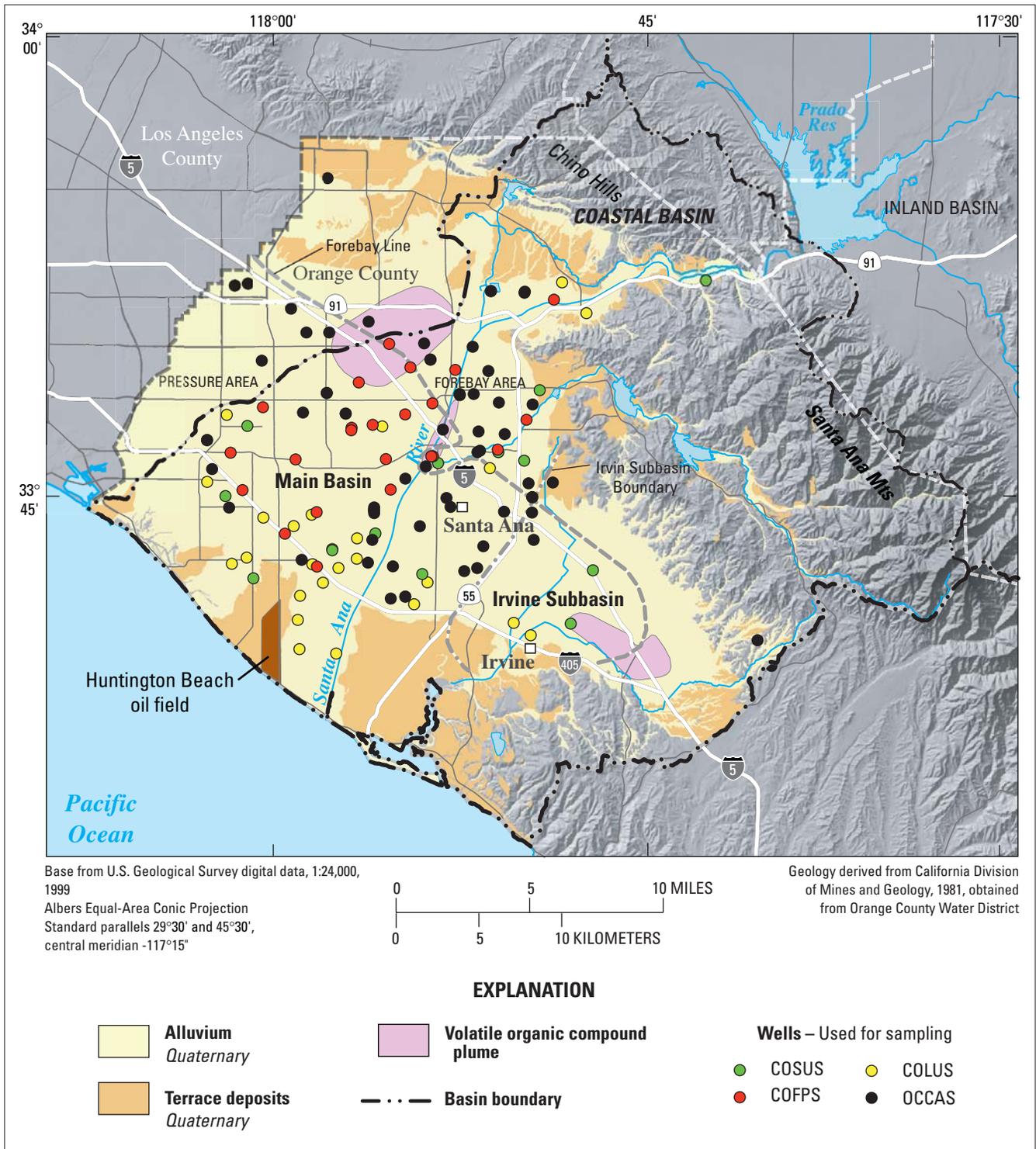


Figure 2. Coastal subunit study area and locations of sampled wells, Santa Ana NAWQA, California.

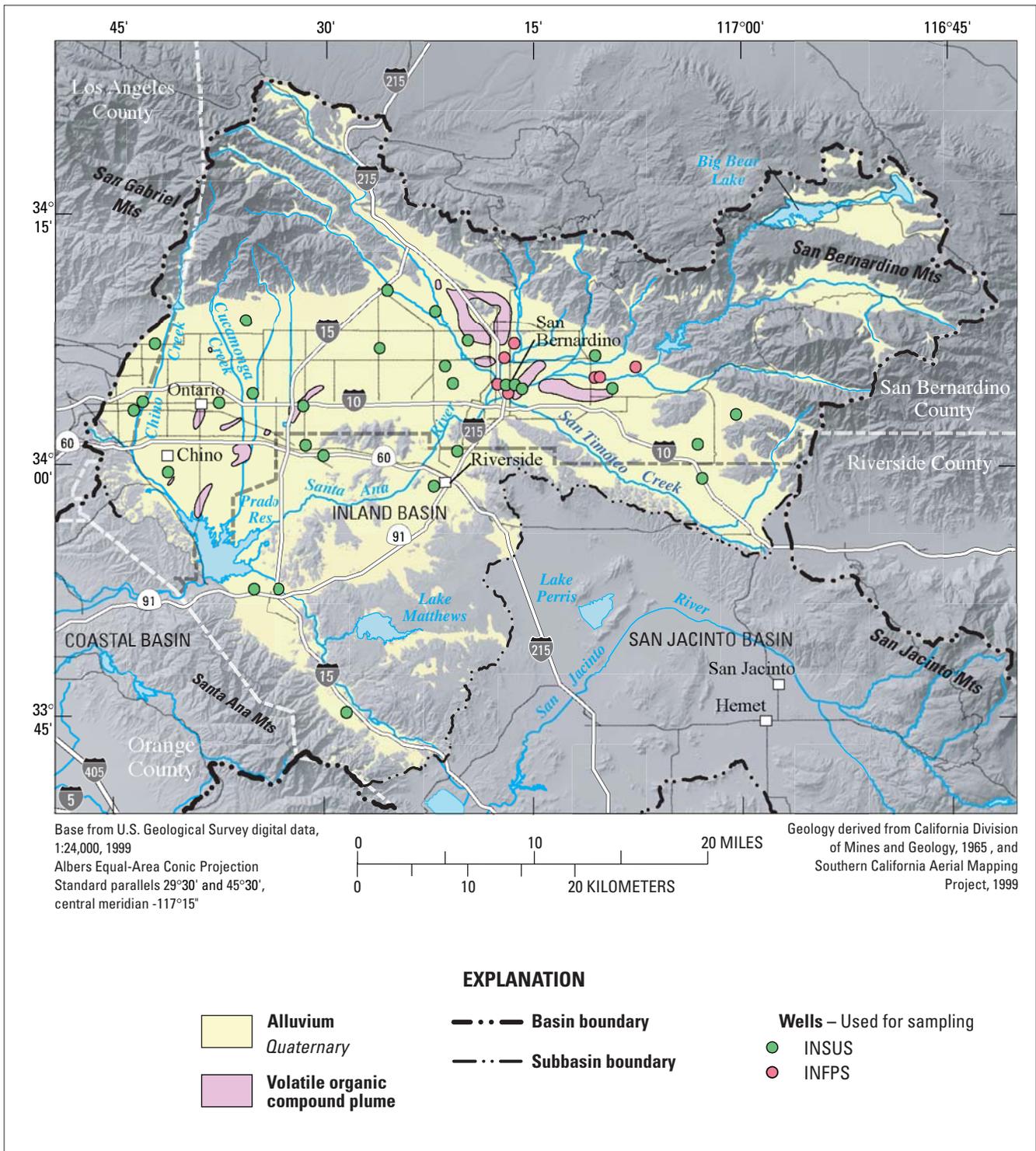


Figure 3. Inland subunit study area and locations of sampled wells, Santa Ana NAWQA, California.

The aquifer system of the San Jacinto Basin consists of a series of interconnected alluvium-filled valleys bounded by steep-sided bedrock mountains and hills. The thickness of deposits in these valleys typically ranges from 200 to 1,000 ft (Wildermuth Environmental, Inc., 2000). Collectively, alluvium covers about one-half of the total area in the subunit. Prior to development, recharge to the flow system was from infiltration of mountain streams, primarily the San Jacinto River. Presently, recharge is largely from irrigation return flows and from percolation ponds filled with reclaimed water. Ground-water discharge occurs primarily by ground-water pumpage. Water levels in the alluvium-filled subbasins are greatly affected by local management practices, including augmentation of ground-water pumpage by use of imported water and recharge with reclaimed water.

In addition to the USGS NAWQA assessment of water quality, numerous local studies have been conducted in the SANA ground-water basin by local, State, and Federal agencies. It is beyond the scope of this report to review those studies.

The Santa Ana Watershed Project Authority (SAWPA) was formed in 1972 to plan and build facilities to protect water quality in the Santa Ana watershed (Santa Ana Watershed Project Authority, 1998). The SAWPA encompasses five major water districts in the basin. There are several local agencies that collect and interpret water-quality data in the Santa Ana Basin; OCWD, Inland Empire Utilities Agency (IEUA), and Eastern Municipal Water District (EMWD). OCWD has implemented programs to recharge the Coastal ground-water basin, has developed new wastewater-treatment processes, and manages a number of programs to protect the quality of available water supplies. OCWD performs about 300,000 analyses per year on more than 15,000 samples collected from about 700 wells in the basin.

The IEUA, formerly Chino Basin Municipal Water District, encompasses several water agencies, including the San Bernardino Municipal Water District and the Western Municipal Water District. The IEUA and Western Municipal Water District are located immediately upstream from OCWD in the Inland Basin. The Chino Basin Water Master manages ground-water use and has implemented programs to reclaim wastewater and to remove salts from areas of saline ground water. The main water-quality issues in this subbasin, as in most of the Santa Ana Basin, are high concentrations of nitrate and dissolved solids.

Additionally, VOC plumes have impacted water quality in several areas. The USGS has conducted studies in the Inland Basin in cooperation with local water agencies to investigate nitrate and VOC contamination of ground water, to evaluate ground-water chemistry and recharge, and to optimize ground-water use and pumpage (Klein and Bradford, 1979; Duell and Schroeder, 1989; Izbicki and others, 1998; Woolfenden and Kadhim, 1997; Rees and others, 1994; Danskin and Freckleton, 1992).

The EMWD is located within the San Jacinto Basin and has implemented programs to reclaim wastewater and optimize ground-water use to reduce dependence on imported water. The USGS has conducted studies in cooperation with EMWD to describe geohydrology and water quality in the basin (Burton and others, 1996; Kaehler and others, 1998).

Purpose and Scope

This report presents data that describe ground-water quality in the Santa Ana study unit of the USGS NAWQA program. The purpose of this report is twofold: (1) to compile, organize, and present data collected during eight ground-water studies conducted in the Santa Ana watershed and (2) to discuss ground-water quality in the context of drinking-water standards established by the U.S. Environmental Protection Agency (EPA). The studies collected data to define overall water-quality conditions in the basins, to define flow paths in the Coastal and Inland Basins, to determine shallow ground-water quality in the Coastal Basin, and to determine the susceptibility of aquifers to potential contamination.

Two hundred and seven wells, of which about two-thirds were used for municipal supply, were sampled between April 1999 and August 2001 during the course of the eight studies. Typical chemical analytes determined included 10 major ions, 6 nutrients, dissolved organic carbon (DOC), 22 trace elements, uranium, radon-222, tritium, stable isotopes, more than 100 pesticides, and more than 80 volatile organic compounds (VOCs). In addition to these determinations, field parameters were measured including water temperature, specific electrical conductance, dissolved oxygen, pH, turbidity, and alkalinity.

Water quality in the three ground-water basins is described overall by using trilinear diagrams and box plots. These data are also discussed in the context of EPA standards established to regulate constituents that may be harmful to human health (primary maximum contaminant levels) or affect the aesthetic quality of drinking water (secondary maximum contaminant levels). Percentages of analytes that exceed EPA drinking water standards are presented for each basin.

Acknowledgments

The authors thank the many water purveyors and companies that allowed the USGS to sample their wells: Agri Empire, Cucamonga County Water District, Diamond Brothers, East Orange Water Company, East Valley Water District, Elsinore Valley Municipal Water District, Fontana Water Company, Irvine Ranch Water District, Jurupa Community Services District, Lake Hemet Municipal Water District, Mesa Consolidated Water District, Serrano Water District, Southern California Water Company, The Irvine Company, University of California at Riverside, West San Bernardino County Water District, Yucaipa Valley Water District; and the cities of Anaheim, Chino Hills, Colton, Corona, Fountain Valley, Garden Grove, Hemet, Huntington Beach, Newport Beach, Nuevo, Ontario, Orange, Pomona, Redlands, Riverside, San Bernardino, San Jacinto, Santa Ana, Tustin, and Westminster.

We also thank the water districts that coordinated sampling efforts within their boundaries: Orange County Water District in the Coastal Basin and Eastern Municipal Water District in the San Jacinto Basin. Without their cooperation, this study would not have been possible.

STUDY DESIGN

NAWQA studies are designed to provide an integrated assessment of water quality and provide data that is consistent with and comparable to data from other NAWQA study units. The suite of analytes for

NAWQA studies is extensive; more than 20 trace elements, 100 pesticides, and 80 volatile organic compounds. In addition, detection limits for VOCs, pesticides, and trace elements are commonly much lower than regulatory guidelines and limits established for drinking water. Quality-assurance and quality-control activities have been designed to guide data-collection methods and to quantify measurement variability, respectively (Koterba and others, 1995).

The SANA ground-water study was divided into three components: (1) a regional assessment of water quality (subunit survey, or SUS), (2) characterization of spatial and temporal variations in water quality along a ground-water flow path (flow-path study, or FPS), and (3) an evaluation of water quality in shallow ground water associated with recent urban development (urban land-use study, or ULUS). Protocols for NAWQA studies are described in detail by Gilliom and others, 1995. Additional wells were sampled for VOCs and tritium-helium in cooperation with the California Aquifer Susceptibility (CAS) program. Three regional SUS assessments were completed in the Coastal (COSUS), Inland (INSUS), and San Jacinto (SANSUS) Basins (figs. 2–4). Variation of water quality in the SUS subbasins is primarily related to hydraulic constraints (for example, confined versus unconfined system, and location along flow paths), distribution and quality of recharge (imported water versus local sources), and occurrence of contaminant sources (type and distribution). Wells sampled for the Coastal flow-path study define radial flow extending from recharge facilities in the upper part of the basin toward the coast (fig. 3). A second flow-path study was completed in the Inland Basin (INFPS) (Dawson, 2002). The Coastal urban land-use study (COLUS) evaluates factors that affect shallow ground-water quality in the immediate vicinity of the wells. VOC and tritium data collected during two CAS studies permit a more detailed evaluation of ground-water flow in the Coastal and San Jacinto Basins.

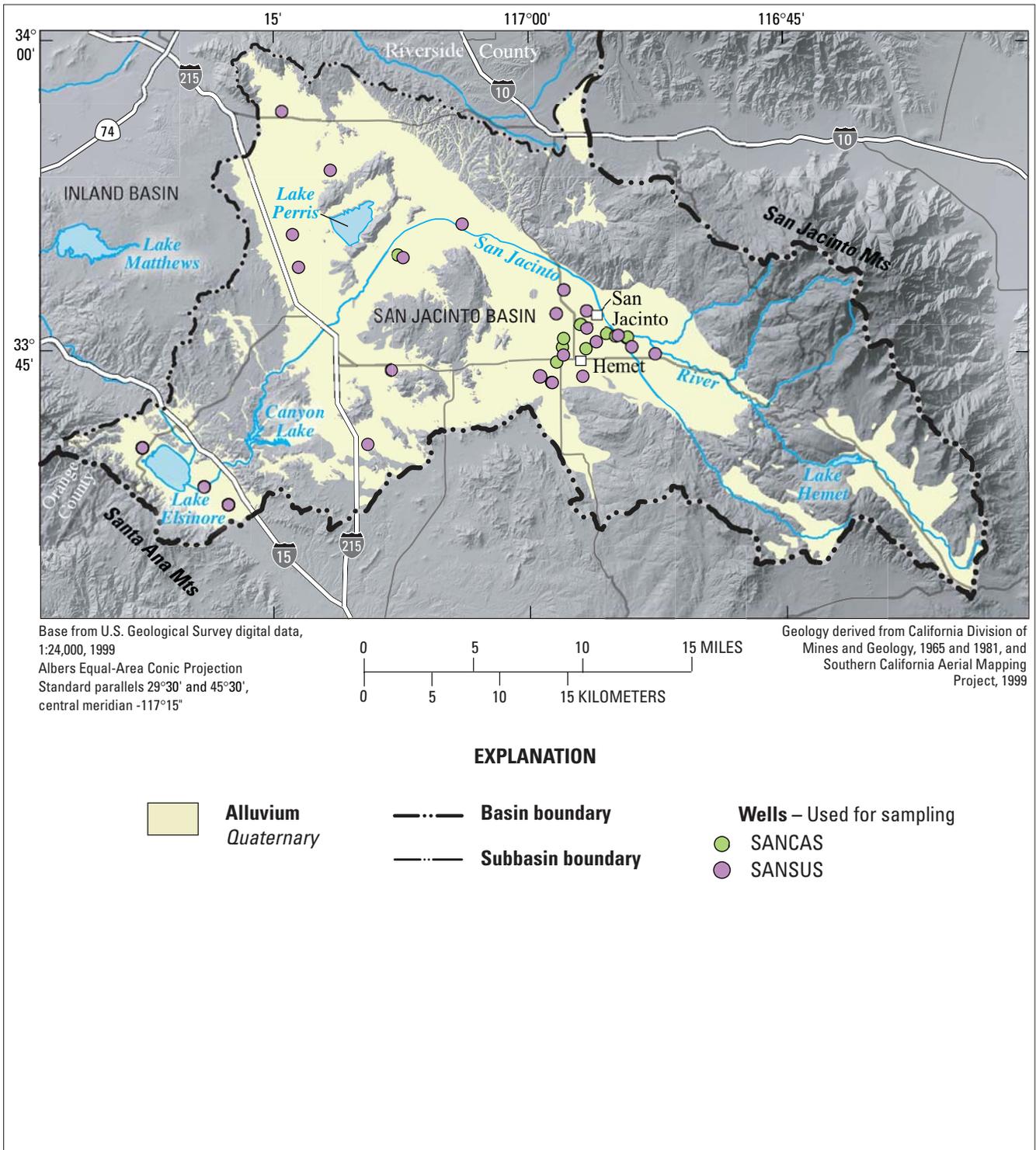


Figure 4. San Jacinto subunit study area and locations of sampled wells, Santa Ana NAWQA, California.

Subunit Surveys

The SANA study provides an integrated, regional assessment of ground-water quality in the Santa Ana watershed. The results of smaller scale studies are evaluated in the context of the regional characterization of ground-water quality. The primary objectives in the selection of wells for NAWQA subunit survey (SUS) assessments are to attain a sampling density of at least one well per 40 mi² (100 km²), randomly select at least 20 wells per SUS, and minimize variability in well type to adequately characterize the quality of the ground-water resource used for public supply (Gilliom and others, 1995). In the Santa Ana watershed, production wells are used for public supply and provide the best definition of water quality in the main aquifer systems. Wells were selected for each SUS using a grid-based program to produce equal-area, random cells (Scott, 1990). The program was used to generate 20 cells in the smaller Coastal Basin (COSUS), and 30 cells each in the Inland (INSUS) and San Jacinto (SANSUS) Basins. An attempt was made to select one well per cell. Wells from adjacent cells were used to populate cells that either had no active wells or contained wells that did not meet NAWQA selection criteria, such as those lacking well-construction data. Twenty wells were sampled during the COSUS assessment, achieving a sampling density of about 1 well per 14 mi² (35 km²). Twenty-nine wells were sampled for the INSUS assessment to achieve a density of about one well per 23 mi² (60 km²). Twenty-three wells were sampled for the SANSUS assessment, resulting in a sampling density of about 1 well per 17 mi² (45 km²).

Flow-Path Studies

The primary objectives of NAWQA flow-path studies (FPS) are to characterize the distribution of water-quality constituents in relation to ground-water flow, improve understanding of the natural and human factors that effect water quality along flow paths, and evaluate the relation between surface- and ground-water quality (Gilliom and others, 1995). When possible, FPS assessments are located at or near existing research sites to take advantage of databases established by previous study.

In both the Coastal and Inland flow-path studies (figs. 2 and 3), the flow paths originate in the “headwaters” of the ground-water basin and extend toward a discharge area. The COFPS was designed to characterize variation in ground-water quality as water moves from recharge facilities located in the forebay of the Coastal Basin toward the natural discharge area at the coast. As a result of urbanization in the basin, pumpage from production wells is now the primary component of ground-water discharge. Sources of recharge include treated wastewater, imported water, runoff from urban, agricultural, and undeveloped areas. Ground-water flow in the deep aquifers becomes mostly confined a few miles from the recharge facilities and is generally insulated from overlying land uses. The COFPS is defined by data from 23 wells that are completed in the intermediate-depth aquifer zone; most depths are between 200 and 800 feet, and average depth is about 500 ft. Data from these wells were used to determine the extent of recharged water in the main ground-water basin and indicate large-scale replacement of native ground water by imported water (Shelton and others, 2001). Results from studies in the Coastal Basin also indicate that anthropogenic chemicals (such as VOCs and tritium) are good tracers of imported recharge water in the ground-water system (Shelton and others, 2001).

The INFPS is located in the Inland Basin along a losing reach of the Santa Ana River, ending near the San Jacinto Fault, which forms a partial barrier to ground-water flow. Recharge originates in the San Gabriel and San Bernardino Mountains and is relatively free of contamination. Potential contaminant loading in this unconfined system is from overlying land use, which is primarily urban. The study is based on two convergent flow paths defined by 20 monitoring wells and 7 production wells. Data from six of the seven production wells were collected as part of the INSUS assessment. The flow paths originate near the San Gabriel and San Bernardino Mountains and converge in a discharge area near the city of San Bernardino (fig. 3). Numerous VOC plumes in the Inland Basin illustrate the length-scale over which point sources of contaminants affect ground-water quality, typically 3 to 6 miles (5 to 10 km) (fig. 3).

Urban Land-Use Studies

The primary objectives of NAWQA Land-Use Studies are to assess the occurrence of water-quality constituents in recently recharged ground water in a specific land-use setting and to develop an understanding of the natural and human factors that affect ground-water quality (Gilliom and others, 1995). In general, between 20 and 30 wells are sampled for each LUS.

The Coastal Urban LUS (COLUS) was designed to assess the effect of recent urban development on shallow ground-water quality in the Coastal Basin. Areas of new urban development were delineated by comparing residential and urban land uses from mid-1960s topographic coverages with those from 1993 coverages generated by the Southern California Association of Governments. These areas were surrounded by buffer zones to exclude potential effects from highways and railroads and then subdivided into 30 random, equal-area cells using a grid-based program (Scott, 1990). This analysis yielded a total area of 15 mi² (39 km²), in which 31 shallow wells were drilled. Wells were located at least 0.6 mi (1 km) apart to avoid the potential effect of overlapping land uses on ground-water quality (Squillace and Price, 1996). The wells were constructed to sample the upper 10 to 15 ft of the unconfined aquifer (water-table) system and were generally less than 25 ft deep. Twenty-six wells were sampled as part of the COLUS assessment.

California Aquifer Susceptibility Studies

In response to concern about potential degradation of ground-water quality, the California State Water Resources Control Board (SWRCB) implemented the California Aquifer Susceptibility (CAS) program with the objectives of assessing water quality and determining the susceptibility of ground water used for public supply to contamination resulting from anthropogenic activities. The sampling program utilizes age-dating and low-level VOC analysis to evaluate the condition of the ground-water resource. This comprehensive ground-water monitoring plan was developed after public-supply wells became unusable when methyl tert-butyl ether (MTBE) and industrial solvents were detected in well water. The USGS NAWQA program is collaborating with the SWRCB,

the California Department of Health Services (DHS), the California Department of Water Resources (DWR), and the Lawrence Livermore National Laboratory (LLNL) to implement the CAS assessment.

The CAS studies utilize estimates of water age, coupled with low-level VOC analysis conducted by the USGS, to evaluate the susceptibility of public-supply wells and, by inference, the potential for assessment of the contamination of specific aquifers (Shelton and others, 2001). These studies rely on tritium-helium analysis conducted by LLNL to estimate ground-water age. Age dating is used to determine the presence of young water (recharged within 50 years) in the well. In some cases, the presence of low-level VOC concentrations may provide early warning of contamination moving toward a public-supply well. These data can be evaluated in relation to location of potential sources of contaminants and to hydrogeology in order to determine factors that control vulnerability of the ground-water resource. Two CAS studies were done in the Santa Ana Watershed; the OCCAS study and the SANCAS study. The OCCAS study encompassed wells in Orange County and includes an area slightly larger than the COSUS study ([fig. 2](#)). The SANCAS study utilized production wells located in the San Jacinto Basin.

STUDY METHODS

Description of Sampled Wells

Only production wells were sampled for the SUS, COFPS, and CAS assessments: most of the wells sampled were municipal- supply wells and were determined to provide the best representation of the ground-water resource in the Santa Ana Watershed used for public supply. Municipal wells are the primary source of water supply. A smaller number of domestic and irrigation wells were used to obtain geographic coverage in areas where municipal-supply wells were not available.

A mix of production and existing monitoring wells were sampled for the INFPS. Monitoring wells were installed and sampled for the COLUS assessment. Well-construction data for these eight studies are summarized in Appendix 1.

Unique NAWQA identification numbers (IDs) were assigned to each well sample using a three-letter prefix based on the study and a numerical suffix representing sampling order. For example, the first well sampled for the COSUS study was given the ID COS-1. Prefixes assigned for the other studies were COL (COLUS), COF (COFPS), INS (INSUS), INF (INFPS), OCC (OCCAS), SAS (SANSUS), and SAC (SANCAS).

One hundred and twenty-three wells were sampled during studies in Orange County, which includes the Coastal Basin ([fig. 2](#)). Twenty production wells sampled for the COSUS study included 17 municipal-supply wells and 3 irrigation wells. These wells ranged in depth from 98 to 1,550 ft; median depth was 910 ft. Screened intervals in these wells ranged from 24 to 1,040 ft; median screen length was 575 ft. Of the 23 wells sampled for the COFPS assessment, 19 were municipal-supply wells, 3 were irrigation wells, and 1 was an industrial well. These wells ranged in depth from 214 to 1,310 ft; median depth was 447 ft. Screened intervals in these wells ranged from 9 to 780 ft; median screen length was 161 ft. One well (COF-8) was previously sampled as part of the COSUS study (COS-11). Fifty-six municipal-supply wells were sampled for the Orange County CAS (OCCAS) study and consisted entirely of municipal-supply wells. These wells ranged in depth from 306 to 1,132 ft; median depth was 495 ft. The screened intervals in these wells ranged from 26 to 1,132 ft; median screen length was 495 ft. Five of the OCCAS wells were previously sampled as part of the COSUS study; OCC-3 (COS-2), OCC-7 (COS-20), OCC-17 (COS-18), OCC-20 (COS-19), and OCC-26 (COS-6). Twenty-six monitoring wells were sampled as part of the COLUS study. These monitoring wells ranged in depth from 18.5 to 143.5 ft; median depth was 24 ft. Most of the well screens are 5 ft long; however, several wells were installed with 10-foot screens. The tops of the screens were generally set about 5 ft below the water table.

Fifty wells were sampled during studies conducted in the Inland Basin ([fig. 3](#)). The 29 wells sampled for the INSUS assessment included 23 municipal-supply wells, 5 domestic wells, and 1 irrigation well. Six of the INSUS wells are along one of the two flow paths selected for the INFPS. Data from

these wells (INS-5, -18, -19, -20, -27, and -28) were evaluated in conjunction with data collected for the INFPS. The additional 21 wells sampled for the INFPS included 20 monitoring wells and 1 municipal-supply well. Most of the monitoring wells have a 10- to 20-foot screen and casing depths between 45 and 950 ft; median well depth was 455 ft. The depths of production wells used for the INFPS ranged from 396 to 1,020 ft; median depth was 580 ft. Screened depth for these wells ranged from 92 to 434 ft; median screen length was 250 ft. The production wells sampled for the INSUS study ranged in depth from 225 to 1,180 ft; median depth was 585 ft. Screened length for these wells ranged from 50 to 740 ft; median screen length was 266 ft.

Thirty-four wells were sampled for studies conducted in the San Jacinto Basin ([fig. 4](#)). No wells were sampled in the Lake Hemet area because only a few production wells tap shallow alluvium (about 350 ft thick) in this part of the basin. The 23 wells sampled for the SANSUS study included 18 municipal-supply wells and 5 irrigation wells. Eleven municipal-supply wells were sampled as part of the San Jacinto CAS (SANCAS) study. The production wells sampled for the SANSUS assessment ranged in depth from 328 to 1,720 ft; median well depth was 696 ft. Screened length for these wells ranged from 154 to 1,320 ft; median screen length was 457 ft. Production wells sampled for the SANCAS study ranged in depth from 580 to 1,696 ft; median well depth was 1,030 ft. Screened length for these wells ranged from 200 to 1,312 ft; median screen length was 710 ft.

Municipal-supply, domestic, and irrigation wells were constructed of steel casing that may be a source of iron, manganese, and other dissolved metal species in the sampled water. No correlation was observed between VOC detections and type of motor lubrication (water or oil) for the sampled wells. Shallow monitoring wells for the COLUS study were installed with a hollow-stem auger rig to avoid alteration of water quality by drilling fluids typically used during installation of production wells. The deep monitoring wells sampled for the INFPS were installed with a hydraulic rotary rig using bentonite drilling mud. Monitoring wells were constructed of threaded, 2-inch PVC casing to avoid use of glue, which is a potential source of VOC contamination in well water.

Samples from production wells were collected from discharge valves located as close to the well head as possible and before any inline water treatment, such as chlorination. Monitoring wells were sampled using a stainless-steel submersible pump that maintained positive pressure on the water. Sampling lines consisted of Teflon® tubing.

Within each basin, wells were selected to sample different zones of the ground-water system. Wells for the urban land-use study tap shallow ground water in recently urbanized areas of the Coastal Basin. This water is not used for public supply or irrigation. Monitoring wells near the coast may reflect pre-development conditions, during which much of the area was a saltwater marsh. COFPS and some OCCAS wells were completed in an aquifer of intermediate depth used for public supply. Most subunit survey and CAS wells tap main, deep aquifer systems developed for public supply in the Coastal, Inland, and San Jacinto Basins. The INFPS monitoring wells have 20-foot screens installed in the main, deep aquifer zone.

Sample Collection and Analysis

Water-quality samples were collected between April 1999 and August 2001 following NAWQA guidelines established for ground-water data collection (Koterba and others, 1995). To ensure that the well had been completely purged, approximately three casing volumes were removed prior to sample collection. During purging, field parameters including water temperature, specific conductance, dissolved oxygen, and pH (Appendix 2) were monitored in a flow-through chamber until measurements stabilized, indicating that a representative sample could be collected. For all sites except one, samples were collected using Teflon® tubing and stainless steel fittings. One irrigation well (COS-9) in the COSUS study could be run only for several minutes at a time. A composite sample was collected at this site from a spigot at the well head and later split into sub-samples for processing and analysis.

Samples collected for determination of major ions, nutrients, and trace elements were filtered using a 0.45- μm capsule filter. The cation and trace-element samples were adjusted to a pH of 2 using nitric acid. Most samples for dissolved organic carbon (DOC) determination were collected in a stainless steel or Teflon® chamber and filtered through a 0.45- μm silver membrane. DOC samples collected for the COLUS assessment were processed using capsule filters as recommended by interim NAWQA protocols in effect at that time. All nutrient and DOC samples were stored in a sealed cooler on ice and transported to the NWQL for analysis. Pesticide samples were either filtered in the field using a glass-fiber filter in an aluminum filter assemblage or sent to the NWQL for filtering prior to analysis. Pesticide samples were collected in 1-L baked amber glass bottles and chilled with ice during storage and transport to the NWQL. Unfiltered VOC samples were collected in 40-mL septum vials leaving no air space, preserved with 1:1 hydrochloric acid, and chilled with ice. Temperature of the chilled samples was maintained at 4 degrees Celsius ($^{\circ}\text{C}$) to minimize the potential for chemical and (or) biological degradation of dissolved constituents. Radon samples were collected by inserting a syringe through a septum in the pressurized sample line and allowing 10 mL of water to collect in the chamber. This sample was then injected below mineral oil in a glass scintillation vial to prevent degassing of radon. Alkalinities were determined in the field by incrementally titrating a filtered sample with a standard solution of sulfuric acid to pH 4.5.

After sampling at each site, the Teflon® tubing was cleaned using a 0.1-percent solution of nonphosphate detergent. The tubing was then rinsed using about 3 gal (10 L) of tap water followed by de-ionized water. After cleaning, the tubing was stored in a clean, sealed, plastic bag. The DOC and pesticide filtration assemblies and radon sampler were also rinsed using the detergent solution, followed by tap water and de-ionized water. The pesticide filtration assembly was given a final rinse using pesticide-free methanol, wrapped in aluminum foil, and stored in ziplock plastic bags.

The samples were analyzed at the USGS National Water-Quality Laboratory (NWQL) for inorganic and organic constituents. The following analytical methods were used: inorganics by various methods (Fishman and Friedman, 1989; Fishman, 1993); DOC by UV-promoted persulfate oxidation and infrared spectrometry (Brenton and Arnett, 1993); radon-222 by liquid scintillation counting (American Society for Testing and Materials, 1992); pesticides by solid-phase extraction (SPE) technology on a C-18 cartridge and gas chromatography/mass spectrometry (Zaugg and others, 1995); and VOCs by purge and trap capillary gas chromatography/mass spectrometry (Rose and Schroeder, 1995). In addition to the established analytical schedule used for pesticides, a provisional analytical schedule was used for the COSUS, COLUS, INSUS, and SANSUS assessments. This method is described by Furlong and others (2001).

Quality Control

Quality-control samples were collected and analyzed to qualify the interpretation of water-quality data and to describe bias and variability in data associated with sample collection, processing, transportation, and laboratory analysis (Koterba and others, 1995). Blank samples (blanks) consisting of inorganic- and organic-free water were analyzed by the same methods used for ground-water samples. Four types of blanks were collected; field, source-solution, equipment, and trip. Quality-control sample data from eight ground-water studies in the Santa Ana River Basin from 1999 to 2001 were used for this analysis (Appendix 3). Data for constituents that were questionable on the basis of field-blank analyses were identified and are summarized in Appendix 3.

The USGS NWQL collects quality-control data on a continuing basis to determine long-term method detection levels (LT-MDLs) and laboratory reporting levels (LRLs). These values are re-evaluated on an

annual basis using current quality-control data and may change periodically. The LT-MDL controls false positive error. The chance of falsely reporting a concentration greater than the LT-MDL for a sample that did not contain an analyte is 1 percent or less. The LRL controls false negative error. The chance of falsely reporting a nondetection for a sample that contained an analyte at a concentration equal to or greater than the LRL is 1 percent or less (Childress and others, 1999). LRLs vary for different analytes in relation to chemical behavior and may change when laboratory analytical techniques are modified or new instrumentation is used. Additionally, some concentrations below the LRL are reported by the NWQL when specific analytical criteria were met, and these concentrations are compiled in separate appendixes. LRLs are generally twice the value of LT-MDLs (Childress and others, 1999).

Field-blank data were used to evaluate potential sample contamination and bias introduced during sample collection and analysis. Field blanks were prepared on site using water that was certified free of the selected constituents. The blank water was pumped through the sampling equipment, processed, and transported using the same methods used for the ground-water samples. Fourteen field blanks were prepared and analyzed for major ions, 14 for trace elements, 9 for DOC, 14 for pesticides, and 26 for VOCs. A constituent may be of potential concern if it is detected in one or more blanks and is detected in ground-water samples, and the minimum concentration detected in ground water is less than the maximum concentration detected in the blanks. Concentrations of analytes in ground water that were detected in a blank and were below the LRL are flagged in tables listed in the appendixes.

Six major ions were detected in blanks at concentrations lower than the minimum concentration detected in ground-water samples (Appendix 3A). Therefore, major inorganic constituent concentrations appear to be unaffected by contamination or bias.

Five nutrients and DOC were detected in blanks and in ground water, and the maximum concentration detected in the blanks was greater than or equal to the minimum concentration detected in ground-water samples (Appendix 3A). With the exception of ammonia plus organic nitrogen, the concentrations detected in blanks were below the respective laboratory reporting limits (LRLs); concentrations below LRL are qualified as estimated (E) in the Appendixes. The maximum concentration of ammonia plus organic nitrogen was 0.33 mg/L, which is greater than the LRL of 0.1 mg/L; concentrations in ground-water samples below 0.33 mg/L may be less than the reported value. Detections of nutrients at or near the LRL are well below the applicable EPA maximum contaminant levels (MCLs), and therefore do not affect interpretation of nutrient data.

Seven trace elements were detected in blanks and ground water (Appendix 3A). Barium was detected in blanks, but at concentrations lower than the minimum concentration detected in ground-water samples. Selenium was detected in a field blank at a concentration below the LRL; concentrations in ground water below the LRL are qualified as estimated. Boron and manganese were detected in a single field blank that was prepared 2 hours after sampling an INFPS well that had high concentrations of both constituents. There were a number of other constituents, especially VOCs, detected in the same field blank. These detections may indicate carry-over of constituents from the previously sampled well. Boron and VOC concentrations were greater in ground water from the next well sampled after blank preparation; given the relatively large volume of water passed through the sampling apparatus during the sampling of a well in comparison with the volume of blank water used, the concentration in this sample is considered representative of concentration in ground water. The manganese concentration, however, in water from the next well was lower than that observed in the blank; this value may reflect carryover and is flagged with braces in Appendix 7. Manganese was not detected in two wells subsequently sampled, indicating adequate cleaning of the sampling and processing equipment.

Aluminum, copper, and zinc were each detected in two or more blanks, the maximum concentration was greater than both the LRLs and the minimum concentration detected in a ground-water sample (Appendix 3A). Ground-water samples that had concentrations near the maximum blank concentrations may not represent actual concentrations in ground water. Concentrations observed in blanks were well below applicable MCLs, and therefore do not affect interpretations of trace-element data presented in this report.

Two pesticides were detected in field blanks and in ground-water samples; concentrations detected in the field blanks were above the LRLs and greater than the minimum concentration detected in ground-water samples (Appendix 3A). Although detected in a field blank collected as part of the INSUS study (Appendix 3B), p,p'-DDE was detected only in ground-water samples collected as part of the COFPS and COLUS assessments. Considering the separation in time and space of these studies, the detection of p,p'-DDE in a field blank is not considered related to detections in ground water. Molinate was detected in a field blank and in ground-water samples collected as part of the SANSUS study (Appendix 3B). The field blank was prepared subsequent to sampling a well where molinate was not detected; the molinate concentration in the blank was more than ten times higher than the LRL. The occurrence of a relatively high concentration in the blank and non-detection in the well previously sampled suggests that contamination was limited to the blank. No ground-water samples were collected after the field blank was collected.

Eighteen VOCs were detected in field blanks (Appendix 3A); of these, 17 were also detected in ground-water samples. Because of the large number of VOCs detected in field blanks, the data were evaluated on a study-by-study basis (Appendix 3B). Concentrations in blanks for each study were compared with concentrations detected in ground-water samples from the same study. If the concentration of a VOC detected in a blank sample was greater than the minimum concentration in associated ground-water samples, then the concentration(s) determined for ground water may be influenced by contamination.

If a VOC was detected in a field blank in a particular study, then the concentration detected in the field blank was compared with the concentration detected in the associated source-solution blank. If the source solution was identified as the source of the detection in the field blank, then contamination of water samples by the VOC was not of concern in that study. If the detection could not be related to a detection in the source solution, the concentration in the field blank was compared to the concentration detected in ground-water samples collected prior to the blank for possible carryover. If carryover was identified as the cause of the detection in the blank, then subsequent ground-water samples and subsequent field blanks were evaluated for evidence of additional carryover. Values potentially affected by carryover are flagged (identified by braces) in the appendixes. Alternatively, if a detection in a blank was above or near the LRL, and was accompanied by many nondetections in ground-water samples obtained prior to and subsequent to the field blank, then the contamination was assumed to be limited to the blank. And finally, if a detection in a blank could not be related to the source solution, to carryover, or to contamination limited to the blank, then all ground-water samples with concentrations lower than the maximum blank value are of potential concern.

Many of the VOCs detected in field blanks were not related to concentrations detected in ground-water samples. Toluene in the COLUS blanks and chloroform in the OCCAS blanks are related to contamination in the source solution. PCE and TCE in the INSUS blanks and chloroform, carbon disulfide, isopropyl benzene, and n-propylbenzene in the INFPS blanks are attributed to carryover, but affect only the field blanks. Two of the VOCs detected in field blanks were accompanied by numerous nondetections in ground-water samples obtained before and after the field blank; CFC 11 in the OCCAS study and INFPS assessment, and TCE in the INFPS assessment.

There are 5 VOCs that may have contaminated both blanks and ground-water samples. Benzene and ethylbenzene detected in INFPS field blanks were

attributed to carryover that may have affected a subsequent ground-water sample. Toluene in the COSUS, OCCAS, and INFPS field blanks; MTBE in the COLUS field blanks; and chloromethane in the COFPS field blanks could not be attributed to a specific cause. The values that may be affected by contamination are flagged (placed in braces) in Appendixes 11 and 12. Flagged concentrations were not excluded from computation of detection frequencies.

Replicate samples were collected to assess variability of the analyses for inorganic constituents, nutrients, dissolved organic carbon (DOC), pesticides, and VOCs. The mean relative standard deviation (MRSD) was used for this assessment, which is defined as 100 times the standard deviation divided by the mean concentration for each replicate pair of samples. If one value in a sample pair was reported as a nondetection and the other value was reported as an estimate below the LRL, the MRSD was set to zero because the values are mathematically identical. If one value in a sample pair was reported as a nondetection and the other value was greater than the LRL, then the nondetection value was set equal to one-quarter of the LRL and the MRSD was calculated (Childress and others, 1999). The MRSDs for all constituents except nickel (about 28 percent) were less than 20 percent; most were below 10 percent (Appendix 3C). Values of MRSD less than 20 percent are considered acceptable in these studies. High MRSD values for a constituent may indicate analytical uncertainty at low concentrations, particularly for concentrations below the LRL.

Surrogates (compounds that behave similarly to pesticide or VOC analytes, but are not usually present in ground water) were added to all pesticide and VOC samples at NWQL before sample analysis to evaluate the accuracy of laboratory analytical methods. The mean recoveries of the surrogates in all ground-water and quality-control samples analyzed for pesticide and VOCs were between 70 and 130 percent, which is considered acceptable.

Field- and laboratory-spike samples are made by adding solutions containing known amounts of pesticides and VOCs to replicate ground-water samples. Spike recoveries for these analytes are used to evaluate bias of the analytical results related to matrix interference or methods of sample collection and analysis. Replicates of pesticide and VOC field-spiked samples also were collected. The compounds with relatively low recoveries are of potential concern if environmental concentrations are close to the MCLs; a non-exceedance of an MCL could be falsely indicated. Compounds at concentrations below established MCLs and with recoveries less than 70 percent were either not detected in environmental samples or were detected at concentrations less than one tenth of the MCL, and all recoveries were greater than 20 percent. Therefore, it is unlikely that there is false under-reporting of MCL exceedances for these compounds. The compounds with relatively high recoveries are of potential concern if the environmental concentrations exceed MCLs, since a high recovery could falsely indicate an exceedance of MCL. With the exception of benzene and naphthalene, there were no exceedances of MCLs for compounds with recoveries above 130 percent. If corrected for high recoveries, benzene (523 percent) and naphthalene (159 percent) data also are below MCLs.

Concentrations of forty-seven pesticides (laboratory schedule 2001) were measured in field-spiked samples; 42 of these had mean spike recoveries between 70 and 130 percent (Appendix 3F). The mean relative standard deviation of all pesticide-spike replicate pairs was less than 10 percent. Most pesticides that had mean recoveries in spiked samples of less than 70 percent or greater than 130 percent were not detected in ground-water samples. Spike recovery for carbaryl was slightly high (152 percent), but correction for this did not affect carbaryl detection frequency. Carbofuran also had a slightly high mean

recovery (141 percent), but it was not detected in ground-water samples. Mean recoveries of three pesticides p,p' DDE, permethrin, and disulfoton were lower than 70 percent (49, 54, and 58 percent, respectively), indicating that these pesticides may not have been detected if present in low concentrations in some ground-water samples. The pesticide p,p' DDE was detected in several samples at concentrations below the LRL in the COLUS and COFPS assessments; permethrin and disulfoton were not detected in any ground-water samples.

Concentrations of sixty-five pesticides (laboratory code 9060) were measured in laboratory-spiked samples because field-spike solutions were not available; forty-four of these had mean recoveries between 70 and 130 percent (Appendix 3G). Of the pesticides detected in ground-water samples, imazethpyr was only present in concentrations less than the LRL and had a mean recovery of 149 percent, indicating that low concentrations of imazethpyr may be overestimated. Five other pesticides had mean recoveries greater than 130 percent, but they were not detected in ground-water samples. The mean recoveries of 16 pesticides were less than 70 percent (21 to 68 percent), indicating that these pesticides may not have been detected if present in low concentrations in some ground-water samples. One of these pesticides, deisopropylatrazine had a low mean recovery (49 percent), but it was detected in 23 ground-water samples; 18 detections were below the LRL. None of the other 15 pesticides with low mean recoveries were detected in ground-water samples. The MRSD of the replicate pairs for five pesticides was greater than 20 percent (Appendix 3G); these five pesticides also had low mean recoveries, less than 70 percent. Of these pesticides, only deethyldeisopropylatrazine was detected at a concentration above the LRL.

Eighty-five VOCs were evaluated with field-spiked samples; 51 had mean recoveries between 70 and 130 percent (Appendix 3H). The mean recoveries of 12 VOCs were high (144 to 701 percent). Eight of the 12 VOCs were detected in ground-water samples; m- and p- xylene, naphthalene, sec-butyl benzene, dichlorodifluoromethane, iso-propylbenzene, benzene, methyl acrylonitrile, and n-propylbenzene. Naphthalene, iso-propylbenzene, methyl acrylonitrile, and n-propylbenzene were detected only in one well. Concentrations determined for compounds with high recoveries may be over-estimated in samples relative to actual concentrations in ground water. The mean recoveries of 21 VOCs were low (56 to 69 percent), indicating that they may not have been detected if present in low concentrations in ground-water samples. Of these 21 VOCs, 7 were detected in ground-water samples; methylene chloride, cis-1,2-dichloroethylene, 1,1-dichloroethylene, o-xylene, trichloroethylene, 1,1-dichloroethane, 1,3,5-trimethylbenzene, and trans-1,2-dichloroethylene. The MRSDs of the replicate pairs for all but one VOC (dichlorodifluoromethane) were less than 20 percent (Appendix 3). Field-spiked samples of dichlorodifluoromethane had a mean relative standard deviation of 23 percent, and also a high mean recovery of 181 percent. Dichlorodifluoromethane was detected in only one well at a concentration near the LRL.

In summary, field-blank data indicate that major inorganic data were unaffected by contamination or bias. Based on field-blank results, concentrations of ammonia plus organic nitrogen greater than 0.33 mg/L may be over-estimated; results for the remaining nutrients and DOC do not affect interpretation of the data. Environmental concentrations of seven trace elements detected in blanks (barium, selenium, boron, manganese, aluminum, copper, and zinc) are well below MCLs and interpretation of the data was not affected. Two pesticides (p,p'-DDE and molinate) were detected in blanks; contamination appeared to be limited to the blanks. Eighteen VOCs were detected in field blanks; most of these VOCs were not related to concentrations detected in ground-water samples. Five VOCs may have contaminated both blanks and ground-water samples; benzene, ethylbenzene, toluene,

MTBE, and chloromethane. Mean relative standard deviations (MRSDs) for replicate samples were low for all constituents except nickel. High MRSD values may indicate analytical uncertainty at low concentrations. Most mean spike recoveries were within acceptable ranges for pesticides. Detection frequencies were not affected for pesticides with high spike recoveries. Pesticides with low spike recoveries (p,p'-DDE, permethrin, disulfoton, deisopropylatrazine, and several others) may not be detected if present in low concentrations in ground water. Eight of the twelve VOCs that had high mean spike recoveries were detected in ground-water samples; these concentrations may be over-estimated. The mean spike recoveries of 21 VOCs were low, indicating that they may not have been detected if present in low concentrations. Seven of these 21 VOCs were detected in ground water; methylene chloride, cis-1,2-dichloroethylene, 1,1-dichloroethylene, o-xylene, trichloroethylene, 1,1,1-dichloroethane, 1,3,5-trimethylbenzene, and trans-1,2-dichloroethylene.

GROUND-WATER QUALITY

In this section of the report constituents in ground water are discussed in groups of related analytes; major ions, nutrients and dissolved organic carbon, trace elements, isotopes, pesticides, and VOCs. Major-ion data are used to classify water types. The discussion of nutrients centers primarily on nitrate in the context of redox condition. Trace elements are discussed in the context of water-quality standards and, where applicable, in relation to redox stability of dissolved species. Stable isotopes of hydrogen and oxygen are used to help classify water types and sources. Pesticides and VOCs are discussed in relation to frequency of detection above the laboratory reporting limit (LRL). The order of discussion of pesticide and VOC data for individual ground-water basins is determined by relative detection frequencies, beginning with the basin having the greatest number of detections.

Data from each of the eight studies are compared to EPA water-quality standards. In each section, such as “Major Ions,” data from each study are discussed in order of exceedance frequency of EPA standards. Primary maximum contaminant levels (MCLs) for drinking water establish the permissible level of a contaminant in drinking water to protect human health. MCLs are legally enforceable. Secondary MCLs were established to protect the aesthetic qualities of water and are recommended levels that are not enforceable. Proposed MCLs (PMCLs), such as for radon and uranium, are not currently enforceable. In addition to the PMCL, there is also an alternative PMCL (APMCL) for radon gas that is linked to a “multimedia mitigation” program to reduce radon in drinking water to acceptable levels (US EPA, 1999b).

Major Ions

Water samples were analyzed for the major ions calcium, magnesium, sodium, potassium, chloride, sulfate, fluoride, bromide, and silica (Appendix 4). Alkalinity, bicarbonate, and carbonate were determined in the field. The total concentration of dissolved solids also is reported as a calculated sum of total dissolved solids (TDS) and as residue on evaporation at 180 degrees Celsius. Significant differences between the two values may result from high concentrations of dissolved organic compounds not included in the TDS value, which accounts only for inorganic parameters.

Trilinear diagrams showing relative concentrations of major ions were constructed for the Coastal, Inland, and San Jacinto Basins ([figs. 5, 6, and 7](#)) to identify major groupings and geochemical trends. These diagrams are useful in displaying the effects of mixing water from two different sources. A mixture of water will plot along a straight line between the source compositions, as long as the mixed solution composition was not altered by processes such as ion exchange, precipitation, or dissolution of salts.

Production wells sampled in the Coastal Basin yielded water in which the dominant cations were calcium or sodium; dominant anions varied between bicarbonate, chloride, and sulfate ([figs. 5, 6, and 7](#)). Relative magnesium percentages were generally low for all studies. Water from some urban land-use wells shows evidence of seawater intrusion on the basis of elevated relative sodium and chloride percentages

([fig. 5](#)). These monitoring wells are not typical of the other studies, which utilized deep, production wells; the COLUS wells tap shallow ground water that is not used for supply or irrigation. Many of these shallow monitoring wells near the coast may reflect predevelopment conditions; much of the area was marshland in which evaporation and geochemical conditions have affected water quality. Aside from this influence, the urban land-use wells probably reflect soil chemistry and the effect of landscape-maintenance practices in the immediate vicinity many of these wells. Shallow COLUS wells near the Huntington Beach oil field may be affected by disposal of petroleum brines or upwelling of brine from deeper aquifers. In the past, disposal of petroleum brine was handled by discharge to streams or “evaporation ponds” (Todd, 1980). Oil companies began discharging wastewater and brines to lagoons at the southern end of the Huntington Beach oil field near the coast in 1938. Constituents found in the wastewater included phenol, benzene, xylene, toluene, sulfuric acid, chromic acid, and lead (Schou, 1997). These wells are located in the historic discharge zone of the coastal aquifer system and therefore shallow ground water may have dissolved constituents derived from the deep ground-water system.

Ground water in the Coastal Basin had the greatest range in major-ion composition. The range in composition reflects the influences of activities and conditions in upgradient areas of the Santa Ana Basin ([fig. 1](#)). Other factors that may affect ground-water quality include artificial recharge to the ground-water basin using water from the Santa Ana River, infiltration of imported water used to reduce ground-water pumpage, and infiltration of recycled wastewater that constitutes the majority of base flow in the Santa Ana River. Ground water in the Coastal Basin may be divided into three general zones based on lateral distance from recharge facilities in the forebay. Ground water near the recharge basins reflects the recent quality of recharge water. The quality of ground water at the distal end of the flow system in the confined aquifers near the coast represents predevelopment conditions (native ground water) and, in some areas, may be affected by seawater intrusion. Ground-water quality in the intermediate area between the recharge basins and distal zone reflects historical variation in recharge water quality and mixing with native ground water.

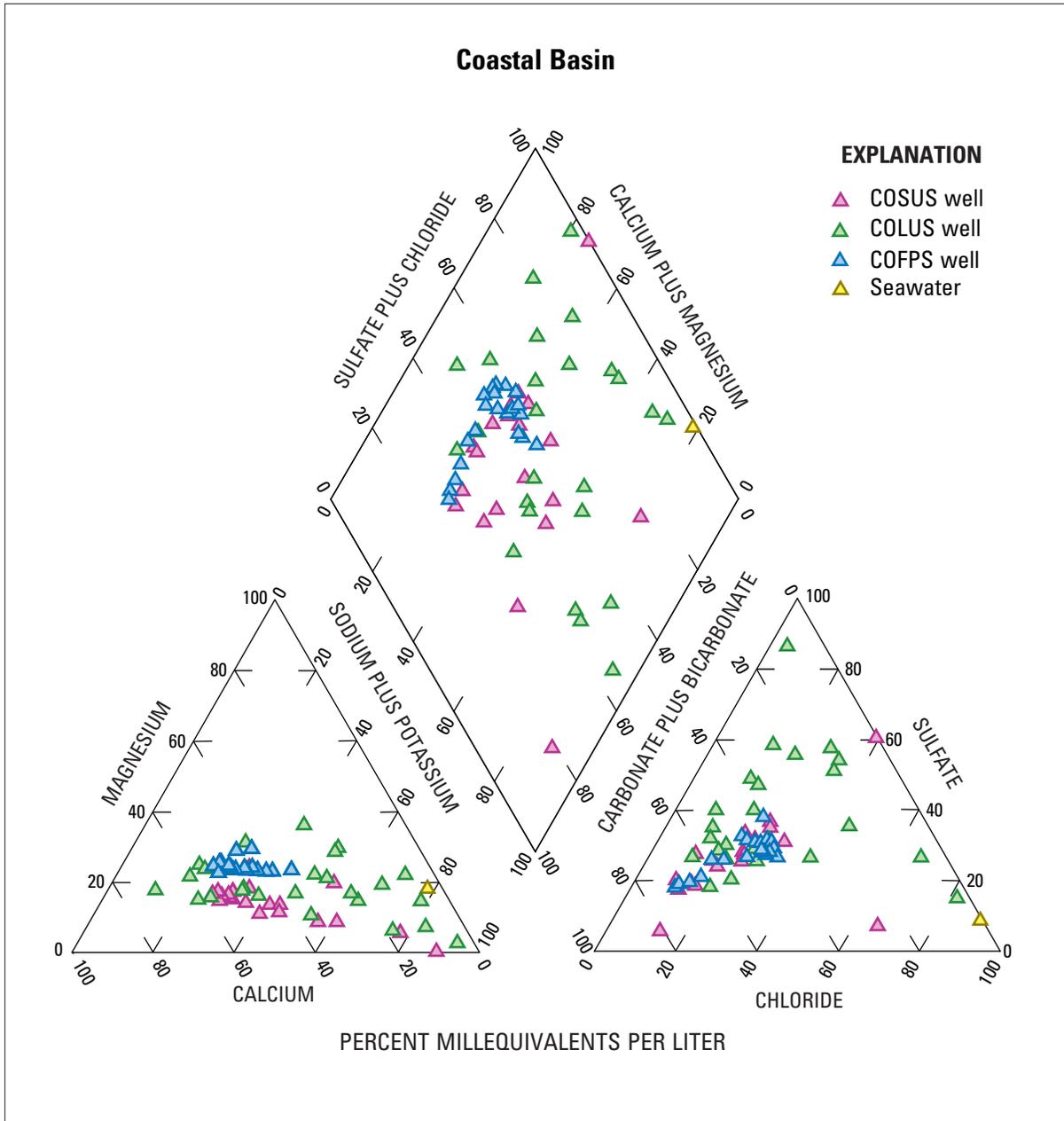


Figure 5. Major-ion composition of ground-water samples from the Coastal Basin., Santa Ana NAWQA, California

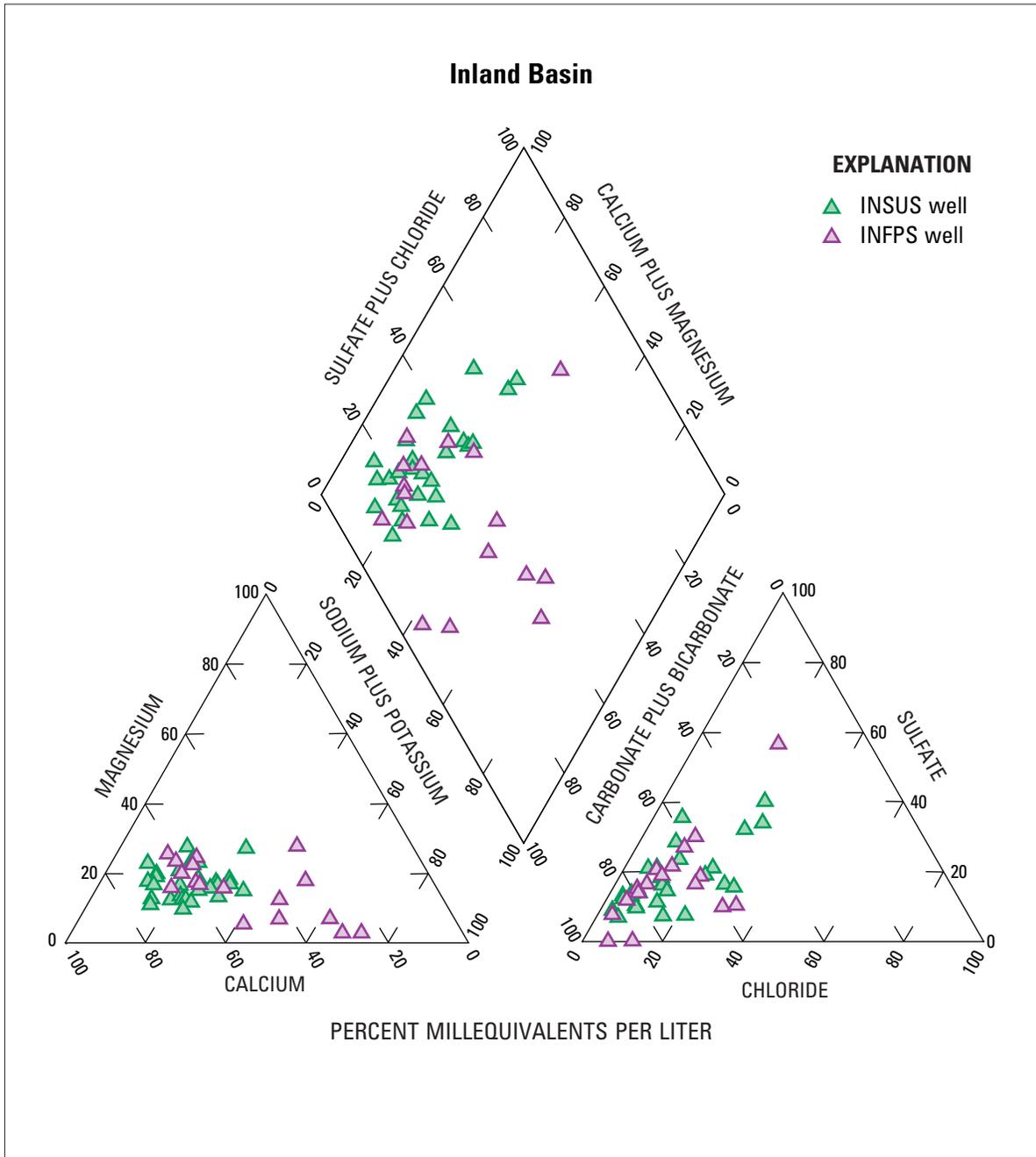


Figure 6. Major-ion composition of ground-water samples from the Inland Basin, Santa Ana NAWQA, California.

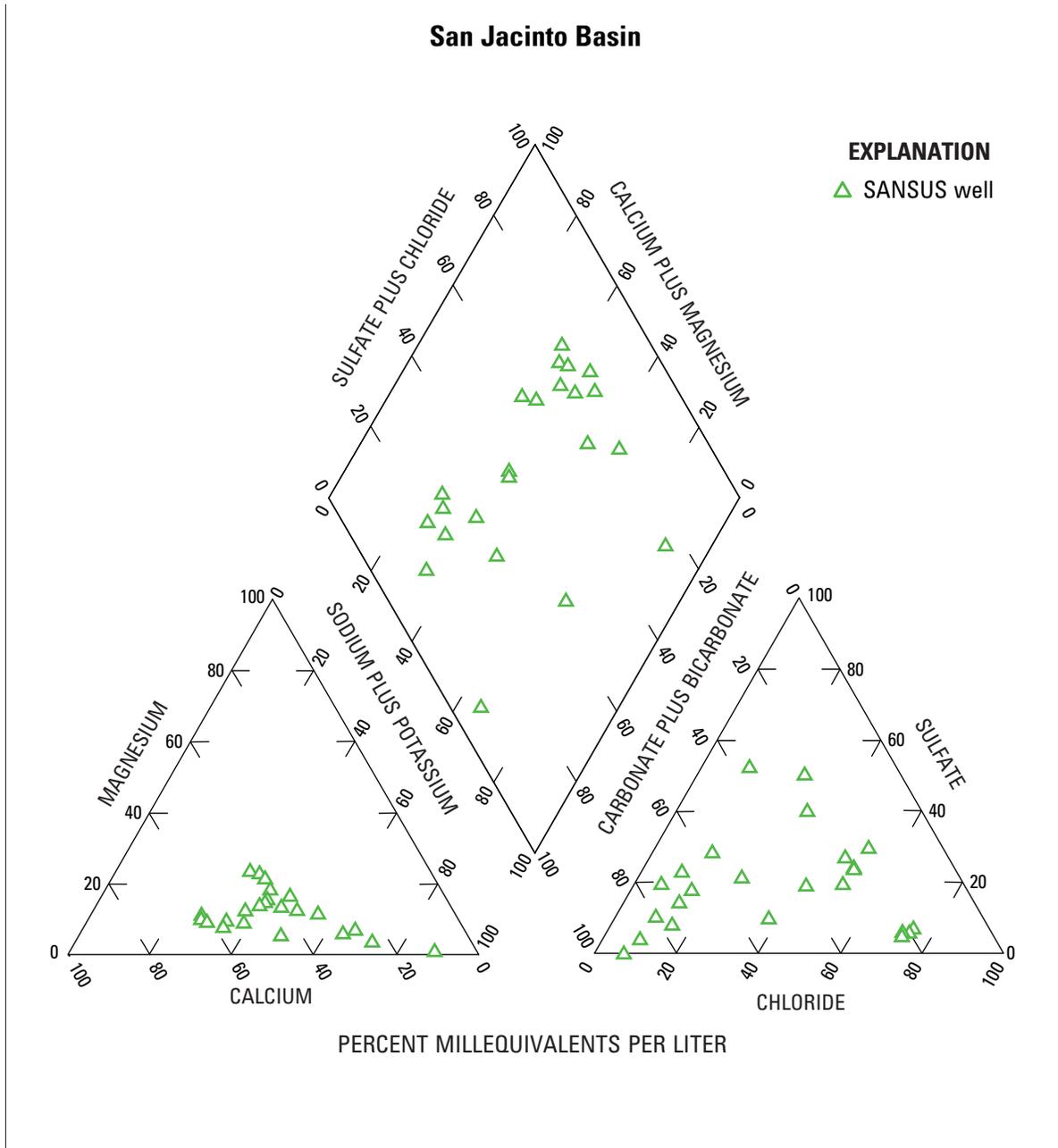


Figure 7. Major-ion composition of ground-water samples from the San Jacinto Basin, Santa Ana NAWQA, California.

Additionally, studies in the Coastal Basin reflect vertical variability in water quality in shallow (COLUS), intermediate (COFPS, OCCAS), and deep (COSUS, OCCAS) aquifers. The quality of shallow ground water sampled for the COLUS study, generally within a few tens of feet of the land surface, is likely related to the historical marsh lands in much of the area and to recent land use near the wells, such as landscape maintenance. The deeper wells sampled for the other studies reflect lateral zonation of water quality along ground-water flow paths.

Most wells sampled in the Inland and San Jacinto Basins produce water from deep aquifer zones. Most samples of ground water in the Inland Basin were a calcium-bicarbonate type, which may reflect the quality of recharge originating in pristine, high-altitude areas of the adjacent San Gabriel and San Bernardino Mountains (figs. 3 and 6). Other factors that influence ground-water quality in the Inland Basin include recharge from the Santa Ana River, discharge of recycled wastewater to the river, and use of imported water in the basin. Because the sampled wells tap unconfined aquifers, ground-water quality also may be influenced by introduction of compounds generated by overlying land-use activities.

Composition of most samples of ground water in the San Jacinto Basin (fig. 7) ranged between calcium-bicarbonate to sodium-calcium sulfate types. Samples from some wells were high in bicarbonate and low in sulfate. Izbicki (1991) suggest that ground water enriched in bicarbonate and depleted in sulfate may have resulted from sulfate reduction. The presence of methane gas in some wells is evidence of localized reducing conditions in the aquifer. Major factors that may affect ground-water quality include high evaporation rates due to the arid climate of this basin, extensive use of imported water, use of recycled wastewater for ground-water recharge, and recharge of low-TDS, calcium-bicarbonate water originating in the adjacent San Jacinto Mountains.

Boxplots are used to display variability in TDS (figs. 8 and 9) and nitrate concentrations in the Santa Ana ground-water studies. Boxplots illustrate features of data distribution, including the median (central) value, the interquartile range encompassing the central 50 percent of the data, and outlying data points, which

are outside the expected range. All outliers for the current studies were above the 90th percentile and are represented by circles.

The EPA secondary maximum contaminant level (MCL) for TDS (500 mg/L; US EPA, 1996) was exceeded in water from 39 percent of all production wells sampled and from 92 percent of the COLUS monitoring wells. One COLUS sample had a TDS concentration of 25,500 mg/L (Appendix 4). The quality of water from these shallow monitoring wells may reflect the historical marsh environment in much of the area and the effect of landscape maintenance practices in the vicinity of the wellhead. Wells in the Coastal Basin generally had greater TDS concentrations than did wells in the other two basins (figs. 8 and 9). The TDS secondary MCL was exceeded in 71 percent of the COFPS wells, which tap an intermediate aquifer zone used for water supply. The TDS secondary MCL was exceeded in 45 percent of the COSUS wells, which tap a deep aquifer zone used for water supply. Higher TDS concentrations in the COFPS relative to the deeper COSUS wells may reflect closer proximity to engineered recharge facilities and shorter flow paths in the COFPS system. TDS concentrations have increased in municipal-supply wells as a consequence of recharge of high TDS water from the Santa Ana River and from imported Colorado River water (Herndon and others, 1997). High TDS concentrations in ground water from the Irvine subbasin in the southeastern part of the Coastal Basin, relative to the main subbasin, may be related to recharge of saline water from marine sediments in the adjacent Santa Ana Mountains and to irrigation practices (Singer, 1973).

The secondary MCL for TDS was exceeded in water from 39 percent of the wells sampled in the San Jacinto Basin. This exceedance probably reflects recharge by low-TDS runoff from the adjacent San Jacinto Mountains. Factors that may contribute to increasing TDS in the basin include recharge of high-TDS recycled and imported waters. Only 10 percent of the wells sampled in the Inland Basin yielded water with TDS concentrations that exceeded the secondary MCL. This may be explained by the widespread recharge by fresh water in the basin, particularly from the adjacent San Gabriel and San Bernardino Mountains.

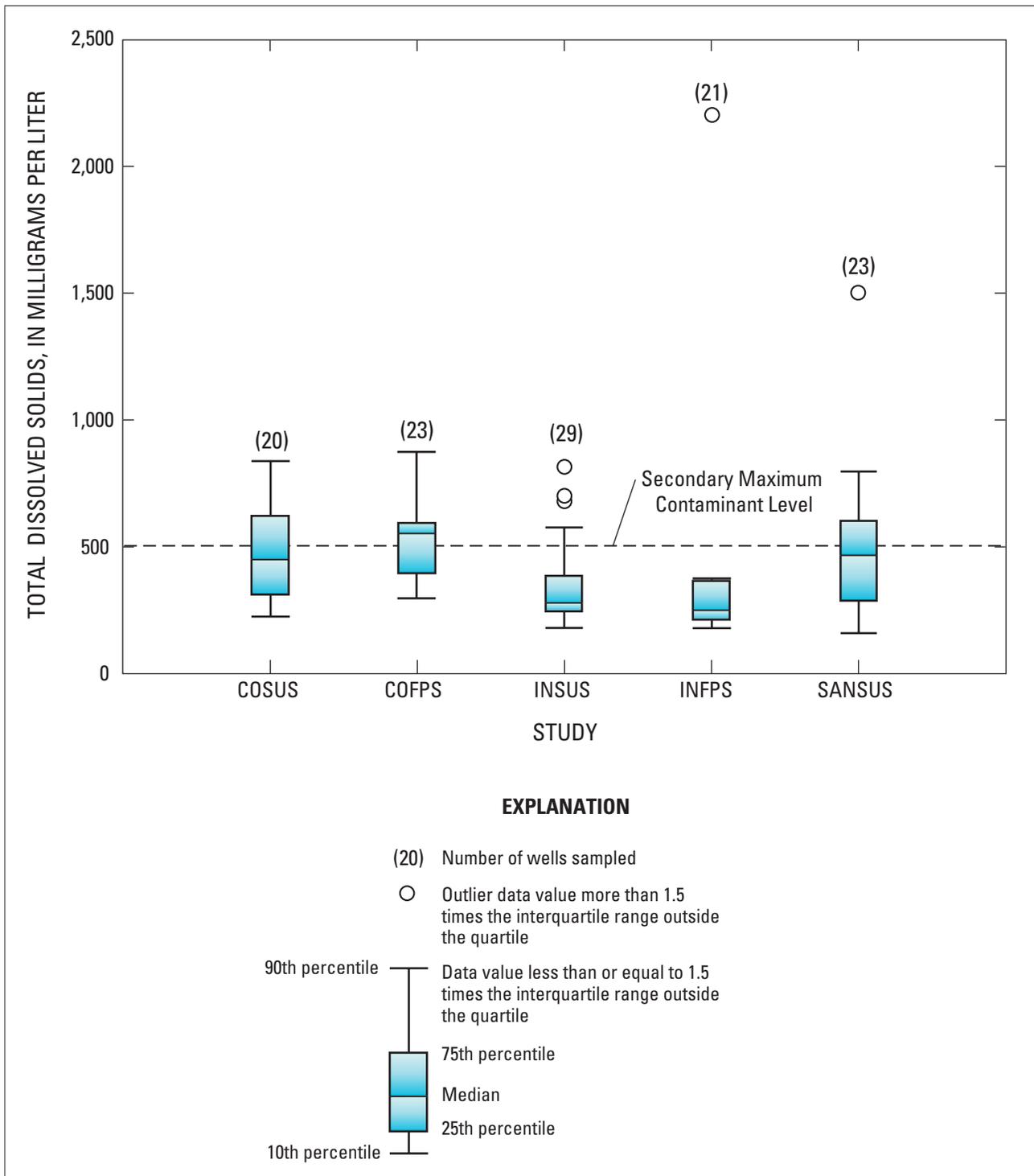


Figure 8. Comparison of concentrations of total dissolved solids for ground-water samples from the COSUS, COFPS, INSUS, INFPS, and SANSUS studies, Santa Ana NAWQA, California.

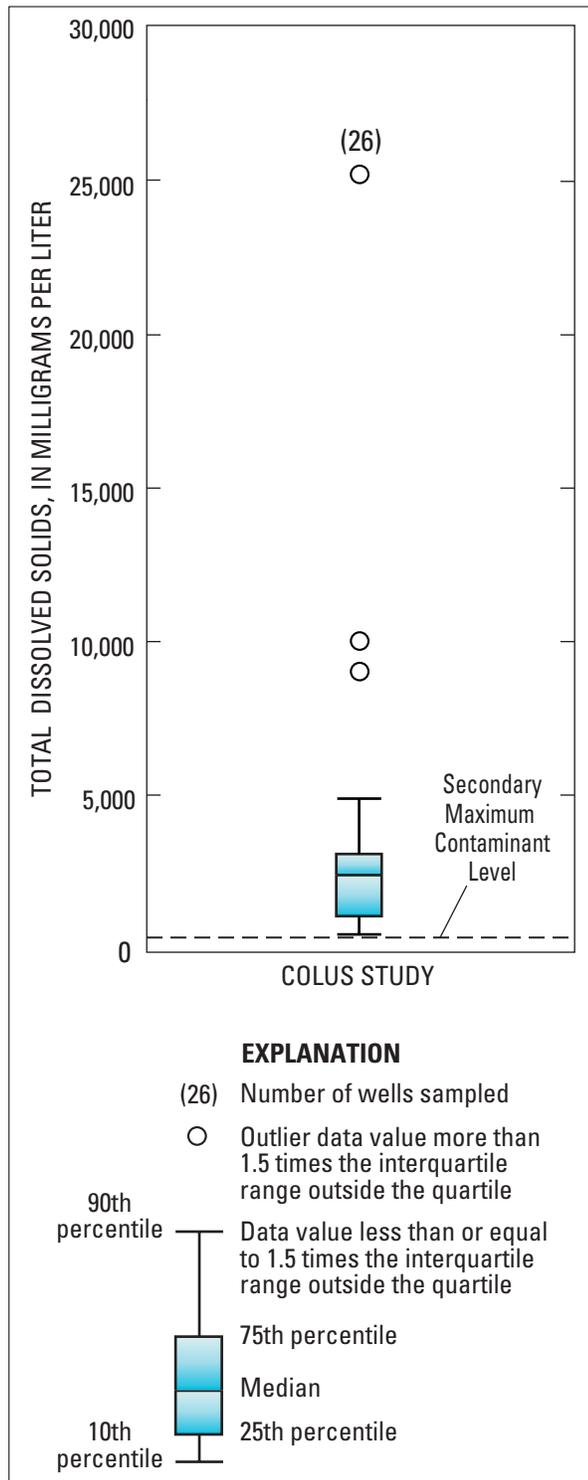


Figure 9. Total dissolved solids concentrations for water samples from the Coastal Land-Use assessment, Santa Ana NAWQA, California.

The secondary MCL for chloride is 250 mg/L (US EPA, 1996). The highest chloride concentrations and the greatest number of samples exceeding the chloride secondary MCL were—as they were for TDS—from shallow urban land-use wells in the Coastal Basin. The greatest chloride concentration was 9,430 mg/L; 40 percent of the samples exceeded the chloride secondary MCL (Appendix 4). Potential sources of high chloride concentrations in the COLUS monitoring wells are seawater, evaporation associated with the historical marsh environment, and oil-field brines. Oil-field brines, which have chloride concentrations ranging between 1,750 and 100,000 parts per million, historically were discharged to natural depressions in the vicinity of the Huntington Beach oil field (Piper and others, 1953). One production well located in the Irvine subarea of the Coastal Basin had a chloride concentration of 324 mg/L; this well may have been affected by irrigation-return flow. Two production wells in the San Jacinto Basin had chloride concentrations (345 mg/L and 454 mg/L) that slightly exceeded the secondary MCL. Possible sources of the elevated chloride concentrations in ground water from the San Jacinto Basin include irrigation-return flow, recharge of recycled wastewater, and infiltration of evaporated water. Infiltration from animal feeding operations (dairies) is another potential source of chloride to ground water in the San Jacinto Basin. Chloride concentrations in all samples from wells in the Inland Basin were below the secondary MCL.

The highest sulfate concentrations and the greatest percentage of samples exceeding the sulfate secondary MCL (250 mg/L; US EPA, 1996) were—again as they were for TDS and chloride—from shallow wells sampled for the urban land-use study in the Coastal Basin. The highest concentration of sulfate was 5,270 mg/L; 80 percent of the COLUS samples exceeded the secondary MCL (Appendix 4). Sulfate concentration in seawater is high (about 2,700 mg/L) and may influence shallow ground-water quality in the historical marsh environment. The sulfate concentration that exceeded seawater concentration may have been derived from evaporation or some other mechanism operating in the marsh environment. Other potential sources of high sulfate concentrations are brine disposal associated with the Huntington Beach

Oil Field and upwelling of deep ground water in the coastal discharge area. Two COLUS wells near the oil field yielded water with sulfate concentrations (4,170 and 5,270 mg/L) that exceeded the concentration in seawater (2,700 mg/L; Hem, 1985). Chloride concentrations in these wells (1,540 and 9,430 mg/L) were less than seawater concentration (19,000 mg/L; Hem, 1985). Relative to seawater, native salty water and brine have excess sulfate (Piper and others, 1953). One production well in the Coastal Basin had a sulfate concentration (270 mg/L) slightly above the secondary MCL. Water from this irrigation well may reflect infiltration of irrigation-return flow. Two wells in each of the INFPS and SANSUS assessments also had sulfate concentrations that exceeded the secondary MCL. Possible sources of elevated sulfate include naturally occurring minerals and infiltration from agricultural activities.

Nutrients and Dissolved Organic Carbon

Nutrients in ground water, primarily nitrate and phosphorus, can originate from a variety of sources, including atmospheric deposition and dissolution of natural deposits. Elevated concentrations in ground water are commonly the result of human activities, such as exfiltration from sewer lines, recharge of recycled wastewater, and agricultural practices. Most environmental nitrate is derived from oxidation (nitrification) of ammonia that forms during decomposition and leaching of animal wastes, organic material, and fertilizers. Where sufficient dissolved oxygen is present, nitrate is the most common stable form of nitrogen. Nitrate in anaerobic systems can be reduced by bacteria to nitrous oxide or nitrogen gas and lost from solution (Hem, 1985). Dissolved nitrate occurs as an anion and is highly mobile in ground water. Nitrogen also occurs as ammonium cations, which are strongly adsorbed on mineral surfaces. Elevated concentrations of nitrate in drinking water have been associated with “blue-baby” syndrome (methemoglobinemia) and with increased incidence of stomach cancer, birth defects, miscarriage, and leukemia (U.S. Environmental Protection Agency, 1996).

The EPA has not established a drinking-water standard for dissolved organic carbon (DOC). However, DOC in water has been correlated with the formation of trihalomethane compounds, as a result of chlorination of the water for potable use (Fujii and others, 1998). These compounds are regulated by the EPA. DOC in ground water is commonly derived from decomposition and dissolution of organic material in soils and is a constituent of some of the water used for recharge. DOC in ground water can affect dissolved-oxygen concentration, which controls redox conditions. The redox state of the water, either reducing or oxidizing, can affect nutrient, iron, and manganese concentrations (Hem, 1985). Ground-water samples from the COLUS wells had the highest concentrations of DOC, ranging from 0.3 mg/L to 25 mg/L and the highest median concentration (3.4 mg/L; Appendix 5). Potential sources of elevated DOC include organic soil material from the historical marsh environment and seepage from the Huntington Beach oil field in the southwest part of the Coastal Basin (fig. 2). Median concentrations of DOC for all the other six studies were 0.4 mg/L; individual concentrations ranged from 0.1 to 6.6 mg/L.

In this report, concentrations of nitrate plus nitrite are reported as nitrate. Nutrient samples were not collected for the OCCAS and SANCAS studies. Nitrite was less than 0.01 mg/L in 109 of the 120 wells sampled in the Santa Ana Basin. Six of the monitoring wells sampled for the COLUS assessment had nitrite concentrations ranging from 0.01 to 1.62 mg/L. However, associated nitrate concentrations (1.9 to 31 mg/L) were considerably higher than the nitrite concentrations. Nitrite was detected (0.46 mg/L) in a shallow irrigation well sampled for the COSUS study; nitrate concentration was 5.5 mg/L in this well. Similarly, nitrite also was detected (0.03 mg/L) in a shallow irrigation well sampled for the COFPS; nitrate concentration in this well was 2.9 mg/L. Nitrite was detected in two public supply wells (0.02 and 0.05 mg/L) and in one irrigation well (0.02 mg/L) sampled for the SANSUS study; associated nitrate

concentrations ranged from 2.1 to 14 mg/L. All wells sampled for the INSUS study yielded nitrite concentrations below the LRL (0.01 mg/L).

Most ground-water samples had nitrate concentrations below the MCL (10 mg/L; U.S. Environmental Protection Agency, 1996). Boxplots are used to show ranges in nitrate-nitrogen concentration in the Santa Ana ground-water studies (figs. 10 and 11). These data are compiled in Appendix 5. Nitrate concentrations exceeded the MCL in 22 percent of the production wells sampled in the San Jacinto Basin; exceedances occurred in both municipal-supply and irrigation wells. The highest nitrate concentration in these samples was 16.6 mg/L. Of the ground-water basins, the San Jacinto Basin has the greatest percentage of land used for agricultural purposes. Potential sources of nitrate in the San Jacinto Basin are recycled municipal wastewater used for ground-water recharge and infiltration of wastewater from animal feeding facilities.

All municipal-supply wells sampled in the highly urbanized Coastal Basin had nitrate concentrations below the MCL. However, 19 percent of the shallow monitoring wells sampled for the urban land-use study had nitrate concentrations exceeding the MCL (fig. 11). This observation probably reflects the use of fertilizer and irrigation practices in the vicinity of these shallow wells. The highest nitrate concentration from the COLUS samples was 53.3 mg/L; the highest nitrate concentrations were associated with DOC concentrations below 5 mg/L, which may indicate oxidizing conditions. Conversely, non-detections of nitrate and the highest ammonium concentrations were associated with the highest DOC concentrations and dissolved oxygen concentrations less than 1 mg/L, indicating reducing conditions (Appendix 5). Sources of nitrate in water from municipal-supply wells in the Coastal Basin include recharge from the Santa Ana River (about 2 to 8 mg/L nitrate-nitrogen) and infiltration from agricultural activities, past and present (Herndon and others, 1997).

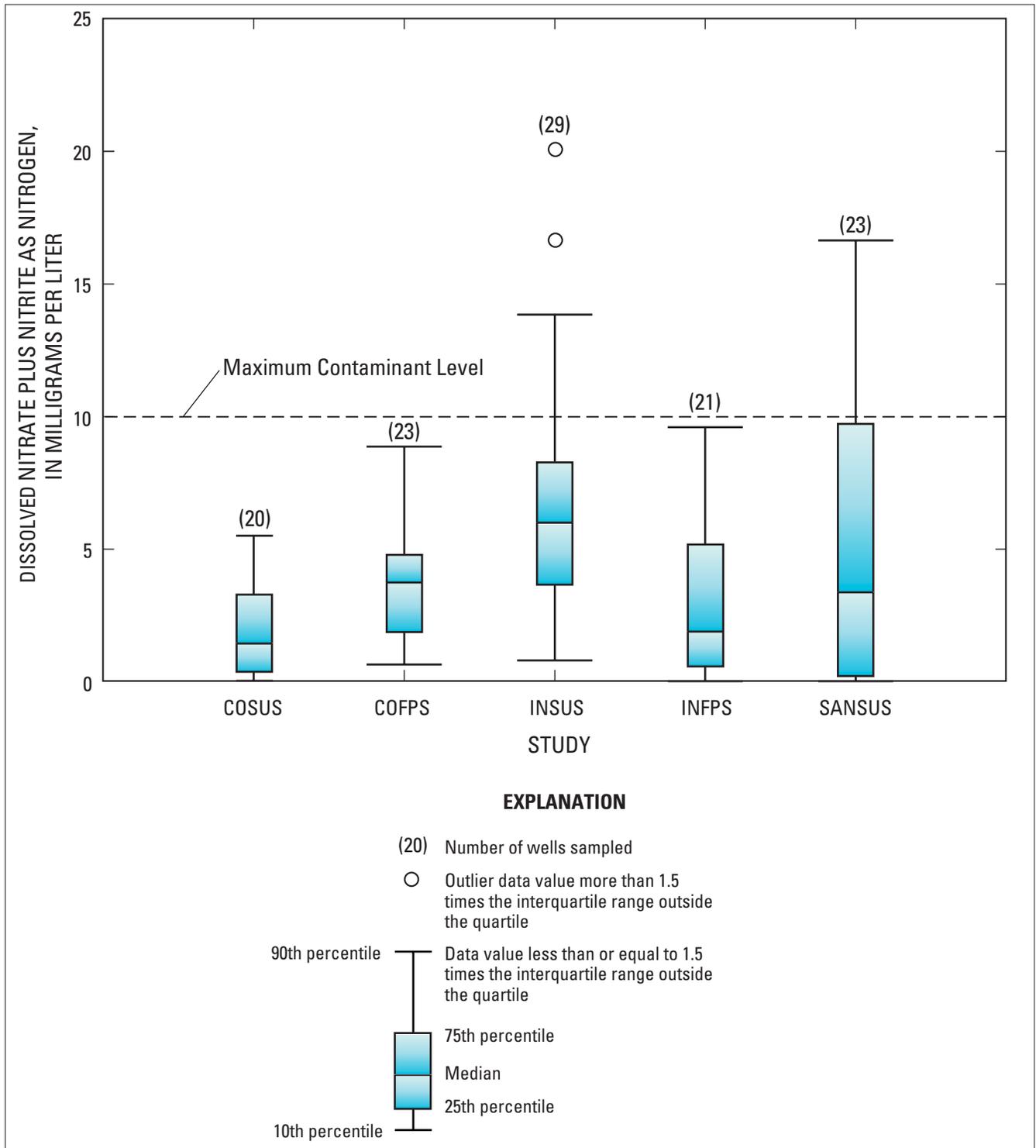


Figure 10. Dissolved nitrate plus nitrite for ground-water samples from the COFPS, COSUS, INSUS, INFPS, and SANSUS studies, Santa Ana NAWQA, California.

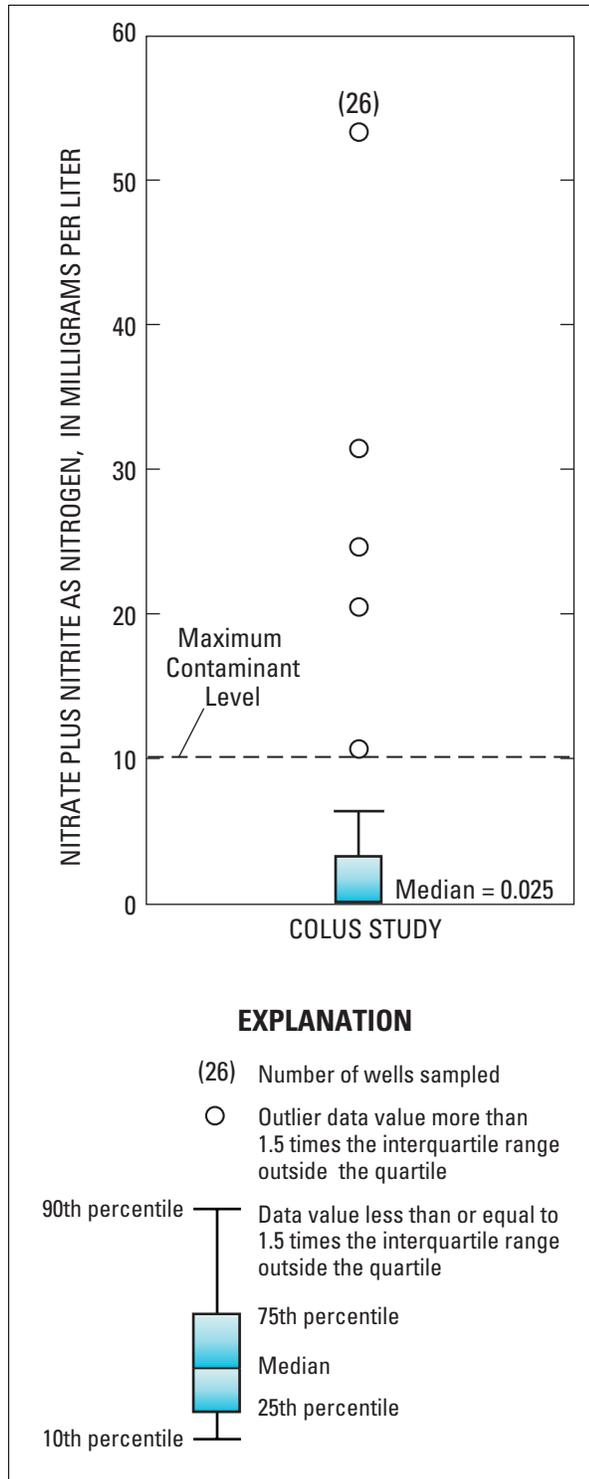


Figure 11. Dissolved nitrate plus nitrite for ground-water samples from the Coastal Land-Use assessment, Santa Ana NAWQA, California.

Nitrate concentrations exceeded the MCL in 14 percent of the production wells sampled in the Inland Basin reflect a greater percentage of agricultural land use in comparison with the Coastal Basin. Exceedances occurred in both municipal-supply and irrigation wells. The highest nitrate concentration in water from a production well was 20.1 mg/L. In general, sources of nitrate in ground water include fertilizers, exfiltration from sewer pipes, infiltration from agricultural activities, and discharge of reclaimed water. Another potential source of nitrate in ground water in the northwestern part of the Inland Basin ([fig. 3](#)) is infiltration of wastewater from animal feeding facilities. No wells were sampled in the Chino area where infiltration from dairy farms has led to elevated nitrate concentrations in the underlying ground water. Most wells in this area do not have construction data necessary for use in NAWQA studies. Runoff from cattle feedlots can have high concentrations of ammonia, which can produce average nitrate concentrations ranging from about 70 to 120 mg/L (Miller, 1980).

Past and present agricultural activities in the Inland and San Jacinto Basins may be the source of many of the elevated nitrate concentrations in ground-water samples from production wells screened in unconfined aquifers. The deep COSUS production wells had the lowest nitrate concentrations of the USGS studies and reflect the confined nature of the deep aquifer in the Coastal Basin. The COLUS assessment yielded the highest nitrate concentrations but very low median and quartile values in comparison with the other USGS studies ([figs. 10 and 11](#)). Many of the COLUS monitoring wells tap the shallow water table in landscaped areas that are irrigated and commonly maintained using soil supplements and fertilizers.

Trace Elements and Isotopes

Trace elements and isotopes that exceed water-quality standards, and variation in stable- isotope ratios are discussed in this section of the report. Analyses for trace elements in ground water from the Santa Ana basins (Appendixes 6 and 7) include aluminum, antimony, arsenic, barium, beryllium, boron, cadmium, chromium, cobalt, copper, iron, lead, lithium, manganese, molybdenum, nickel, selenium, silver, strontium, thallium, vanadium, and zinc. The results of analyses for stable and radioactive isotopes are given in Appendix 8. The stable isotopes of hydrogen and oxygen that form water molecules are reported as ratios in per mil relative to Standard Mean Ocean Water. Radioisotopes include radon-222, uranium, tritium, and carbon-14.

Concentrations of dissolved arsenic in all sampled wells were below the current standard of 50 $\mu\text{g/L}$ (US EPA, 1996). However, about 19 percent of the monitoring wells sampled for the Coastal land-use study had arsenic concentrations exceeding the proposed MCL of 10 $\mu\text{g/L}$ (EPA, 2001). The new standard will become effective in January 2006. Arsenic may be derived from naturally-occurring minerals. Arsenic has been used as a component of pesticides and thus may enter streams or ground water through waste disposal or agricultural drainage (Hem, 1985). Arsenic also has been detected in some fertilizers, along with other toxic elements (California Public Interest Group Charitable Trust, 2001). One analysis of a fertilizer used in California yielded an arsenic concentration of 12 parts per million (ppm) or 12 $\mu\text{g/g}$. Elevated concentrations of arsenic in the shallow land-use monitoring wells may result from concentration of natural sources and from local pesticide and fertilizer use. With the exception of one production well in the San Jacinto Basin, none of the wells sampled for the other studies exceeded the arsenic proposed MCL.

The secondary MCL for iron is 0.3 mg/L (US EPA, 1996). Iron concentrations were below the secondary MCL for all the studies, except the urban land-use study, where 44 percent of the sites had iron concentrations that exceeded the secondary MCLs and the Inland flow-path study. Some values for shallow ground water sampled for the Coastal land-use study were very high; 6 wells yielded iron concentrations between 2 and 39 mg/L (Appendix 6). Only one monitoring well from the Inland flow-path study yielded an iron concentration (7.4 mg/L) that exceeded the secondary MCL. Iron is an essential element in the metabolism of animals and plants. However, high concentrations of iron in drinking water affect taste and may produce red oxyhydroxide precipitates that can stain laundry and plumbing fixtures. Many of the PVC monitoring wells installed for the COLUS are located in the historical marsh area; soils have a high content of organic matter, including peat, which may produce high concentrations of dissolved iron (Hem, 1985). Reducing conditions related to the marsh environment would favor dissolved iron species. Additionally, most of the wells were installed in areas that are landscaped and maintained using soil supplements and fertilizers, which also may be sources of dissolved iron. Some of the dissolved iron in the COLUS samples may reflect the common use of iron supplements, such as iron sulfate, to reverse the effects of iron chlorosis, which is indicated by yellow foliage.

The secondary MCL for manganese is 0.05 mg/L (US EPA, 1996). Manganese chemistry is similar to that of iron and both are commonly found together in ground water. Manganese is an essential element in plant metabolism. However, high concentrations in drinking water can cause a brown discoloration of the water and affect taste. High manganese concentrations in drinking water are undesirable because of the tendency to deposit black manganese-oxide stains on laundry fixtures (Hem, 1985). Dissolved species of manganese are generally more stable than solid phases under reducing conditions and in water with acidic pH.

Samples from several of the current studies had manganese concentrations that exceeded the secondary MCL.

About 80 percent of the shallow monitoring wells sampled for the Coastal urban land-use study assessment had manganese concentrations exceeding the secondary MCL (Appendix 7). Some values were very high; 6 sites yielded manganese concentrations between 1 and 8 mg/L. Manganese oxide may accumulate with other materials in bog deposits. High manganese concentrations for wells located in the historical marsh area may result from reducing conditions that allow the dissolution of manganese compounds. Another source of dissolved manganese in landscaped areas of the land-use study may be the common use of manganese supplements, such as manganese sulfate, to counteract the effects of manganese deficiency in plants. As with iron chlorosis, manganese deficiency in plants is characterized by yellow foliage.

About 29 percent of the water samples from the Inland flow-path study had manganese concentrations that exceeded the secondary MCL. These samples were from monitoring wells that have PVC casings and were not used for public supply. Manganese concentrations in these samples were much lower than those samples from the Coastal land-use wells, ranging between 0.08 and 0.4 mg/L.

Three irrigation wells sampled in the Coastal Basin study (15 percent of all wells sampled) had manganese concentrations that exceeded the secondary MCL, ranging from 0.15 to 0.67 mg/L. The highest concentration is from a shallow well (less than 100 ft deep) in an irrigated park adjacent to the Santa Ana River. Coatings of manganese oxides in streambeds occur in many places under oxidizing conditions (Hem, 1985); reducing conditions may result in dissolution of these deposits and consequent increase in manganese concentration in associated ground water. Water from one irrigation well had a manganese concentration (0.51 mg/L) that exceeded the secondary MCL. This shallow well (less than 250 ft deep) was located on the bank of the Santa Ana River.

Natural uranium occurs as several isotopes, of which uranium-238 is predominant (Hem, 1985). Isotopes are atoms of the same element with the same number of protons and different numbers of neutrons. Uranium-238 decays to radium-226 in a radioactive decay series that ends with the stable isotope lead-206. Uranium is present in concentrations between 0.1 and 10 µg/L in most natural water. However, concentrations greater than 1,000 µg/L also can occur in water associated with uranium-ore deposits. The solubility of uranium is dependent upon the redox state and pH of the water. In general, reduced uranium species are only slightly soluble; uranium has a greater mobility in solutions that are oxidizing and (or) have a high pH (Hem, 1985). Numerous uranium deposits are widely distributed throughout the watershed of the Colorado River in western Colorado, eastern Utah, northeastern Arizona, and northwestern New Mexico; seepage from these deposits and (or) mining activities are potential sources of uranium to ground water and associated river water (Park and MacDiarmid, 1975). Colorado River water is imported to the Santa Ana Basin to augment existing water supply. However, concentrations of dissolved uranium in the water are substantially lower than current and proposed EPA standards.

High concentrations of uranium and radon in the South Platte River Basin in Colorado were related to crystalline rocks, primarily granitic, and to marine shales and coal deposits (Dennehy and others, 1998). Zielinski and others (1997) assessed the relative importance of soils and fertilizers as sources of uranium to water in southeastern Colorado. Fertilizer with trace amounts of uranium had been applied for decades to croplands in the area. Geochemical associations indicated that uranium-rich, shaley soils were the primary source of uranium in surface water. It was concluded that similar studies in other areas would be needed to evaluate the mobility of fertilizer-derived uranium. Leaching of rock and soil by irrigation water, coupled with evaporation in a semiarid climate, can produce concentrations of dissolved uranium in surface water and shallow ground water that may threaten nearby drinking-water supplies (Zielinski and others, 1995). Uranium deposits are commonly associated

with granite and may result in high levels of radon in ground water (Otton and others, 1993; Lindsey and Ator, 1996; Grady and Mullaney, 1998).

The EPA has proposed a MCL of 30 µg/L for uranium that would become effective in December 2003 (US EPA, 2000). Water from about 48 percent of the shallow monitoring wells sampled for the Coastal land-use study exceeded the proposed MCL for uranium, with concentrations ranging from 43 to 312 µg/L (Appendix 8). These wells are located in the area of the historical marsh environment in which geochemical conditions may tend to concentrate some trace elements, particularly those sensitive to redox potential. With the exception of one deep irrigation well sampled for the subunit survey in the Inland Basin, uranium concentrations in deep production wells from the five other studies were all below the proposed MCL.

Elevated levels of uranium found in shallow ground water sampled during the Coastal land-use study may have been derived from local soils and concentrated by evaporation and geochemical conditions in the marsh environment. The highest uranium concentration (312 µg/L) determined in all studies was in water from a COLUS monitoring well, located nearest to the Huntington Beach Oil Field. Radionuclides, such as uranium and radium, may be associated with oil-field brines (Zielinski and others, 1999). Fertilizer also may be a source of uranium (California Public Interest Group Charitable Trust, 2001). One fertilizer used in California was found to have a uranium concentration of 2.9 ppm (2.9 µg/g). Uranium shows a positive correlation with chloride concentrations less than 5,000 mg/L, indicating that evaporation may have produced elevated levels of uranium in some of the COLUS water samples.

Decay of naturally occurring radium-226 in sediments and bedrock is a source of radon gas (radon-222) to ground water (Hem, 1985). Radon is soluble in water and readily volatilizes. In addition to degassing, radon is lost from ground water by radioactive decay. Where ground water doesn't have the opportunity to lose radon to the atmosphere, such as under confined conditions, the concentration can substantially exceed 1,000 pCi/L (Hem, 1985).

The EPA has developed a proposed MCL of 300 pCi/L for radon in drinking water (US EPA, 2000). An alternative MCL of 4,000 pCi/L for radon in drinking water was determined as the radon concentration in water needed to produce the average radon concentration in ambient air of about 4 pCi/L during activities such as bathing, showering, and cooking (US EPA, 2000). The alternative MCL will apply only to states and (or) community water systems that develop multimedia mitigation (MMM) programs to address radon levels in indoor air. Because most of the radon in indoor air is derived from soil in comparison to radon derived from household use of water, MMM programs will target sources other than drinking water. Only about 1 to 2 percent of radon in indoor air comes from drinking water (U.S. EPA, 1999b). States that do not develop MMM programs will be required to meet the proposed MCL. Breathing radon in the indoor air of homes is the second leading cause of lung cancer after smoking tobacco products and is responsible for about 20,000 deaths each year in the United States (US EPA, 2000).

In the Coastal Basin, about 95 percent of the wells sampled for the subunit survey had radon concentrations exceeding 300 pCi/L, ranging between 313 and 719 pCi/L with a median value of 474 pCi/L; this is the highest percentage of wells in all the study areas. High levels of radon in some of these wells probably are related to the composition of aquifer materials and degree of aquifer confinement. The second highest concentration of radon (644 pCi/L) was in a sample from a shallow irrigation well (COS-9) adjacent to the Santa Ana River. Most of the lowest radon concentrations were from wells located in the zone of native ground water not affected by artificial ground-water recharge. About 75 percent of the shallow monitoring wells sampled for the Coastal land-use study had radon concentrations exceeding the proposed MCL, ranging from 301 to 965 pCi/L with a median value of 339 pCi/L. The source of radon may be reflect redox conditions in the historical marsh

environment as well as irrigation practices and fertilizer use. Another potential source of radon in the Coastal Basin is from decay of radium-226 possibly associated with brines from the Huntington Beach oil field (fig. 2). Under reducing conditions radium mobility is increased and, if present, would travel with petroleum brines (Zielinski and others, 1999).

In the Inland Basin, about 79 percent of the sites sampled for the INSUS study had radon concentrations exceeding the proposed MCL, ranging from 306 to 4,560 pCi/L with a median value of 403 pCi/L. Many of these wells are screened in deposits derived from granitic mountains on the north side of the basin (fig 3). The alternative MCL was exceeded at a single site; one production well in the Inland Basin yielded a radon concentration of 4,560 pCi/L. This well is screened in deposits derived from nearby granitic mountains.

In the San Jacinto Basin, about 60 percent of the sites sampled for the subunit survey had radon concentrations exceeding the proposed MCL, ranging from 305 to 1,800 pCi/L with a median value of 324 pCi/L. The highest radon concentration (1,800 pCi/L) in the SANSUS study was from a well located in the southwestern part of the San Jacinto Basin. The remaining wells with high radon concentrations (greater than 900 pCi/L) are located in the northwestern part of the basin. High radon concentrations are probably related to granitic bedrock and mountains in the vicinity and may reflect the relatively shallow depth to bedrock in these areas of the basin.

Several USGS studies in the Santa Ana Basin have utilized analysis of the stable isotopes of hydrogen and oxygen that compose the water molecule to determine the source of recharge to ground water and to trace its movement (Izbicki and others, 1998; Woolfenden and Kadhim, 1997; Kaehler and others, 1998; Rees and others, 1994). Stable-isotope data are given in Appendix 8 and presented graphically in [figure 12](#).

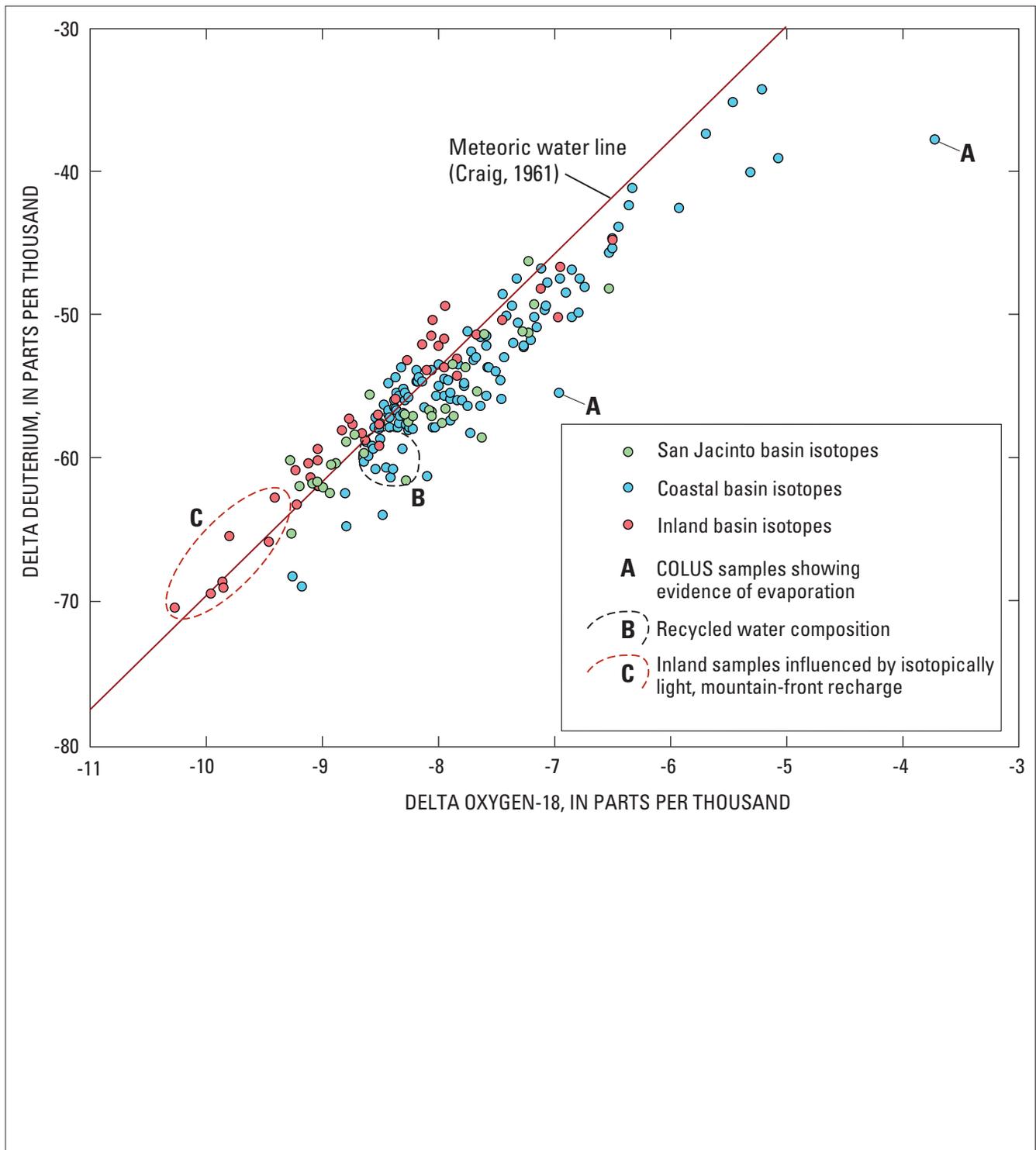


Figure 12. Stable-isotope composition of ground-water samples from the COSUS, COLUS, COFPS, OCCAS, INSUS, INFPS, SANSUS and SANCAS studies, Santa Ana NAWQA, California.

The stable isotopes that compose the water molecule, ^2H , ^1H and ^{18}O , and ^{16}O , can be used to identify water types and to trace the movement of water. The isotopes oxygen-18 (^{18}O) and deuterium (^2H) have more neutrons and a greater atomic mass (weight) than do the more common isotopes, ^{16}O and ^1H . This difference in weight results in differences in the physical and chemical behavior. The ^{18}O and ^2H abundances are expressed as ratios, in delta notation (δ), as per mil (parts per thousand) differences, relative to the standard known as Standard Mean Ocean Water (SMOW) (Freeze and Cherry, 1979). Most precipitation throughout the world originates from the evaporation of seawater and, as a result, the oxygen-18 ($\delta^{18}\text{O}$) and deuterium (δD) composition of precipitation throughout the world is linearly correlated in a relation referred to as the “meteoric water line” (Craig, 1961). Precipitation near the coast and at low altitudes is isotopically heavier than precipitation farther inland and at high altitudes because the lighter isotopes tend to remain in water vapor relative to the heavier isotopes, which are fractionated into the precipitation. Similarly, water that has been partly evaporated is enriched by fractionation of the heavier isotopes relative to the original isotopic composition; these values plot to the right of the meteoric water line. Stable-isotope data may also be used to show the effects of mixing waters from various sources.

Four distinct sources of recharge in the Santa Ana Basins can be identified on the basis of stable-isotope data; Colorado River water, water from the State Water Project, water derived from high-altitude precipitation, and water derived from low-altitude precipitation (Williams, 1997; Williams and Rodini, 1997). Imported water from the Colorado River has the lightest composition, with values of $\delta^{18}\text{O}$ and δD clustering around -12 and -100 per mil, respectively. Water from the State Water Project is somewhat heavier, with values of $\delta^{18}\text{O}$ and δD near -9 and -70 per mil, respectively. Water samples from the Coastal Basin that have light isotopic compositions may reflect the use of imported Colorado River water for ground-water recharge. The water generally has $\delta^{18}\text{O}$ and δD values less than about -8 and -60 per mil, respectively. Ground water with isotopic ratios in this range may result from mixing of one, or more, of these source

waters with locally-derived ground water. Water derived from high-altitude precipitation in the San Bernardino Mountains is used for recharge in the Inland Basin and at times contributes flow to the Santa Ana River, which is used for recharge in the Coastal Basin. Ground water enriched in heavy isotopes probably reflects recharge by precipitation and local meteoric runoff from low-altitude sources, such as the near-coastal Santa Ana Mountains (Williams, 1997).

The dry-season flow in the Santa Ana River is primarily maintained by discharge from wastewater-treatment plants (Burton and others, 1998). The isotopic composition of recycled water reflects mixed use of imported water and local ground water for public supply. Based on a limited data set, the isotopic composition of this recycled water was tightly clustered by δD ranging from -61.5 to -58 per mil and $\delta^{18}\text{O}$ ranging from -8.65 to -8.27 per mil (Williams, 1997). The actual range in isotopic composition could be wider. Ground water flows from the Inland Basin to the Coastal Basin. Additionally, almost all of the base flow of the Santa Ana river is used to recharge the Coastal ground-water basin. The isotopic composition of Santa Ana River water is nearly identical to a group of wells sampled in a study of recharge in the forebay area of Orange County (Williams, 1997).

Evaporation of water prior to recharge produces isotopic compositions enriched in the heavy isotopes that plot below and to the right of the meteoric water line; evidence of evaporation is observed in many of the shallow Coastal land-use wells. These samples plot in the ranges of δD -30 to -40 per mil and $\delta^{18}\text{O}$ -4 to -6 per mil (fig.). However, many of the stable-isotope data from deep production wells in the coastal area that plot below the meteoric line can be explained by mixing locally derived water with isotopically light (more negative) imported water. Evaluation of isotope and trace-level VOC data collected for CAS studies in the coastal area indicate the extent that water used for recharge had displaced native ground water (Shelton and others, 2001). Modern water (less than 50 years old), including isotopically light Colorado River water and State Water Project used for recharge, typically contains trace amounts of VOCs and other compounds released from anthropogenic activities.

Stable-isotope ratios for ground-water samples collected in the Inland Basin generally fall on or near the meteoric water line and probably reflect recharge from high-altitude precipitation derived from the San Bernardino Mountains. Water samples that plot in the lower left area of the meteoric line also may reflect the effects of the mixing locally-derived ground water with isotopically light (more negative) recharge water.

Several wells sampled for the INSUS (INS-18, -20, -28) and the INFPS (INF -6, -7, 8, -9) assessments yielded the lightest isotope ratios (fig. 12) of wells sampled in the Inland Basin. These wells are downgradient from a recharge facility and are near the San Bernardino Mountains. Therefore, light isotope ratios may result from recharge by isotopically light imported water and (or) recharge by runoff derived from high-altitude precipitation. A few samples with heavy (less negative) isotopic ratios that plot to the right of the meteoric line may reflect evaporative effects.

Stable-isotope ratios for ground-water samples collected in the San Jacinto Basin also are shown in figure . Isotopically light samples that plot in the lower left area of the meteoric water line reflect recharge by water depleted in heavy isotopes, such as imported water and runoff derived from high-altitude precipitation in the San Jacinto Mountains. The isotopic composition of samples collected at three locations along the San Jacinto River ranged from -8.32 to -9.59 for $\delta^{18}\text{O}$ and from -59.1 to -63.4 for δD (Williams and others, 1993). Aqueducts for both State Project water and Colorado River water pass through the San Jacinto Basin. Lake Perris in the northwest part of the basin (fig. 4) serves as a storage reservoir for State Project water. Both of these imported waters have been utilized in the region for irrigation and artificial recharge (Williams and others, 1993). In general, most ground water in the San Jacinto Basin appears to be

dominated by recharge from high-altitude precipitation via the San Jacinto River; relatively few wells are affected by isotopically heavy recharge from low-altitude precipitation (Williams and others, 1993). Some of the ground-water samples collected in the San Jacinto Basin that plot below and to the right of the meteoric water line may reflect the effects of evaporation.

Pesticides

Pesticides are used to eliminate plant or insect pests and are generally applied to cropland in rural areas and to rights-of-way, lawns, gardens, and residential/business structures in urban areas. Some pesticides volatilize during and after application, spread over great distances, and return to the soil via atmospheric deposition (Majewski and Capel, 1995). Most pesticides are designed to stay in the soil zone; many are prone to sorb to solids and organic matter and have relatively low solubilities in water (Rao and Alley, 1993). Pesticide concentrations tend to decrease in the unsaturated zone as the compounds are degraded by abiotic and biotic processes. The likelihood of detecting one pesticide in ground water in comparison with another is related to the laboratory detection limit for a particular compound; the extent to which a particular compound is used; the degree of partitioning into the aqueous phase, relative to soil organic matter or soil; and the relative resistance to chemical transformation in soil, with or without mediation by microorganisms (Barbash and others, 1999). In general, longer ground-water flow paths allow for greater residence time and increase opportunities for sorption, degradation, and dispersion, which may cause decreases in pesticide concentration (Savoca and others, 2000).

Table 1. Pesticide compounds and predominant source or use for USGS laboratory analytical schedule 2001

[CAS, Chemical Abstract Services]

Compound	Description	CAS No.	Compound	Description	CAS No.
2,6-Diethylalanine	Degradation product	579-66-8	Malathion	Insecticide	121-75-5
Acetochlor	Herbicide	34256-82-1	Metolachlor	Herbicide	51218-45-2
Alachlor	Herbicide	15972-60-8	Metribuzin	Herbicide	21087-64-9
alpha-HCH	Degradation product	319-84-6	Molinate	Herbicide	2212-67-1
Atrazine	Herbicide	1912-24-9	Napropamide	Herbicide	15299-99-7
Azinphos-methyl	Insecticide	86-50-0	p,p'-DDE	Degradation product	72-55-9
Benfluralin	Herbicide	1861-40-1	Parathion	Insecticide	56-38-2
Butylate	Herbicide	2008-41-5	Parathion-methyl	Insecticide	2998-00-0
Carbaryl	Insecticide	63-25-2	Pebulate	Herbicide	1114-71-2
Carbofuran	Insecticide	1563-66-2	Pendimethalin	Herbicide	40487-42-1
Chlorpyrifos	Insecticide	2921-88-2	Phorate	Insecticide	298-02-2
cis-Permethrin	Insecticide	54774-45-7	Prometon	Herbicide	1610-18-0
Cyanazine	Herbicide	21725-46-2	Propachlor	Herbicide	1918-16-7
Dacthal	Herbicide	1861-32-1	Propanil	Herbicide	709-98-8
Deethylatrazine	Degradation product	6190-65-4	Propargite	Insecticide	2312-35-8
Diazinon	Insecticide	333-41-5	Propyzamide	Herbicide	23950-58-5
Dieldrin	Insecticide	60-57-1	Simazine	Herbicide	122-34-9
Disulfoton	Insecticide	298-04-4	Tebuthiuron	Herbicide	34014-18-1
EPTC	Herbicide	759-94-4	Terbacil	Herbicide	5902-51-2
Ethalfuralin	Herbicide	55283-68-6	Terbufos	Insecticide	13071-79-9
Ethoprophos	Insecticide	13194-48-4	Terbutylazine	Herbicide	5915-41-3
Fonofos	Insecticide	944-22-9	Thiobencarb	Herbicide	28249-77-6
Lindane	Insecticide	58-89-9	Tri-allate	Herbicide	2303-17-5
Linuron	Herbicide	330-55-2	Trifluralin	Herbicide	1582-09-8

Table 2. Pesticide compounds and predominant source or use for USGS laboratory analytical code 9060

[CAS, Chemical Abstract Service]

Compound	Description	CAS No.	Compound	Description	CAS No.
2,4-D	Herbicide	94-75-7	Diphenamid	Herbicide	957-51-7
2,4-d methyl ester	Insecticide	1928-38-7	Diuron	Herbicide	330-54-1
2,4-DB	Herbicide	94-82-6	Fenuron	Herbicide	101-42-8
2-Hydroxyatrazine	Degradation product	2163-68-0	Flumetsulam	Herbicide	98967-40-9
3(4-chlorophenyl) methyl urea	Degradation product	5352-88-5	Fluometuron	Herbicide	2164-17-2
3-Hydroxycarbofuran	Degradation product	16655-82-6	Imazaquin	Herbicide	81335-37-7
3-Ketocarbofuran	Degradation product	16709-30-1	Imazethaphyr	Herbicide	81335-77-5
Acifluorfen	Herbicide	50594-66-6	Imidacloprid	Insecticide	138261-41-3
Aldicarb	Insecticide	116-06-3	Linuron	Herbicide	330-55-2
Aldicarb sulfone	Degradation product	1646-88-4	MCPA	Herbicide	94-74-6
Aldicarb sulfoxide	Degradation product	1646-87-3	MCPB	Herbicide	94-81-6
Atrazine	Herbicide	1912-24-9	Metalaxyl	Fungicide	57837-19-1
Bendiocarb (Ficam)	Insecticide	22781-23-3	Methiocarb	Insecticide	2032-65-7
Benomyl	Fungicide	17804-35-2	Methomyl	Insecticide	16752-77-5
Bensulfuron-methyl	Herbicide	83055-99-6	Methomyl-oxime	Insecticide	13749-94-5
Bentazon	Herbicide	25057-89-0	Metsulfuron methyl	Herbicide	74223-64-6
Bromacil	Herbicide	314-40-9	Neburon	Herbicide	555-37-3
Bromoxynil	Herbicide	1689-84-5	Nicosulfuron	Herbicide	111991-09-4
Caffeine	Sewage tracer	58-08-2	Norflurazon	Herbicide	27314-13-2
Carbaryl	Insecticide	63-25-2	Oryzalin	Herbicide	19044-88-3
Carbofuran	Insecticide	1563-66-2	Oxamyl	Insecticide	23135-22-0
Chloramben, methyl ester	Herbicide	7286-884-2	Oxamyl oxime	Insecticide	30558-43-1
Chlorimuron ethyl	Herbicide	90982-32-4	Picloram	Herbicide	1918-02_1
Chlorothalonil	Fumigant	1897-45-6	Propham	Herbicide	122-42-9
Clopyralid	Herbicide	1702-17-6	Propiconazole	Fungicide	60207-90-1
Cycloate	Herbicide	1134-23-2	Propoxur	Insecticide	114-26-1
Dachthal monoacid	Herbicide	887-54-7	Siduron	Herbicide	1982-49-6
Deethylatrazine	Degradation product	6190-65-4	Sulfometuron methyl	Herbicide	74222-97-2
Deethyldeiso-propylatrazine	Degradation product	3397-62-4	Tebuthiuron	Herbicide	34014-18-1
Deisopropylatrazine	Degradation product	1007-28-9	Terbacil	Herbicide	5902-51-2
Dicamba	Herbicide	1918-00-9	Tribenuron-methyl	Herbicide	101200-48-0
Dichlorprop	Herbicide	120-36-5	Triclopyr	Herbicide	55335-06-3
Dinoseb	Herbicide	88-85-7			

Two USGS NWQL analytical schedules were used for these studies. Laboratory schedule 2001 ([table 1](#)) includes 48 compounds (herbicides, insecticides, and degradation products). Laboratory code (LC) 9060 ([table 2](#)) includes 65 compounds (herbicides, insecticides, fungicides, degradation products, a fumigant, and caffeine). Analytical results for pesticides determined by LC 9060 for SANA NAWQA studies (April 1999 to April 2001) reflect the implementation of new laboratory procedures and analytical equipment. During initial implementation of this method, samples were held beyond the maximum recommended laboratory holding time of 30 days (Edward Furlong, U.S. Geological Survey, written commun., 2002). This back-log included samples from the COSUS study. The holding time for COSUS samples submitted for analysis by LC 9060 in April and May of 1999 ranged from 95 to 124 days, with a median holding time of 101 days. Consequently, concentrations of compounds determined by LC 9060 for the COSUS study are likely to be biased low relative to actual concentrations in ground water (Jeffrey Martin, U.S. Geological Survey, oral commun., 2002). Another consequence of the long holding times is that some pesticide compounds may be present in COSUS ground-water samples, but were not detected by LC 9060 analysis.

Both schedules were used for samples collected for the COLUS, COSUS, INSUS, and SANSUS studies. Only schedule 2001 was used for the COFPS and INFPS studies. Pesticide samples were not collected for the OCCAS and SANCAS studies. Discussions of the results of these analyses are grouped by ground-water basin and are in order of decreasing detection frequency of pesticides for individual studies. Pesticide concentrations are tabulated in Appendix 9 for detections above the LRL and in Appendix 10 for detections below the LRL. Detections above the LRL are discussed in this section of the report.

Pesticides and metabolites were detected above LRL in 66 wells of the 133 production and monitoring wells sampled. Atrazine, deethylatrazine, simazine, tebuthiuron, and prometon were the five most commonly detected pesticides in the USGS studies (5 to 29 percent of wells sampled). All pesticides detected in the current studies were below MCLs established by the EPA.

Atrazine is a potential carcinogen and has a MCL of 3 µg/L (US EPA, 1996). Atrazine, detected in 28 percent of the wells sampled (Appendix 9), is a triazine herbicide used primarily for selective control of broadleaf and grassy weeds in agricultural settings and as a nonselective herbicide on industrial and fallow lands. It may be used legally only by licensed operators. It is moderately persistent and, because of its basic pH, sorbs to soil particles (Weber, 1994). Atrazine has a half-life of about 8 years in ground water and about 40 days in surface water.

Deethylatrazine, detected in 29 percent of the wells sampled, is a metabolite formed by biologically mediated degradation of atrazine. A MCL has not been established for deethylatrazine.

The MCL for simazine is 4 µg/L (US EPA, 1996). Simazine, detected in 28 percent of the wells sampled (Appendix 9), may only be used by licensed operators and is generally used to control weeds and other vegetation primarily along roads, driveways, right-of-ways, parking lots, and utility corridors. Simazine also has a basic pH that results in sorption to acidic soil particles (Weber, 1994). Simazine has a half-life of 90 days in neutral soils. In the context of nationwide pesticide application, simazine use is relatively high in California largely as a consequence of its extensive application to orchards, vineyards, and alfalfa (Barbash and others, 1999).

Tebuthiuron, detected in 8 percent of the wells sampled (Appendix 9), is a herbicide commonly used on road right-of-ways. An MCL for tebuthiuron has not been established. Like the other commonly detected pesticides, tebuthiuron has a basic pH, but has a greater solubility and a lesser sorption coefficient than the other pesticides (Weber, 1994). Tebuthiuron degrades slowly in soils, with a half-life of 360 days.

Prometon, detected in 5 percent of the wells sampled (Appendix 9), is a nonselective, long-lasting, pre- and post-emergent herbicide used to control perennial broadleaf weeds and grasses on right-of-ways (Sine, 1993) and is primarily applied in urban areas (Barbash and others, 1999). An MCL for prometon has not been established. Like atrazine and simazine, prometon has a basic pH, and degrades relatively slowly in soils; the estimated half life is between 200 and 500 days (Weber, 1994).

Pesticides were detected most frequently in deep production wells sampled for the subunit survey conducted in the Inland Basin (83 percent). The most frequently detected pesticides were atrazine; one of its degradation products, deethylatrazine; and simazine. Pesticides were detected less frequently in the deep monitoring and production wells sampled for the INFPS than the INSUS (Appendix 9E). The most commonly detected pesticides were simazine and atrazine. Detected concentrations of simazine and atrazine were well below the respective MCLs set by the EPA (US EPA, 1996).

The large number of pesticide detections for sites sampled in the Inland Basin probably reflects generally unconfined conditions in the ground-water system, past agricultural land use, and relatively low organic content of aquifer materials. The lower frequency of detection of pesticides in the INFPS most likely reflects the proximal location of these wells to relatively pesticide-free, mountain-front recharge. Most of the production wells sampled for the INSUS study were located in areas of the basin farther from mountain-front recharge; these wells represent distal locations in ground-water flow paths that are influenced by overlying developed land.

Pesticides were detected less frequently in the deep production wells sampled for the subunit survey in the San Jacinto Basin than in the subunit survey in the Inland Basin. The most commonly detected pesticides were simazine, atrazine, and atrazine degradates (Appendix 9F). All pesticide detections were below drinking-water standards established by the EPA (US EPA, 1996). The SANSUS assessment was the only USGS study in which frequency of detection of atrazine was greater than that for its degradation products, primarily deethylatrazine. This observation may be explained by relatively shorter flow paths in

comparison with other studies and (or) aquifer conditions that enhance mobility and stability of the parent pesticide.

The San Jacinto Basin is the least urbanized of the SANA ground-water basins and has the highest percentage of agricultural land. As mentioned previously, the occurrence of simazine is probably related to extensive agricultural applications in California. The predominance of atrazine is consistent with its primarily agricultural use.

Pesticides were detected least frequently in the Coastal Basin. Samples from the intermediate-depth production wells sampled for the Coastal flow-path study had the highest percentage of pesticide detections (43 percent) in the Coastal Basin (Appendix 9C). These wells are along a flow path that is close to engineered recharge facilities along the Santa Ana River. About 38 percent of the shallow, water-table wells sampled for the Coastal land-use study had pesticide detections (Appendix 9B). The deep, confined wells sampled for the subunit survey had the lowest number of detections (25 percent) for production wells in the Coastal Basin. The low number of detections for the Coastal subunit survey probably results from degradation and adsorption of pesticides along relatively long flow paths in comparison with the other studies.

Atrazine, deethylatrazine, simazine, and tebuthiuron were detected in samples from each of the Coastal studies (Appendix 9A–C). All pesticide detections were below drinking-water standards set by the EPA; no MCL has been established for tebuthiuron (US EPA, 1996). Prometon was the most commonly detected pesticide in the land-use study, and it was also detected in one industrial well sampled for the flow-path study (Appendix 9C).

Pesticide detections in the Coastal Basin reflect the relatively confined and extensively urbanized nature of the ground-water basin. Consequently, the distribution of pesticides in ground water is affected by proximity to source and length of flow paths. Pesticide concentrations and detection frequencies generally are highest in ground water in the unconfined forebay near the recharge facilities and decrease along radial flow paths. The occurrence of trace concentrations of pesticides in the intermediate (COFPS) and deep (COSUS) flow systems may be related to recharge from spreading grounds that utilize water from the Santa Ana River and to applications of pesticides in the forebay area. The most commonly detected pesticides in Coastal ground water (atrazine, dehyaltrazine, simazine, and tebuthiuron) were among the most frequently detected pesticides in the Santa Ana River below Prado Reservoir (Izbicki and others, 2000). During the dry season, the recharge water consists of treated wastewater that constitutes the base flow in the river. Pesticides and other contaminants may be present in the wastewater and (or) introduced to the river water as it flows through urban areas upstream of the recharge operations. The predominance of prometon and tebuthiuron, pesticides commonly used in urban areas, in the COLUS assessment probably reflects the urban land use in the vicinity of these wells and the shallow water table.

Volatile Organic Compounds

Volatile organic compounds (VOCs) are carbon-based compounds that readily evaporate in the normal range of temperature and atmospheric pressure. VOCs are used in many products including fuels, solvents, dry-cleaning agents, paints, adhesives, deodorizers, refrigerants, and pesticides. These compounds are also present in vehicle exhaust, in chlorinated drinking water, and chlorinated wastewater. VOCs can be introduced to ground water by infiltration from spills, leakage from underground storage tanks, recharge by

surface water containing VOCs, infiltration of precipitation containing VOCs, and gas-phase transfer from the atmosphere (Stackelberg and others, 2000; Baehr and others, 1999).

The USGS NWQL schedule 2020 (table 3) was used to determine concentrations of VOCs in samples from 207 wells and consists of 85 compounds, including solvents, refrigerants, fumigants, disinfection byproducts, and gasoline compounds; 38 VOC compounds were detected in the wells sampled. Of the VOCs detected, many (25) were in only one to five wells. VOC concentrations are tabulated in Appendix 11 for detections above the LRL and in Appendix 12 for detections below the LRL. Detections above LRL are discussed in this section of the report. Discussions of the results of these analyses are organized by ground-water subbasin and study and are in order of decreasing detection frequency of VOCs for individual studies.

VOCs were detected in 115 wells of the 207 wells sampled in the Santa Ana Basin. The ranking of basins based on VOC detections is the same as that derived on the basis of pesticide-detection frequency; Inland Basin, San Jacinto Basin, and the Coastal Basin. VOCs detected in at least 5 percent of the wells are, in order from high to low detection frequency, chloroform, trichloroethylene (TCE), 1,1,1-trichloroethane (TCA), trichlorofluoromethane (CFC 11), 1,1,2-trichloro-1,2,2-trifluoroethane (CFC 113), tetrachloroethylene (PCE), bromodichloromethane, methyl tert-butyl ether (MTBE), 1,2-dichloroethene (1,2-DCE), and 1,1-dichloroethene (1-1-DCE). Napthalene and benzene were detected in one INFPS monitoring well (INF-4) above the EPA MCLs of 20 and 5 µg/L, respectively (Appendix 11f). Both compounds had mean recoveries greater than 100 percent as indicated by laboratory spikes and, therefore, the exceedances of MCLs may be due to overestimates of the environmental concentrations. However, other gasoline compounds in addition to benzene were detected at this well.

Table 3. Volatile organic compounds and predominant source or use for USGS laboratory analytical schedule 2020

[CAS, Chemical Abstract Services]

Compound	Primary Use or Source	CAS No.	Compound	Primary Use or Source	CAS No.
1,1,1,2-Tetrachloroethane	Solvent	630-20-6	Carbon tetrachloride (tetrachloromethane)	Solvent	56-23-5
1,1,1-Trichloroethane (TCA)	Solvent	71-55-6	Chlorobenzene	Solvent	108-90-7
1,1,2,2-Tetrachloroethane	Solvent	79-34-5	Chloroethane	Solvent	75-00-3
1,1,2-Trichloroethane	Solvent	79-00-5	Chloroform (trichloromethane)	Disinfection byproduct	67-66-3
1,1,2-Trichlorotrifluoroethane (CFC-113)	Refrigerant	76-13-1	Chloromethane	Refrigerant	74-87-3
1,1-Dichloroethane	Solvent	75-34-3	Dibromochloromethane	Disinfection byproduct	124-48-1
1,1-Dichloroethylene	Organic synthesis	75-35-4	Dibromomethane	Solvent	74-95-3
1,1-Dichloropropene	Organic synthesis	563-58-6	cis-1,2-Dichloroethylene	Solvent	156-59-2
1,2,3,4-Tetramethylbenzene (prehnitene)	Hydrocarbon	488-23-3	cis-1,3-Dichloropropene	Fumigant	10061-01-5
1,2,3,5-Tetramethylbenzene (isodurene)	Hydrocarbon	527-53-7	trans-1,2-Dichloroethylene	Solvent	156-60-5
1,2,3-Trichlorobenzene	Organic synthesis	87-61-6	trans-1,3-Dichloropropene	Fumigant	10061-02-6
1,2,3-Trichloropropane	Solvent	96-18-4	trans-1,4-Dichloro-2-butene	Organic synthesis	110-57-6
1,2,3-Trimethylbenzene	Gasoline	526-73-8	Dichlorodifluoromethane (CFC-12)	Refrigerant	75-71-8
1,2,4-Trichlorobenzene	Solvent	120-82-1	Diethyl ether	Solvent	60-29-7
1,2,4-Trimethylbenzene	Organic synthesis	95-63-6	Diisopropyl ether	Gasoline	108-20-3
1,2-Dibromo-3-chloropropane	Fumigant	96-12-8	Ethyl methacrylate	Organic synthesis	97-63-2
1,2-Dibromoethane	Solvent	106-93-4	Ethyl tert-butyl ether (ETBE)	Gasoline	637-92-3
1,2-Dichlorobenzene	Solvent	95-50-1	Ethylbenzene	Gasoline	100-41-4
1,2-Dichloroethane	Solvent	107-06-2	Hexachlorobutadiene	Organic synthesis	87-68-3
1,2-Dichloropropane	Solvent	78-87-5	Hexachloroethane	Solvent	67-72-1
1,3,5-Trimethylbenzene	Gasoline	108-67-8	Isopropylbenzene	Organic synthesis	98-82-8
1,3-Dichlorobenzene	Solvent	541-73-1	m- and p-Xylene	Gasoline	108-38-3 106-42-3
1,3-Dichloropropane	Organic synthesis	142-28-9	Methyl acrylate	Organic synthesis	96-33-3
1,4-Dichlorobenzene	Fumigant	106-46-7	Methyl acrylonitrile	Organic synthesis	126-98-7
2,2-Dichloropropane	Organic synthesis	594-20-7	Methyl tert-butyl ether (MTBE)	Gasoline	1634-04-4
2-Butanone	Solvent	78-93-3	Methyl iodide	Organic synthesis	74-88-4
2-Chlorotoluene	Solvent	95-49-8	Methyl methacrylate	Organic synthesis	80-62-6
2-Hexanone	Solvent	591-78-6	Methylene chloride (dichloromethane)	Solvent	75-09-2
3-Chloropropene	Organic synthesis	107-05-1	Naphthalene	Organic synthesis	91-20-3
4-Chlorotoluene	Solvent	106-43-4	n-Propylbenzene	Solvent	103-65-1
4-Isopropyl-1-methylbenzene	Organic synthesis	99-87-6	o-Ethyl toluene	Hydrocarbon	611-14-3
4-Methyl-2-pentanone	Solvent	108-10-1	o-Xylene	Gasoline	95-47-6
Acetone	Solvent	67-64-1	sec-Butylbenzene	Organic synthesis	135-98-8
Acrylonitrile	Organic synthesis	107-13-1	Styrene	Organic synthesis	100-42-5
Benzene	Gasoline	71-43-2	tert-Butyl methyl ether	Gasoline	1634-04-4
Bromobenzene	Solvent	108-86-1	tert-Butylbenzene	Organic synthesis	98-06-6
Bromochloromethane	Organic synthesis	74-97-5	Tetrachloroethylene (PCE)	Solvent	127-18-4
Bromodichloromethane	Disinfection byproduct	75-27-4	Tetrahydrofuran	Solvent	109-99-9
Bromoethene	Organic synthesis	593-60-2	Toluene	Gasoline	108-88-3
Bromoform (tribromomethane)	Disinfection byproduct	75-25-2	Trichloroethylene (TCE)	Solvent	79-01-6
Bromomethane	Fumigant	74-83-9	Trichlorofluoromethane (CFC-11)	Refrigerant	75-69-4
Butylbenzene	Organic synthesis	104-51-8	Vinyl chloride	Organic synthesis	75-01-4
Carbon disulfide	Organic synthesis	75-15-0			

The EPA has established an MCL of 100 µg/L for total trihalomethanes (US EPA, 2000), which include chloroform and other disinfection byproducts. Chloroform, also known as trichloromethane, is a common disinfection by-product formed during chlorination of drinking water; occurrences in ground water are associated with residential water used for irrigation and with treated wastewater. It was detected in 36 percent of the wells sampled. Primary sources include water utilities, sewage-treatment plants, pulp and paper mills, and pharmaceutical plants (Verschueren, 1983). Minor sources include automobile exhaust, pesticides, tobacco smoke, decomposition of TCE, and combustion of plastics (Verschueren, 1983). Chloroform also is used as a solvent in industrial applications. Bromodichloromethane, also a disinfection by-product, was detected in 10 percent of the wells sampled. None of the wells sampled for any of the studies exceeded the EPA MCL for these compounds.

The EPA has established MCLs for TCE (5 µg/L) and TCA (200 µg/L) that were developed to minimize potential health effects, including liver and kidney damage (US EPA, 2000). TCE and TCA are commonly used industrial and commercial solvents and have been produced in large quantities since the 1960s (Stackleberg and others, 2000). TCE and TCA were detected in 13 percent and 12 percent of the wells sampled, respectively. The widespread occurrence of TCE and TCA may reflect their use in household products used for cleaning, painting, and car care. Industrial uses of TCA include degreasing of metal parts in repair shops and in electronic manufacturing (Pankow and Cherry, 1996). The MCL for TCE was exceeded in two INSUS wells used for irrigation. None of the wells sampled for any of the studies exceeded the MCL established by the EPA for TCA.

The EPA MCL for PCE is 5 µg/L (US EPA, 2000). PCE is primarily used as a dry cleaning agent and as a solvent. It was detected in 10 percent of the wells sampled. Samples from two wells in the Inland Basin exceeded the EPA MCL.

CFC 11 and CFC 113 are refrigerants used in air conditioners, coolants, aerosol sprays, cleaning compounds, and solvents during the 1970s. CFC 11 and CFC 113 were detected in 11 percent of the wells

sampled. The EPA has not established MCLs for these compounds. CFC 11 and CFC 113 were the most frequently detected refrigerants in a study of VOC occurrence in the southern California coastal groundwater basin (Shelton and others, 2001). These refrigerants will be phased out of production (US EPA, 1999c).

The EPA has established an MCL of 20 µg/L for MTBE (US EPA, 2000); the California State MCL is 13 µg/L (California Department of Health Services, 2001). MTBE is a fuel oxygenate that was used to enhance octane levels in gasoline beginning in the late 1970s (Zogorski and others, 1996). MTBE was detected in about 7 percent of the wells sampled. MTBE is a suspected carcinogen. MTBE is highly soluble in water and can be easily transported to ground water from road-surface runoff or from precipitation and surface water in areas where it is present in the air (Squillace and others, 1999). None of the wells sampled for any of the studies exceeded the EPA MCL or the California MCL.

The EPA has established an MCL of 7 µg/L for 1,1-DCE and an MCL of 70 µg/L for 1,2-DCE (US EPA, 2000). The primary use of 1,1-DCE is for organic synthesis in making adhesives, synthetic fibers, refrigerants, and food packaging such as plastic wraps (US EPA, 2000). It was detected in 6 percent of the wells sampled. The cis- and trans- forms of 1,2-DCE are used as solvents and also are formed by degradation of TCE (Grady and Casey, 2001). These compounds were detected in about 5 percent of the wells sampled. None of the wells sampled for any of the studies exceeded the EPA MCLs established for these compounds.

VOCs were detected most frequently in the Inland Basin (Appendix 11E,F). The Inland subunit survey yielded the greatest percentage of VOC detections for deep production wells sampled (66 percent). The most frequently detected VOCs were chloroform, TCE, PCE, and DCE. VOCs were detected in 62 percent of the wells sampled for the Inland flow-path study (20 monitoring wells and 1 production well). The most frequently detected VOCs were CFC 11, a variety of gasoline compounds, ethylbenzene, and MTBE.

The only VOCs from the Inland Basin studies that exceeded established MCLs were from 6 production wells sampled for the subunit survey and from 2 monitoring wells sampled for the flow-path study. All of these wells produced water for nonpotable use. TCE exceeded the EPA MCL of 5 µg/L in two irrigation wells, which yielded concentrations of 10.6 and 104 µg/L (Appendix 11E). PCE exceeded the EPA MCL of 5 µg/L in two irrigation wells, which yielded concentrations of 8.3 and 17.8 µg/L (Appendix 11E). Dibromochloropropane (DBCP) exceeded the EPA MCL of 0.2 µg/L in two irrigation wells, which yielded concentrations of 0.4 and 2.8 µg/L (Appendix 11E). DBCP concentration in one flow-path monitoring well (0.3 µg/L) exceeded the EPA MCL (Appendix 11F). Naphthalene and benzene were detected in one flow-path monitoring well above the EPA MCLs of 20 and 5 µg/L, respectively. There were no exceedances of VOC MCLs in the other basins.

VOC detections in sites sampled in the Inland Basin reflect generally unconfined conditions in the ground-water system, agricultural and urban land use, and discharges from industrial operations. Several VOC plumes, delineated by organic solvents, have been mapped in the western and northern parts of the basin (fig. 3; Santa Ana Watershed Project Authority, 1998). The flow-path study had the highest frequency of detection for VOCs of the current studies; it is located in an area of known VOC plumes. Production wells from the Inland subunit survey had the second highest frequency of detection for VOCs of the current studies. Wells with VOC detections were commonly located near known VOC plumes. Wells without VOC detections were generally deep or located near recharge areas above urban development along the mountain front.

VOCs were detected less frequently in the San Jacinto Basin (Appendix 11G, H) than the Inland Basin (Appendix 11, E, F). VOCs were detected in 64 percent of the production wells sampled for the SANCAS study. The most commonly detected VOCs were chloroform and dichloropropane. None of the VOCs detected exceeded MCLs established by the EPA. VOCs were detected in 56 percent of the production wells sampled for the San Jacinto subunit survey. The lower detection frequency in comparison with the

SANCAS study may reflect a mix of irrigation and public supply wells, many of which are in areas less affected by urban development. The most commonly detected VOCs were chloroform and PCE.

The San Jacinto Basin is less urbanized than the Inland Basin and has a high percentage of agricultural land. Lower frequency of VOC detections probably reflects a relatively smaller percentage of urban and industrial land use. However, because the aquifers are generally unconfined, they are susceptible to contamination from surface sources. The potential for contamination of ground water by VOCs can be expected to increase as urban development proceeds.

VOCs were detected least frequently in production wells in the Coastal Basin (Appendix 11A–D). The ranking of VOC detection frequencies for the different studies in the Coastal Basin is the same as the ranking of pesticide detection frequencies; COFPS (52 percent), COLUS (50 percent), and COSUS (45 percent). Pesticide concentrations were not determined in the OCCAS study; VOC detection frequency in the OCCAS was 48 percent. The ranking of VOC detections may be related to the characteristics of the ground-water flow system. As previously mentioned, the flow-path production wells are located along a flow path that is in proximity to engineered recharge facilities along the Santa Ana river that utilize water impacted by upgradient urban land use. The Coastal land-use study utilized shallow monitoring wells generally tapping the first occurrence of ground water. The OCCAS and COSUS studies utilized production wells generally tapping the aquifer system at greater depths than the flow-path study.

The most commonly detected VOCs in the Coastal flow-path study were TCA, CFC 113, chloroform, CFC 11, TCE, and MTBE (Appendix 11C). The most commonly detected VOCs in the Coastal land-use study were chloroform, MTBE, toluene, and dichloroethane (Appendix 11B). The most commonly detected VOCs in the OCCAS study were chloroform, bromodichloromethane, and TCA (Appendix 11D). The most commonly detected VOCs in the Coastal subunit survey were chloroform, CFC 113, bromodichloromethane, and TCA (Appendix 11A).

The highest VOC detection frequencies in production wells sampled for the Coastal flow-path study occur in the forebay (fig. 2; Appendix 11C) and in the confined zone in proximity to the forebay. The VOCs detected in shallow monitoring wells sampled for the Coastal land-use study (Appendix 11B) probably reflect the use of chlorinated water for irrigation (chloroform) as well as atmospheric deposition and proximity to leaky underground storage tanks (source of MTBE). The similarity in VOC-detection frequencies in the deep production wells sampled for COSUS and OCCAS assessments (Appendix 11A, D) probably reflect similar geographic distribution and depth intervals for the wells sampled. The overall lower frequencies of detection in comparison with the other VOC studies probably reflects the greater number of deep wells screened in confined aquifers sampled for these two studies and longer flow paths.

The Coastal Basin is the most highly urbanized of the ground-water basins studied, but most wells are screened in confined aquifers that are isolated from overlying land use. The distribution of VOCs in ground water is related to the location of the well (confined versus unconfined aquifers), well depth, and proximity to sources of recharge. Trace amounts of VOCs in well water, along with age dating, have been used to trace the movement of water from artificial-recharge operations through the ground-water system.

Shelton and others (2001) found that wells sampled in the unconfined forebay area had significantly higher VOC-detection frequencies than those sampled in the confined pressure area. They also found that recharge from the Santa Ana River was a likely source of chloroform and MTBE to ground water.

SUMMARY

Water-quality samples were collected from 207 wells in the Santa Ana Watershed to assess the occurrence and distribution of dissolved constituents in ground water. The Santa Ana Watershed is subdivided into the Coastal, Inland, and San Jacinto subbasins. The wells were sampled during eight studies that were designed to sample the ground-water resource used for water supply at different scales: (1) three subunit surveys (SUS) that characterize water quality at a

regional scale, (2) two flow-path studies (FPS) that focus on variations in water quality along a flow path, (3) an urban land-use study (LUS) that focused on evaluation of water quality in shallow ground water, and (4) two studies (CAS) that were designed to assess aquifer susceptibility to contamination. The purpose of this report was to summarize the data collected for these studies and to compare environmental concentrations with drinking-water standards.

Most of the wells sampled for the regional scale SUS, FPS, and CAS studies were public-supply wells; a small number of irrigation wells were also sampled. The LUS study in the Coastal Basin (COLUS) sampled shallow monitoring wells; the FPS study in the Inland Basin (INFPS) utilized deep monitoring and production wells. Constituents that exceeded primary, secondary, or proposed EPA standards were TDS, chloride, sulfate, nitrate, arsenic, iron, manganese, uranium, radon, TCE, PCE, DBCP, benzene, and naphthalene. Except for VOCs, most exceedances occurred in the shallow monitoring wells sampled for the COLUS study in the Coastal Basin; these wells tap ground water not used for public supply. All VOC exceedances were in the Inland Basin in six wells not used for public supply.

In the Coastal Basin, there were four studies; the COSUS, COLUS, COFPS, and OCCAS assessments. Ground water that occurs in the major aquifers of the Coastal Basin may be divided into three general zones based on lateral distance from recharge facilities along the Santa Ana River in the unconfined forebay area. Ground water near the recharge basins reflects the quality of recent recharge water and influence of land-use activities. The quality of ground water at the distal end of the flow system in the confined areas near the coast represents predevelopment conditions (native ground water). Ground-water quality in the intermediate area between the recharge basins and distal zone reflects historical variation in recharge-water quality, land-use activities in the forebay, and mixing with native ground water. The COSUS, COFPS, and OCCAS assessments sampled these three zones; the COLUS sampled shallow ground water not connected to aquifers used for water supply. The COSUS included wells from relatively deep aquifers used for water supply, the COFPS included wells primarily from intermediate-depth aquifers, and the OCCAS included public-supply wells from intermediate and deep depths.

In the Inland Basin, there were two studies; the INSUS and the INFPS. The Inland Basin is characterized by an unconfined aquifer system in which high-quality recharge is distributed over a broad area near the mountain front. As ground water moves toward areas of discharge, overlying land-use activities impact water quality. Spills and discharges of industrial and commercial chemicals have generated several plumes that demarcate flow paths. Other factors that influence ground-water quality in the Inland Basin include interaction with the Santa Ana River, discharge of recycled wastewater to the river, and use of imported water in the basin. The INSUS study included deep production wells distributed throughout the basin. The INFPS study included monitoring and production wells along two flow paths originating near the San Bernardino Mountains and extending to a discharge area near the San Jacinto Fault.

In the San Jacinto Basin, production wells were sampled for two studies; SANSUS and SANCAS. The San Jacinto Basin is characterized by a series of interconnected alluvial-filled valleys bounded by steep-sided bedrock mountains and hills. These mostly unconfined deposits are recharged largely from irrigation-return flows and from percolation ponds filled with reclaimed water and, to a lesser extent, by infiltration from the San Jacinto River. Ground-water discharge occurs primarily by ground-water pumping. Ground-water quality is affected by agricultural and urban land uses, as well as by use of imported water and reclaimed water for ground-water recharge. The SANSUS study primarily utilized public-supply wells and a few irrigation wells distributed across the basin; the SANCAS assessment utilized public-supply wells mainly in the Hemet area.

Ground water in the Coastal Basin shows a wide range in major-ion composition; the calcium-bicarbonate and sodium-sulfate/chloride water types reflect the long history of engineered recharge replacing native ground water. In contrast, ground-water samples from the Inland Basin are mostly

calcium-bicarbonate in composition, reflecting recharge by runoff from adjacent mountain ranges. The range of composition for ground-water samples in the San Jacinto Basin is similar to that in the Coastal Basin, reflecting extensive use of imported water and recycled wastewater for ground-water recharge. Major-ion composition of ground-water samples from the Coastal land-use study assessment was similar to that of the other studies, except for several samples that are similar in composition to seawater. Many shallow land-use wells are located in a historical marsh area and water quality probably reflects the influence of the marsh environment and local landscape maintenance.

The EPA secondary maximum contaminant level (secondary MCL) for TDS is 500 mg/L. This standard was exceeded in 39 percent of the production wells sampled in all three subbasins and in 92 percent of the Coastal land-use monitoring wells; one monitoring well had a TDS concentration of 25,500 mg/L. The quality of water from these shallow monitoring wells generally reflects the historical marsh environment in much of the area and the effect of landscape maintenance in the vicinity of the wellhead.

Production wells in the Coastal Basin had higher TDS concentrations than in the other two basins; 59 percent of the samples exceeded the EPA secondary MCL. Higher TDS concentrations in the Coastal flow-path relative to the subunit survey wells may reflect closer proximity to engineered recharge facilities and shorter flow paths in the intermediate-depth aquifer sampled by the COFPS wells. The secondary MCL for TDS was exceeded in 39 percent of the production wells sampled in the San Jacinto Basin. This relatively low exceedance probably reflects recharge by low-TDS runoff from the adjacent San Jacinto Mountains. Only 10 percent of the production wells sampled in the Inland Basin had TDS concentrations that exceeded the secondary MCL. This may be explained by the widespread recharge of low-TDS water in the basin, derived from the adjacent mountains.

In the Coastal Basin, water from one production well sampled for the COSUS study slightly exceeded the secondary MCL for chloride (250 mg/L). In contrast, about 40 percent of the samples from the land-use monitoring wells exceeded the secondary MCL; the highest concentration of chloride was 9,430 mg/L. Potential sources of high chloride concentrations in the land-use monitoring wells are deep brines and evaporated water associated with the historical marsh environment. Samples from two production wells in the San Jacinto Basin had chloride concentrations that were above the secondary MCL. All samples from wells in the Inland Basin were below the secondary MCL for chloride. However, no wells were sampled in the area affected by dairy operations near Chino due to lack of well-construction data. Possible sources of the elevated chloride concentrations include irrigation-return flow, recharge of recycled wastewater, infiltration of evaporated water from percolation ponds, and animal feeding operations.

In the Coastal Basin, one production well sampled for the flow-path study had a sulfate concentration slightly above the secondary MCL (250 mg/L). However, 80 percent of the samples from the land-use monitoring wells exceeded the secondary MCL for sulfate. The highest concentration of sulfate was 5,270 mg/L, which exceeds the concentration in seawater (2,700 mg/L). In general, evaporation and geochemical conditions have likely influenced sulfate concentration in shallow ground water in the historical marsh environment. Water from two wells in the Inland Basin sampled for the flow-path study had sulfate concentrations that exceeded the secondary MCL. Similarly, two production wells sampled for the subunit survey in the San Jacinto Basin had sulfate concentrations that exceeded the secondary MCL. The most likely sources of elevated sulfate concentration in production wells sampled are recharge of recycled wastewater and infiltration from agricultural activities.

The San Jacinto Basin had the greatest percentage of exceedances for the nitrate MCL of 10 mg/L; 22 percent of the production wells sampled for the subunit survey exceeded the MCL. The highest nitrate concentration from these samples was 16.6 mg/L. Potential sources are agricultural activities and recycled water used for ground-water recharge. Nitrate concentrations in the Inland Basin exceeded the MCL in 10 percent of the production wells sampled for the INSUS study; the highest nitrate concentration was 20.1 mg/L. General sources of nitrate to ground water

include fertilizers, exfiltration from sewer pipes, infiltration from agricultural activities, and discharge of reclaimed wastewater.

All sampled municipal-supply wells in the confined Coastal Basin had nitrate concentrations below 10 mg/L. However, 19 percent of the shallow monitoring wells sampled in the Coastal Basin had nitrate concentrations exceeding the MCL. These exceedances may reflect the fertilizer use and irrigation practices in the vicinity of these shallow wells.

Water-quality samples were collected for 22 trace elements. Of the 94 production wells sampled for trace elements, samples from 3 irrigation wells in the Coastal Basin exceeded the secondary MCL for manganese (50 µg/L). All other production wells were in compliance with EPA standards for all other trace elements, including the proposed MCL for arsenic (10 µg/L).

Some of the monitoring wells sampled for the Coastal land-use and Inland flow-path studies had trace-element concentrations that exceeded EPA MCLs for drinking water. About 19 percent of the shallow monitoring wells sampled for the Coastal land-use study had arsenic concentrations exceeding the proposed EPA MCL of 10 µg/L. Arsenic has been used as a component of pesticides and has also been detected in some fertilizers and may enter ground water by means of agricultural drainage. Elevated concentrations of arsenic in the shallow land-use monitoring wells may be derived from natural sources and from local pesticide and fertilizer use. About 44 percent of the land-use wells sampled had iron concentrations that exceeded the EPA secondary MCL of 0.3 mg/L; six wells had concentrations between 2 and 39 mg/L. The most likely sources of elevated iron concentrations in these shallow monitoring wells are natural sources in the historical marsh area, soil supplements, and fertilizers. One monitoring well sampled for the Inland flow-path study yielded an iron concentration (7.4 mg/L) that exceeded the secondary MCL. About 80 percent of the monitoring wells sampled for the Coastal land-use study had manganese concentrations that exceeded the secondary MCL (0.05 mg/L); six wells had concentrations between 1 and 8 mg/L. The most likely sources of elevated manganese concentrations in the Coastal land-use monitoring wells are natural deposits in the historical marsh area and use of manganese supplements. None of the production wells sampled in the San Jacinto Basin exceeded the secondary MCL for manganese.

Samples for the radioactive elements uranium and radon were collected from 94 production wells and 45 monitoring wells. The EPA has proposed an MCL of 30 µg/L for uranium that would become effective in December 2003. None of the samples from production wells were above the proposed MCL. About 48 percent of the shallow monitoring wells sampled for the COLUS study exceeded the proposed MCL, ranging from 43 to 312 µg/L. Elevated levels of uranium are probably derived from local soils and have been concentrated by chemical reactions in the marsh environment and by irrigation practices. Fertilizer also may be a source of uranium.

The EPA has developed a proposed MCL of 300 pCi/L and an alternative MCL of 4,000 pCi/L for radon in drinking water to reduce health risk from breathing radon in indoor air. In the Coastal Basin, about 95 percent of the production wells sampled for the COSUS study had radon concentrations exceeding the proposed MCL. About 75 percent of the monitoring wells sampled for the COLUS assessment had radon concentrations exceeding the proposed MCL. In the Inland Basin, about 79 percent of the production wells sampled for the INSUS study had radon concentrations exceeding the proposed MCL. Many of these wells are screened in deposits derived from granitic mountains on the north side of the basin; uranium is commonly associated with granitic rocks. In the San Jacinto Basin, about 60 percent of the sites sampled for the SANSUS study had radon concentrations exceeding the proposed MCL; the highest radon concentration (1,800 pCi/L) was from a well located in the southwestern part of the basin. The alternative MCL was exceeded at a single site; one INSUS production well yielded a radon concentration of 4,560 pCi/L. Elevated levels of radon, an end member in the uranium decay series, are most likely related to naturally occurring sources and, in some instances, recharge by imported water.

Pesticides were detected above the LRL in 66 of the 133 wells (50 percent) sampled in the Santa Ana ground-water basins. Five pesticides were detected in at least 5 percent of the wells sampled; deethylatrazine, simazine, atrazine, tebuthiuron, and prometon. All pesticides detected in the current studies were below MCLs established by the EPA. Pesticide detections were most frequent in the unconfined Inland Basin

aquifers (83 percent) and least frequent in the confined Coastal Basin aquifers; pesticides were detected less frequently in the deep production wells of the Coastal Basin (25 percent) than in the intermediate-depth production wells (43 percent). Within the Inland Basin, there were fewer pesticide detections in the wells sampled for the Inland flow-path study than elsewhere. This is likely related to recharge from mountain-front runoff. Pesticides were detected in about 48 percent of the production wells sampled for the subunit survey in the San Jacinto Basin. About 38 percent of the shallow, water-table wells sampled for the COLUS assessment had pesticide detections.

VOCs were detected above LRL in 115 of the 207 wells (56 percent) sampled in the Santa Ana ground-water basins. Ten VOCs were detected in at least 5 percent of the wells sampled: chloroform, trichloroethylene (TCE); 1,1,1-trichloroethane (TCA); trichlorofluoromethane (CFC 11); 1,1,2-trichloro-1,2,2-trifluoroethane (CFC 113); tetrachloroethylene (PCE); bromodichloromethane; methyl tert-butyl ether (MTBE); 1,2-dichloroethene (1,2-DCE); and 1,1-dichloroethene (1-1-DCE). The ranking of basins based on frequency of VOC detections in production wells is the same as that derived from pesticide-detection frequency; Inland Basin (66 percent), San Jacinto Basin (59 percent), and the Coastal Basin (about 48 percent).

The concentrations of VOCs exceeded MCLs in eight wells in the Inland Basin; six wells sampled for the subunit survey and two wells sampled for the flow-path study. All of these wells produced water for nonpotable use. Concentrations of TCE and PCE exceeded the EPA MCL of 5 µg/L for these compounds in two irrigation wells. Concentrations of dibromochloropropane (DBCP) exceeded the EPA MCL of 0.2 µg/L in two irrigation wells and in one flow-path monitoring well (0.3 µg/L). Naphthalene and benzene were detected in one flow-path monitoring well above the EPA MCLs of 20 and 5 µg/L, respectively. However, both compounds had high mean recoveries as indicated by laboratory spikes. Therefore, the exceedances may be due to overestimates of the environmental concentrations. There were no exceedances of VOC MCLs in the other basins.

As with pesticide detections, samples in the Coastal Basin from the intermediate-depth production wells used for the flow-path study had a higher percentage of VOC detections (52 percent) than either the subunit production wells (45 percent) or the land-use monitoring wells (50 percent). VOCs were detected in 48 percent of the public-supply wells sampled for the OCCAS study, in which sampled wells were of intermediate and deep depths.

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APPENDIXES

