# Shallow Ground-Water Quality Beneath Rice Areas in the Sacramento Valley, California, 1997

by Barbara J. Milby Dawson

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.

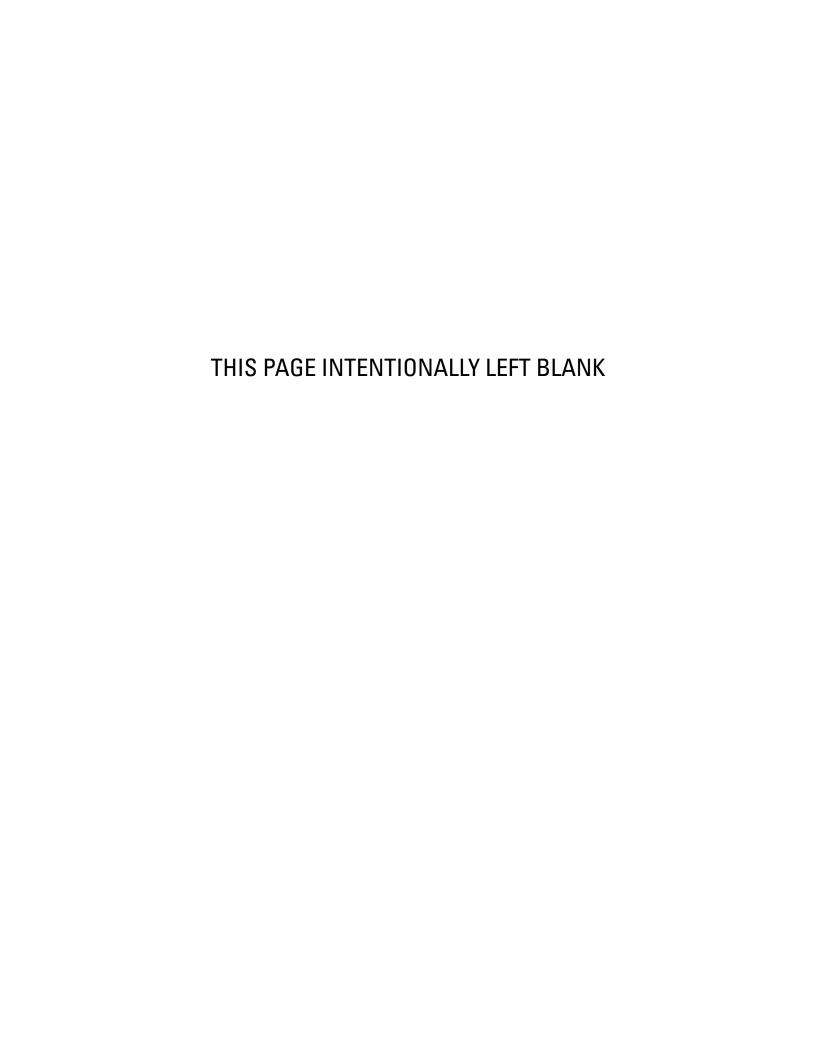
Each assessment is guided by a nationally consistent study design and methods of sampling and analysis. The assessments thereby build local knowledge about water-quality issues and trends in a particular stream or aquifer while providing an understanding of how and why water quality varies regionally 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 water-sheds 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. Hersch

Robert M. Hirsch Associate Director for Water



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#### CONVERSION FACTORS, VERTICAL DATUM, ACRONYMS, AND ABBREVIATIONS

Multiply	Ву	To obtain
centimeter (cm)	0.3937	inch
centimeter per year (cm/yr)	0.3937	inch per year
cubic meter (m <sup>3</sup> )	0.0008107	acre-foot
cubic meter per day (m <sup>3</sup> /d)	35.31	cubic foot per day
cubic meter per square kilometer (m <sup>3</sup> /km <sup>2</sup> )	0.0021	acre-foot per square mile
meter (m)	1.094	yard
meter per day (m/d)	3.281	foot per day
square kilometer (km <sup>2</sup> )	0.3861	square mile

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

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

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

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

#### **Acronyms and Abbreviations**

δ, delta

<sup>2</sup>H, deuterium

<sup>3</sup>H, tritium

<sup>16</sup>O, oxygen-16

<sup>18</sup>O, oxygen-18

μg/L, microgram per liter

µS/cm, microsiemens per centimeter

‰, per thousand

DHS, California Department of Health Services

DNOC, 4,6-dinitro-o-cresol

DOC, dissolved organic carbon

EPA, U.S. Environmental Protection Agency

GC/MS, gas chromatography/mass spectrometry

GMWL, global meteoric water line

HAL, health advisory limit

HPLC, high performance liquid chromatography

MCL, maximum containment level

mg/L, milligram per liter

Mm<sup>3</sup>/d, million cubic meters per day

NAWQA, National Water-Quality Assessment (Program)

NWQL, National Water Quality Laboratory

p, level of statistical significance (Kruskal–Wallis rank-sum test)

pCi/L, picocurie per liter

PVC, polyvinyl chloride

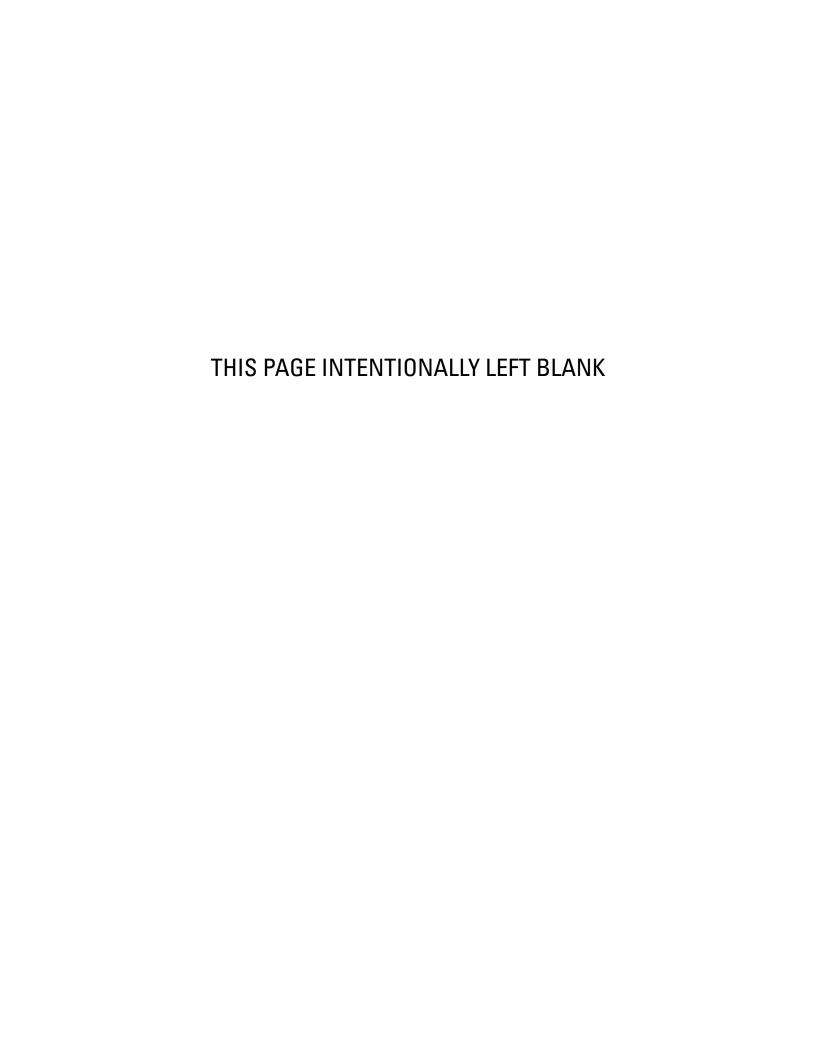
QC, quality control

ρ, Spearman's rho

SMCL, secondary maximum contaminant level

USGS, U.S. Geological Survey

VSMOW, Vienna Standard Mean Ocean Water



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#### **ABSTRACT**

In 1997, the U.S. Geological Survey installed and sampled 28 wells in rice areas in the Sacramento Valley as part of the National Water-Quality Assessment Program. The purpose of the study was to assess the shallow ground-water quality and to determine whether any effects on water quality could be related to human activities and particularly rice agriculture. The wells installed and sampled were between 8.8 and 15.2 meters deep, and water levels were between 0.4 and 8.0 meters below land surface. Ground-water samples were analyzed for 6 field measurements, 29 inorganic constituents, 6 nutrient constituents, dissolved organic carbon, 86 pesticides, tritium (hydrogen-3), deuterium (hydrogen-2), and oxygen-18.

At least one health-related state or federal drinking-water standard (maximum contaminant or long-term health advisory level) was exceeded in 25 percent of the wells for barium, boron, cadmium, molybdenum, or sulfate. At least one state or federal secondary maximum contaminant level was exceeded in 79 percent of the wells for chloride, iron, manganese, specific conductance, or dissolved solids. Nitrate and nitrite were detected at concentrations below state and federal 2000 drinking-water standards; three wells had nitrate concentrations greater than 3 milligrams per liter, a level that may indicate impact from human activities. Ground-water redox conditions were anoxic in 26 out of 28 wells sampled (93 percent).

Eleven pesticides and one pesticide degradation product were detected in ground-water samples. Four of the detected pesticides are or have been used on rice crops in the Sacramento Valley (bentazon, carbofuran, molinate, and thiobencarb). Pesticides were detected in 89 percent of the wells sampled, and rice pesticides were detected in 82 percent of the wells sampled. The

most frequently detected pesticide was the rice herbicide bentazon, detected in 20 out of 28 wells (71 percent); the other pesticides detected have been used for rice, agricultural, and non-agricultural purposes. All pesticide concentrations were below state and federal 2000 drinking-water standards.

The relation of the ground-water quality to natural processes and human activities was tested using statistical methods (Spearman rank correlation, Kruskal–Wallis, or rank-sum tests) to determine whether an influence from rice land-use or other human activities on ground-water chemistry could be identified. The detection of pesticides in 89 percent of the wells sampled indicates that human activities have affected shallow ground-water quality. Concentrations of dissolved solids and inorganic constituents that exceeded state or federal 2000 drinking-water standards showed a statistical relation to geomorphic unit. This is interpreted as a relation to natural processes and variations in geology in the Sacramento River Basin; the high concentrations of dissolved solids and most inorganic constituents did not appear to be related to rice land use. No correlation was found between nitrate concentration and pesticide occurrence, indicating that an absence of high nitrate concentrations is not a predictor of an absence of pesticide contamination in areas with reducing ground-water conditions in the Sacramento Valley.

Tritium concentrations, pesticide detections, stable isotope data, and dissolved-solids concentrations suggest that shallow ground water in the ricegrowing areas of the Sacramento Valley is a mix of recently recharged ground water containing pesticides, nitrate, and tritium, and unknown sources of water that contains high concentrations of dissolved solids and some inorganic constituents and is enriched in oxygen-18. Evaporation of applied irrigation water, which leaves behind salt, accounts for some of the

elevated concentrations of dissolved solids. More work needs to be done to understand the connections between the land surface, shallow ground water, deep ground water, and the drinking-water supplies in the Sacramento Valley.

#### INTRODUCTION

In 1997, the U.S. Geological Survey (USGS) initiated a ground-water quality study in rice areas of the Sacramento Valley in northern California (fig. 1). This study is one component of the USGS's National Water-Quality Assessment (NAWQA) Program, which was initiated in 1994 in the Sacramento River Basin. The NAWQA Program, which began nationwide in 1991, is described in Hirsch and others (1988). Data from studies in the Sacramento River Basin will be compared to similar studies throughout the United States in order to assess the quality of the nation's water resources, to determine any long-term changes in water quality, and to identify natural and human factors that affect water quality. This study of groundwater quality in rice areas of the Sacramento Valley is one of three ground-water studies conducted by the Sacramento River Basin NAWQA Program during 1996-1998. In 1996, the Sacramento River Basin NAWQA group began a study of ground-water quality in the southeastern part of the Sacramento Valley aguifer; in 1998, the Sacramento River Basin NAWQA group began a study of ground-water quality in the Sacramento, Calif., metropolitan area.

The Sacramento River Basin NAWQA study of ground-water quality in rice areas is the type of NAWQA study referred to as a land-use study. The objective of a NAWQA land-use study is to assess the shallow ground-water quality beneath a major land use in the basin. This rice land-use study determined the general water chemistry and quality of the ground water in the upper part of the Sacramento Valley aquifer beneath rice areas, including the occurrence and distribution of nitrate, inorganic constituents, and pesticides. A secondary objective of this study was to determine whether the observed water quality could be related to the overlying rice land-use. Rice was chosen for this study because it is the largest crop acreage in the Sacramento River Basin and rice pesticides have been detected in both surface and ground water. Previous studies have detected the rice pesticides bentazon, 2,4-D, malathion, and molinate in domestic

wells in the Sacramento Valley (Bartkowiak and others, 1998).

#### **Purpose and Scope**

The purpose of this report is to describe the shallow ground-water quality beneath rice areas in the Sacramento Valley and relate that water quality to human activities (land and pesticide use) and natural factors (depth to water level and top of well screen, redox condition, and geomorphology). Ground-water samples from 28 wells (fig. 2) were analyzed for 6 field measurements, 29 inorganic constituents, 6 nutrient constituents, organic carbon, 86 pesticides, <sup>3</sup>H (tritium), <sup>2</sup>H (deuterium), and <sup>18</sup>O (oxygen-18). Observed concentrations were compared to data on geomorphic unit, well depth, ground-water level, land use, and pesticide and fertilizer use.

#### **Acknowledgments**

The author thanks the rice farmers and landowners of the Sacramento Valley for allowing the USGS to install and sample monitoring wells on their property. The author also thanks the counties of Sacramento, Sutter, Butte, Glenn, and Colusa for allowing the USGS to install and sample monitoring wells on county property and for helping to locate sites.

#### STUDY-AREA DESCRIPTION

#### **Climate and Population**

The study area is located in the central part of the Sacramento Valley (fig. 1), which is the northern third of California's Central Valley. The land surface elevations range from sea level to about 152 m above sea level along the edges of the valley. The Sacramento Valley has a Mediterranean-type climate (Blair and Fite, 1957, p. 323) with hot dry summers and wet mild winters. Rainfall in the study area ranges from about 43 to 69 cm/yr (Daly and Taylor, 1998), almost all between late autumn and early spring. The population density ranges from fewer than 100 people per square kilometer throughout most of the rice area to between 965 and 4,806 people per square kilometer in the city of Colusa (Hitt, 1994).

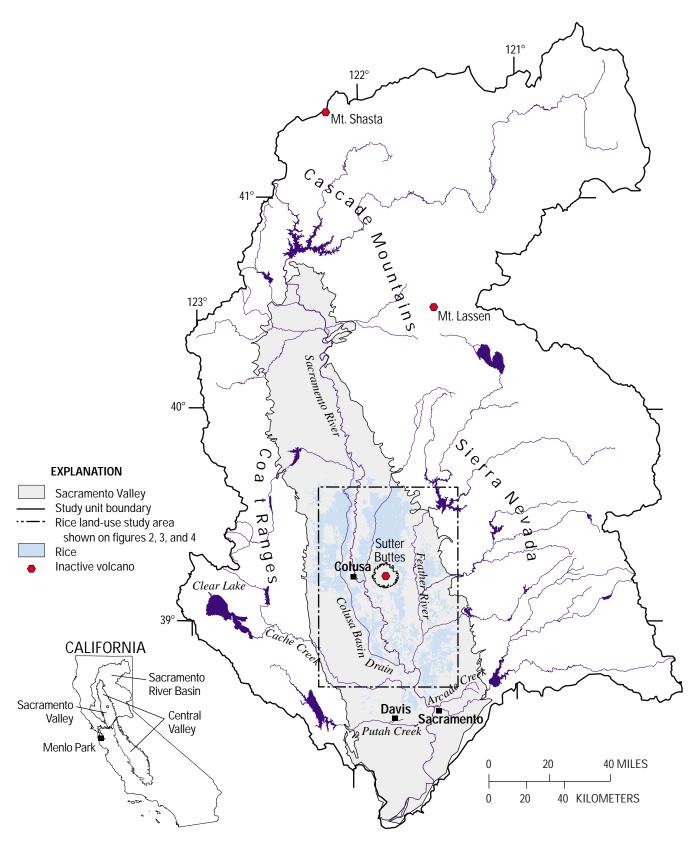


Figure 1. Location of the rice land-use study area and the Sacramento River Basin, California.

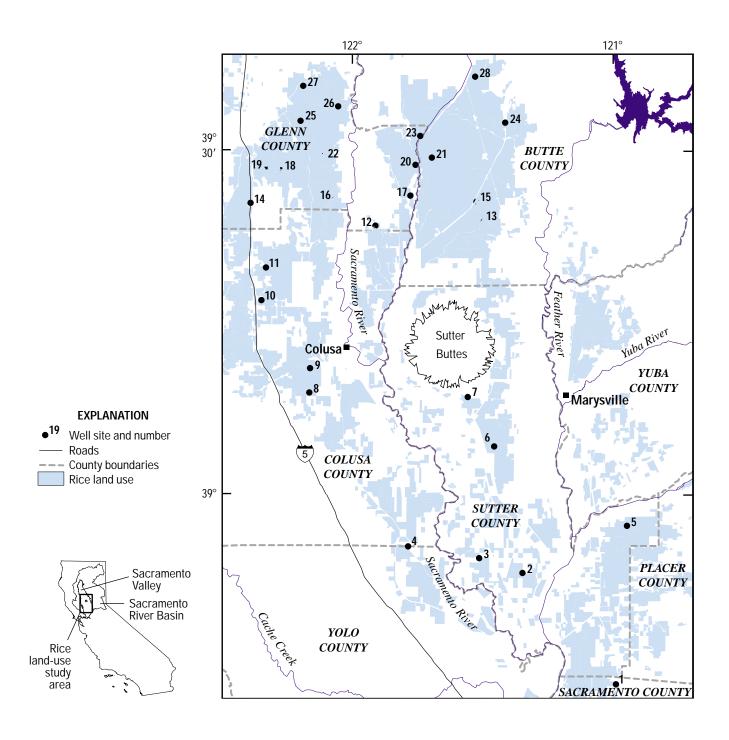


Figure 2. Locations of wells sampled in the rice areas in the Sacramento Valley, California.

#### **Land and Water Use**

Rice has been grown commercially in the Sacramento Valley since the early 1900s. Annual rice growing area currently (2000) is around 2,023 km<sup>2</sup>, and since the 1950s has been between 1,214 and

2,023 km<sup>2</sup>. About 30 percent of the rice fields are rotated with other crops, including safflower, corn, cotton, oats, wheat, grain sorghum, dry beans, sugarbeets, vegetable seed crops, and tomatoes; the majority of rice fields alternate between rice and fallow

Sacramento

seasons (Hill and others, 1997a). In addition to rice, land uses in the study area include alfalfa, grain, orchards, field crops, and wildlife/wetland areas (Domagalski and others, 1998). Rice agriculture in the Sacramento Valley uses as much as 1,800,000 to 2,286,000 m<sup>3</sup>/km<sup>2</sup> of water seasonally. Rice crops are irrigated mostly using surface water and typically are flooded from April to September. Most fields are irrigated with a continuously flooded, flow-through system (Hill and others, 1997a,b). Some rice fields also are flooded during winter months to aid in rice straw decomposition and to provide winter habitat for migrating birds (Hill and others, 1997a). Detections of the rice pesticides molinate and thiobencarb in surface waters prompted a change in irrigation practices beginning in 1983, in which rice-field water must be held or recirculated in rice fields for up to 30 days after treatment in order for those pesticides to degrade or volatilize out of the water (Hill and others, 1997a; Scardaci and others, 1999). Total ground-water use in this study area in 1995 was approximately 4.78 Mm<sup>3</sup>/d, of which about 93 percent was used for irrigation (Perlman, 1999). Both ground water and surface water are used for drinking water and irrigation in the study area. About half of the population in the study area is served by ground water; domestic and public supply ground-water use in 1995 was approximately 0.25 Mm<sup>3</sup>/d (Perlman, 1999).

#### Hydrogeology

The wells sampled during this study tap the shallow ground water in the Sacramento Valley aquifer, a heterogeneous aquifer system with no known continuous confining layers that occupies the northern third of California's Central Valley (fig. 1). The Sacramento Valley aguifer occupies a structural trough surrounded by the Sierra Nevada, Cascade, and Coast Ranges mountains and is made up of thousands of meters of sediment eroded from the surrounding mountains (Page, 1986). Fresh water (less than 3.000 µS/cm) occurs to depths of about 600 m below sea level in the Sacramento Valley; below these depths the aguifer contains saline connate water (Berkstresser, 1973; Olmsted and Davis, 1961). Saline water also occurs in fresh-water parts of the Sacramento Valley aguifer as either perched zones or upward extensions of the deeper connate water (Berkstresser, 1973; Olmsted and Davis, 1961). Dormant and extinct volcanic areas (Norris and Webb, 1990) exist in the

southwestern part of the basin (Clear Lake area, extinct), in the center of the Sacramento Valley (Sutter Buttes, extinct), in the northeastern part of the basin (Mount Lassen volcano, dormant), and in the northern part of the basin (Mount Shasta volcano, dormant) (fig. 1).

Intensive development of both surface- and ground-water sources for water supply and flood control over the last 100 years has greatly altered the hydrologic system in the Sacramento Valley; both discharge and recharge have increased from natural conditions because of ground-water pumping and irrigation return (Bertoldi and others, 1991). Regional ground-water flow is from the sides of the valley toward the center and southward. Ground-water conditions grade downward from unconfined to semiconfined to confined below the upper hundred meters (Williamson and others, 1989). Recharge to the Sacramento Valley aquifer occurs mainly along the upper reaches of river channels in the valley, in irrigated areas, and to some extent from precipitation (Bertoldi and others, 1991). Ground-water discharge occurs as evapotranspiration, loss to streams, and pumpage in the southern part of the Valley (Bertoldi and others, 1991).

Rice fields generally are located on finetextured, poorly drained soils of clay and silt with impervious hardpans or claypans (Hill and others, 1997a). Estimated soil permeabilities over most of the study area generally are less than 6 m/d, with most of the study area being less than 0.6 m/d (Bertoldi, 1974). In most areas, fine-grained sediments make up more than 50 percent of the aquifer system (Page, 1986). The surficial alluvial deposits in the rice areas range in age from Holocene (younger than 10,000 years) to Pliocene (between 1.5 and 5 million years) (Helley and Harwood, 1985) and include three geomorphic units described in Olmsted and Davis (1961, plate 1): low alluvial plains and fans of the Sierra Nevada (referred to in this report as "eastern alluvial plain"), flood basins (referred to in this report as "central flood basins"), and low alluvial plains and fans on the west side of the valley (referred to in this report as "western alluvial plain") (fig. 3). These deposits consist of clay, silt, sand, and gravels eroded from the surrounding mountains, transported and deposited by the Sacramento River and its tributaries. The sediment source areas to the east consist of metamorphic, granitic, and volcanic rock types of the Sierra Nevada and Cascade Ranges; to the west, the sediment source areas consist

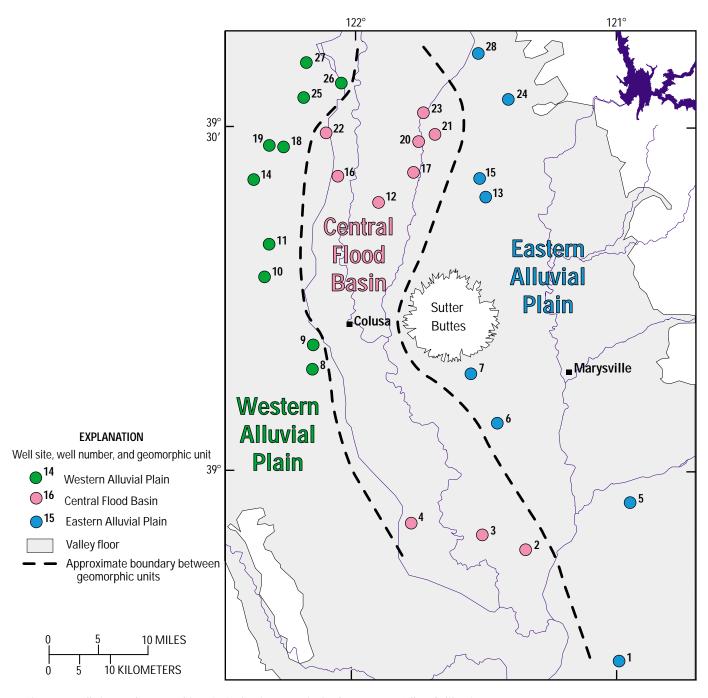


Figure 3. Well sites and geomorphic units in the rice areas in the Sacramento Valley, California.

of metamorphic, volcanic, and marine sedimentary rocks of the Coast Ranges (Helley and Harwood, 1985; Page, 1986).

#### METHODS OF INVESTIGATION

#### **Well Site Selection**

The criteria used for well site selection in this study follow those published in Lapham and others

(1997). The principal criterion used for site selection was that the wells must be located in deposits that make up the Sacramento Valley aquifer. The boundaries for rice land-use areas (fig. 1) located on the Sacramento Valley aquifer were determined from the California Department of Water Resources land-use data (California Department of Water Resources, 1985, 1990, 1991, 1994a,b,c, and 1995a,b) and verified during field inventorying of sites. After the boundaries of the rice land-use areas were

determined, a computer geographic information system was used to divide the total rice area (the blue areas on fig. 1) into 30 equal-area cells (Scott, 1990). A computer program then randomly selected and ordered sites located in each of the 30 cells. The names of property owners were obtained from the County Assessors near the selected sites, and letters were sent to owners explaining this study and requesting permission to drill and sample a monitoring well. Permission also was obtained from some of the counties in which the selected sites were located to install wells on county right-of-way property. Field inventories of the randomly selected sites and a final evaluation of each site for drilling was completed and permission obtained from the land owners. Wells were sited where, at the time of the field inventory, they were surrounded by at least 75 percent rice farmland within 500 m. Because of crop rotations at some sites, some wells are surrounded by less than 50 percent rice farm-land in some years. In many cases, permission could not be obtained to put a well near the randomly selected points, and the search was expanded to other available property within that cell or adjacent cells. Seven wells used in this study are located in right-ofway areas next to rice fields; the rest are located adjacent to rice fields along field roads or rice equipment areas, or in farm or home yards surrounded by rice fields.

#### Monitoring Well Installation

The monitoring wells were drilled between May and July 1997, using a hollow-stem auger rig. All wells were constructed according to the guidelines in Lapham and others (1997) and according to California and local standards for well construction. Casing was 5-cm polyvinyl chloride (PVC) with PVC screens, sand-packed and sealed with bentonite or concrete, or both. All drilling equipment was steam-cleaned on-site before moving to the next drilling site, and well casing and screens were steam-cleaned before installation. After installation, all wells were developed using a combination of pumping and surging until the turbidity was zero or until specific conductance measurements were stable. Lithology was determined from cuttings during drilling by the project hydrologist on-site.

#### Well Descriptions, Water Levels, and Lithology

Well construction data for the wells installed and sampled in this study are shown in table 1. The wells range in depth from 8.8 to 15.2 m below land surface, with most wells being 10.7 m deep. Waterlevel altitudes ranged from 39.7 m above to 1.4 m below sea level, indicating that regional ground-water flow in the shallow part of the Sacramento Valley aguifer is southward and away from the sides of the valley (fig. 4). Lithology, as determined from cuttings during drilling, consisted of clay, silt, sand, and gravels; sediment sizes were generally clay or silt, or both, with varying amounts of sand and gravel. Interlayering and changes in sediment size occurred on scales ranging from centimeters to tens of meters. Although borehole lithology varied between individual wells, no differences in general borehole lithology were found between geomorphic units.

#### **Water Sample Collection and Analysis**

The wells installed for this study were sampled between August and October 1997. Sampling equipment consisted of a portable, stainless-steel submersible pump attached to Teflon lines with stainless-steel fittings. Samples were collected following the protocols in Koterba and others (1995), with the exception of dissolved organic-carbon samples, which were collected using a Teflon filter holder and an electric, oil-free vacuum pump to filter the sample. At wells with low dissolved oxygen or with sulfide odor, samples also were analyzed in the field for the presence or absence of ferrous iron and sulfide, using colorimetric methods. After all the samples were collected, sampling equipment was cleaned and stored in plastic bags. Periodically, quality-control samples were collected to document sample bias and variability. Methods used to analyze water samples are given in table 2. Method reporting limits for pesticides are given in table 3. All samples were analyzed at the USGS's National Water Quality Laboratory (NWQL) in Arvada, Colo., except for tritium samples, which were analyzed at the USGS Tritium Laboratory in Menlo Park, Calif., and stable isotope samples, which were analyzed at the USGS Isotope Laboratory in Reston, Va. All ground-water chemistry data collected in this study are available on the Web at <a href="http://">http://</a> infotrek.er.usgs.gov/wdbctx/nawga/nawga.home>.

**Table 1.** Well construction information for wells sampled in rice areas in the Sacramento Valley, California [masl, meters above sea level; mbls, meters below land surface; USGS, U.S. Geological Survey. mm/dd/yy, month per day per year]

Well number	USGS site ID	State well number	Land surface altitude (masl)	Well depth (mbls)	Screened interval (mbls)	Depth to ground water (mbls)	Water-level altitude (masl)	Date water- level measured (mm/dd/yy)
1	384330121293901	010N004E13F001M	6.7	15.2	10.7-13.7	8.1	-1.4	8/11/97
2	385314121401701	012N003E18H001M	6.7	15.2	12.2-13.7	1.7	5.0	10/3/97
3	385431121451401	012N002E09B002M	6.7	8.8	5.8-7.3	1.4	5.3	9/8/97
4	385528121532001	012N001E05C001M	7.0	10.7	7.6-9.1	1.2	5.8	8/12/97
5	385720121282401	013N004E24Q001M	20.4	14.6	11.6–13.1	4.0	16.4	10/2/97
6	390416121433601	014N002E10R001M	11.0	13.4	10.4–11.9	0.4	10.6	8/18/97
7	390832121463601	015N002E20D001M	12.5	10.7	7.6-9.1	1.7	10.8	8/19/97
8	390856122044301	015N002W16R001M	16.8	10.7	7.6-9.1	0.6	16.1	8/13/97
9	391059122043601	015N002W03E001M	14.9	10.7	7.6-9.1	0.8	14.1	9/17/97
10	391653122101401	017N003W35M001M	22.6	10.7	7.6–9.1	0.5	22.1	8/14/97
11	391947122094501	017N002W14G001M	24.4	10.7	7.6–9.1	1.5	22.9	9/16/97
12	392328121571501	018N001W27B001M	20.7	10.2	7.2 - 8.7	1.4	19.3	9/29/97
13	392358121450301	018N002E21G001M	24.7	13.1	8.5-11.6	1.1	23.6	9/9/97
14	392524122113401	018N003W09R001M	29.3	11.3	8.2-9.8	1.1	28.1	9/17/97
15	392542121452501	018N002E09L001M	26.2	10.7	7.6–9.1	1.1	25.1	8/19/97
16	392545122015201	018N002W12G002M	23.8	10.7	7.6–9.1	2.8	20.9	9/30/97
17	392604121531801	018N001E08D001M	21.9	11.7	8.7-10.2	1.3	20.6	8/21/97
18	392810122080901	019N003W25R001M	29.6	11.7	8.7-10.2	2.1	27.4	9/30/97
19	392824122091401	019N003W25E001M	29.9	10.7	7.6-9.1	0.8	29.1	8/14/97
20	392848121523901	019N001E20R001M	25.3	14.8	10.2–13.3	1.5	23.8	9/10/97
21	392924121504801	019N001E22B001M	26.2	10.7	7.6–9.1	0.4	25.8	8/21/97
22	392931122031701	019N002W23E001M	24.4	10.8	7.8-9.3	0.7	23.7	8/20/97
23	393119121521001	019N001E09C001M	27.7	14.0	11.0-12.5	1.8	25.9	9/10/97
24	393230121422201	020N002E35J002M	37.8	10.7	7.6-9.1	0.9	36.9	9/11/97
25	393235122055301	020N002W32J001M	32.9	10.7	7.6–9.1	1.1	31.8	9/18/97
26	393353122013501	020N002W25A001M	29.3	10.7	7.6–9.1	0.5	28.8	8/15/97
27	393538122053201	020N002W16D001M	38.1	10.8	7.8–9.3	1.5	36.6	10/1/97
28	393630121455401	020N002E08A001M	41.5	10.7	7.6-9.1	1.7	39.7	9/9/97

#### **Data Reporting and Analysis**

In this report, water temperature is reported in degrees Celsius (°C). Specific conductance values are reported in microsiemens per centimeter (μS/cm). Alkalinity and hardness are reported in milligrams per liter as calcium carbonate (mg/L as CaCO<sub>3</sub>). Dissolved concentrations of oxygen, solids (residue-onevaporation at 180°C), organic carbon, and inorganic constituents are reported in milligrams per liter (mg/L). Nitrate plus nitrite, nitrate, nitrite, and

ammonia are reported in mg/L as nitrogen. Phosphorus and orthophosphorus are reported in mg/L as phosphorus. Pesticide concentrations are reported in micrograms per liter (µg/L). Tritium concentrations are reported in picocuries per liter (pCi/L). The stable isotopes  $^2$ H and  $^{18}$ O are reported as ratios per mil (‰, or per thousand) of  $^2$ H to H and  $^{18}$ O to  $^{16}$ O, respectively, and are referenced to Vienna Standard Mean Ocean Water (VSMOW). In the discussion of stable isotopes, the term "lighter" refers to waters with less  $^{18}$ O and  $^2$ H (and therefore more negative per mil

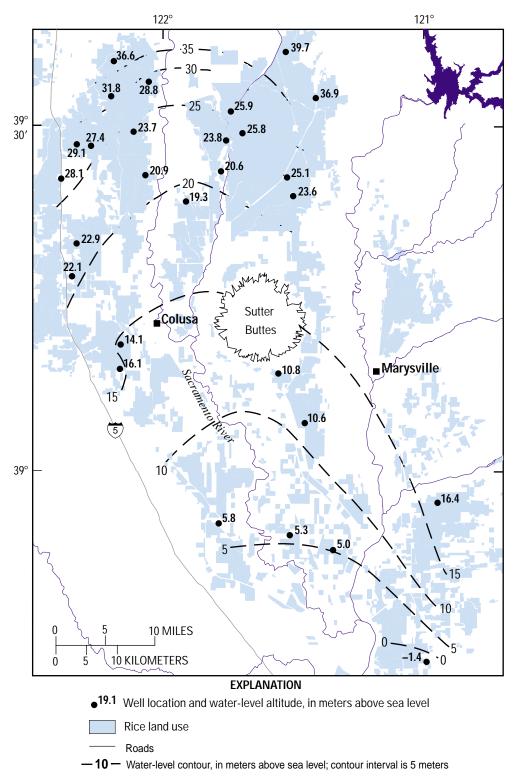


Figure 4. Water-level contours in the rice areas in the Sacramento Valley, California, August to October, 1997.

values), whereas the term "heavier" refers to waters that have more <sup>18</sup>O and <sup>2</sup>H (and therefore less negative per mil values). All chemical constituents except <sup>3</sup>H, <sup>2</sup>H, and <sup>18</sup>O were determined from filtered water samples and reported as dissolved concentrations.

Water-quality constituents were compared to federal 2000 drinking-water standards set by the U.S. Environmental Protection Agency (EPA) (U.S. Environmental Protection Agency, 2000) and California State 2000 drinking-water standards set by the

**Table 2.** Laboratory analysis methods for measured water-quality constituents [<sup>18</sup>O, oxygen-18; <sup>16</sup>O, oxygen-16]

Constituent	Method	Reference		
Deuterium/hydrogen	Hydrogen equilibrium and mass spectrometry	Coplen and others (1991)		
Dissolved organic carbon	Ultra-violet-promoted persulfate oxidation and infrared spectrometry	Brenton and Arnett (1993)		
Major inorganics	Atomic absorption spectrometry, Colorimetry, Ion-exchange chromatography, Inductively-coupled plasma atomic emission spectrometry, and mass spectrometry	Fishman and Friedman (1989), Fishman (1993), and Struzeski and others (1996)		
Nutrients	Colorimetry	Patton and Truitt (1992), Fishman (1993)		
$^{18}{\rm O}/^{16}{\rm O}$	Carbon dioxide equilibrium	Epstein and Mayeda (1953)		
Pesticides	Solid-phase extraction on a carbon-18 cartridge and gas chromatography/mass spectrometry	Zaugg and others (1995)		
Pesticides	Solid-phase extraction on a Carbopak-B cartridge and high performance liquid chromatography with ultraviolet detection	Werner and others (1996)		
Trace inorganics	Atomic absorption spectrometry or Inductively coupled plasma mass spectrometry	Faires (1993)		
Tritium	Electrolytic enrichment with gas counting	Ostlund and Dorsey (1975)		

California Department of Health Services (DHS) (California Department of Water Resources, 1997). DHS standards are used for constituents not currently regulated by the EPA and for those constituents with a DHS standard lower than that set by the EPA. Drinking-water standards used for comparison are the primary maximum contaminant level (MCL), which is the maximum concentration of a contaminant permissible in a public water system; the secondary maximum contaminant level (SMCL), which is a guideline for taste, odor, and other, nonaesthetic effects of drinking water; and the lifetime health advisory limit (HAL), which is the concentration of a chemical in drinking water that is not expected to cause adverse noncarcinogenic effects over a lifetime of exposure (U.S. Environmental Protection Agency, 2000; California Department of Water Resources, 1997).

Summary statistics include median values, and nonparametric statistical methods were used for data analysis, as most ground-water chemistry data have non-normal distributions and many outliers. The Spearman rank correlation test was used to determine the degree of correlation between two variables (Helsel and Hirsch, 1995). The rank-sum test (also known as the Mann-Whitney or Wilcoxon rank-sum test) was used to determine whether one group of data had statistically larger values than a second group (Helsel and Hirsch, 1995). The Kruskal–Wallis test was used to determine whether two or more data groups were statistically different (Helsel and Hirsch, 1995). A significance level of 95 percent was used for all statistical tests in this report. The words "significant" and "correlation" are always used in terms of the statistical results.

#### Quality-Control Data Analyses

Quality control (QC) samples were collected to evaluate the bias and variability of the ground-water chemistry data in this study. QC sample types collected included field blank samples, replicate groundwater samples, and field-spiked ground-water samples.

Table 3. Pesticides analyzed and reporting limits in water samples, in the Sacramento River Basin, California

[\*, transformation product; (0.04) method reporting limit, in micrograms per liter]

Compound	Compound	Compound
	Amides	
Alachlor (0.002) <sup>1</sup>	Napropamide (0.003) <sup>1</sup>	Propanil (0.004) <sup>1</sup>
Metolachlor (0.002) <sup>1</sup>	Propachlor (0.007) <sup>1</sup>	Propyzamide $(0.003)^1$
	Carbamates	
Aldicarb (0.016) <sup>2</sup>	Carbofuran, 3-Hydroxy* (0.014) <sup>2</sup>	Pebulate (0.004) <sup>1</sup>
Aldicarb sulfone* (0.016) <sup>2</sup>	EPTC $(0.002)^1$	Propham $(0.035)^2$
Aldicarb sulfoxide* (0.021) <sup>2</sup>	Methiocarb $(0.026)^2$	Propoxur $(0.035)^2$
Butylate (0.002) <sup>1</sup>	Methomyl $(0.017)^2$	Thiobencarb $(0.002)^1$
Carbaryl $(0.003)^1$ , $(0.008)^2$	Molinate $(0.004)^1$	Triallate $(0.001)^1$
Carbofuran $(0.003)^1$ , $(0.028)^2$	Oxamyl $(0.018)^2$	
	Chlorophenoxy herbicides	
2,4,5-T (0.035) <sup>2</sup>	Dacthal, mono-acid* (0.017) <sup>2</sup>	MCPB (0.035) <sup>2</sup>
2,4-D (acid) $(0.035)^2$	Dichlorprop $(2,4-DP) (0.032)^2$	Silvex $(2,4,5-TP)(0.021)^2$
$2,4\text{-DB} (0.035)^2$	$MCPA (0.05)^2$	Triclopyr $(0.05)^2$
	Dinitroanilines	
Benfluralin (0.002) <sup>1</sup>	Trifluralin (0.002) <sup>1</sup>	Pendimethalin (0.004) <sup>1</sup>
Ethafluralin $(0.004)^1$	Oryzalin $(0.019)^2$	, ,
	Organochlorines	
Chlorothalonil (0.035) <sup>2</sup>	Dichlobenil (0.02) <sup>2</sup>	alpha-HCH* (0.002) <sup>1</sup>
Dacthal (DCPA) (0.002) <sup>1</sup>	Dieldrin (0.001) <sup>1</sup>	GAMMA -HCH (0.004) <sup>1</sup>
$p,p'$ -DDE* $(0.006)^1$		
	Organophosphates	
Azinphos-methyl (0.001) <sup>1</sup>	Ethoprop (0.003) <sup>1</sup>	Parathion (0.004) <sup>1</sup>
Chlorpyrifos (0.004) <sup>1</sup>	Fonofos $(0.003)^1$	Phorate (0.002) <sup>1</sup>
Diazinon (0.002) <sup>1</sup>	Malathion $(0.005)^1$	Terbufos $(0.013)^1$
Disulfoton (0.017) <sup>1</sup>	Methyl parathion (0.006) <sup>1</sup>	
	Triazine herbicides:	
Atrazine (0.001) <sup>1</sup>	Cyanazine $(0.004)^1$	Prometon (0.018) <sup>1</sup>
Atrazine, desethyl* (0.002) <sup>1</sup>	Metribuzin $(0.004)^1$	Simazine (0.005)1
	Uracils	
Bromacil (0.035) <sup>2</sup>	Terbacil $(0.007)^1$	
	Ureas	
Fenuron (0.013) <sup>2</sup>	Fluometuron $(0.035)^2$	Neburon (0.015) <sup>2</sup>
Diuron $(0.020)^2$	Linuron $(0.002)^1$ , $(0.018)^2$	Tebuthiuron (0.010) <sup>1</sup>
	Miscellaneous	
2,6-Diethylanaline* (0.003) <sup>1</sup>	Chloramben $(0.011)^2$	DNOC $(0.035)^2$
Acetochlor $(0.002)^1$	$cis$ -Permethrin $(0.05)^1$	Norflurazon $(0.024)^2$
Acifluorfen (0.035) <sup>2</sup>	Clopyralid (0.05) <sup>2</sup>	Picloram $(0.05)^2$
Bentazon $(0.014)^2$	Dicamba $(0.035)^2$	Propargite $(0.013)^1$
Bromoxynil $(0.035)^2$	Dinoseb $(0.035)^2$	

Solid-phase extraction and gas chromatography/mass spectrometry (GC/MS) correspond to the method reporting limit.

<sup>&</sup>lt;sup>2</sup> Solid-phase extraction and high performance liquid chromatography (HPLC) with ultraviolet light spectrometry correspond to the method reporting limit.

Field-blank samples were collected to evaluate bias in ground-water chemical data from contamination introduced during sample collection and analysis for dissolved organic carbon, pesticides, nutrients, and inorganic constituents. Evidence of contamination from field-blank samples affecting ground-water data was found for aluminum, ammonia, copper, and dissolved organic carbon (DOC). Some of the concentrations of these constituents measured in ground water were within 3 standard deviations of the mean of the concentrations measured in field-blank samples, which indicates that concentrations may be partly or entirely due to contamination introduced during sampling or analysis; these data are not used for analyses in this report. Ammonia was detected in 10 out of 28 wells (36 percent), but in all but one well, ammonia concentrations were within the range of blank sample detections and may be the result of sample contamination. Information from the NWQL indicates that the detections of aluminum in field-blank samples and in all ground-water samples may have been introduced by the nitric acid preservative used in the samples (T. Maloney, USGS NWQL, unpub. data, 1998). Detections of DOC in field blanks indicate that concentrations measuring below 1.8 mg/L in ground water in this study may be partly or entirely due to sample contamination during collection or analysis.

DOC contamination in field-blank samples may have come from the cleaning methods that were used to prevent contamination of other organic constituents during sampling; this contamination may not be present in the ground-water samples because it may only have been introduced into the field-blank samples. Sources of ammonia and copper contamination are not known.

Replicate samples were collected to determine variability of the ground-water chemical data for inorganic constituents and for DOC. A total of 11 replicate sample pairs were used for this evaluation. The mean relative standard deviations between sample pairs for all constituents were less than 25 percent and for most constituents were less than 5 percent (table 4). The relative standard deviation in this study is defined as the ratio of the standard deviation to the mean concentration for each replicate pair of samples. One to three individual replicate pairs for some constituents (as indicated by the footnote in table 4) had a relative standard deviation of greater than 20 percent. Mean relative standard deviations of less than 20 percent are considered acceptable in this report. Data for three constituents with mean relative standard deviations greater than 20 percent—aluminum, cadmium, and chromium—will not be used for analyses in this report.

**Table 4.** Summary of mean relative standard deviations for replicate sample pairs of inorganic compounds, nutrient compounds, and dissolved organic carbon

[%, percent; CaCO<sub>3</sub>, calcium carbonate]

Less than 5%	Less than 10%	Less than 15%	Less than 25%
Arsenic	Ammonia <sup>1</sup>	Boron <sup>1</sup>	Aluminum
Barium	Dissolved organic carbon <sup>1</sup>	Bromide <sup>1</sup>	Cadmium <sup>1</sup>
Calcium	Fluoride <sup>1</sup>	Copper <sup>1</sup>	Chromium <sup>1</sup>
Chloride <sup>1</sup>	Nickel	Orthophosphorus <sup>1</sup>	
Cobalt	Nitrate <sup>1</sup>	Zinc <sup>1</sup>	
Dissolved solids	Phosphorus <sup>1</sup>		
Hardness as CaCO <sub>3</sub>			
Iron			
Magnesium			
Molybdenum			
Nitrite			
Potassium			
Selenium			
Silica			
Sodium			
Sulfate			
Uranium			

<sup>&</sup>lt;sup>1</sup> One to three individual replicate pairs had a relative standard deviation of greater than 20 percent.

Surrogates (constituents that behave like pesticide analytes) were added to all pesticide samples to evaluate the ability of the sampling and analysis methods to detect the pesticides in each ground-water sample and to determine whether the ground-water chemistry of each sample would interfere with the pesticide analysis (generally referred to as matrix interference). The mean recoveries of the surrogates in all ground-water samples for pesticides were within the control limits determined by the NWQL for 1997 (M.P. Schroeder, USGS NWQL, unpub. data, 1998; R. W. Brenton, USGS NWQL, unpub. data, 1998).

Spike solutions containing known amounts of some pesticides were added to some replicate groundwater samples to evaluate bias of those pesticide analyses. Seventy-seven out of eighty-six pesticides were evaluated with field-spiked samples; seventy-six had mean recoveries within NWQL's 1997 control limits, indicating that the methods of sampling and analysis used in this study adequately detected those pesticides and that there were no major matrix interferences on those pesticide analyses. The mean recovery of dicamba was lower than the lower 1997 control limit, indicating that dicamba may not have been detected if present in low concentrations in some ground-water samples. Some pesticides analyzed in this study were not present in the spike solutions, and recoveries for these pesticides could not be evaluated. The pesticides are chloramben, chlorothanlonil, dichlobenil, DNOC (4.6-dinitro-o-cresol), methyl

azinphos, carbaryl, carbofuran, desethyl atrazine, and terbacil.

#### SHALLOW GROUND-WATER QUALITY

#### **General Water Chemistry**

Summary statistics for general water chemistry measurements are listed in table 5. The SMCL drinking-water standard for specific conductance (900 µS/cm) (California Department of Water Resources, 1997) was exceeded in 12 out of 28 wells (43 percent), and the SMCL for dissolved solids (500 mg/L) (U.S. Environmental Protection Agency, 2000) was exceeded in the same wells plus 4 other wells (16 out of 28 wells, or 57 percent). The median concentration for dissolved solids measured in this study (532 mg/L) is higher than the national NAWQA median concentration measured in other shallow ground-water areas (290 mg/L) (Gilliom and others, 1998, p. 18). Three of the wells sampled in this study had dissolved-solids concentrations over 2,000 mg/L. which is considered to be a limit for fresh water (Berkstresser, 1973). The well with the highest dissolved-solids concentration (8,730 mg/L) is located south of Sutter Buttes, an area in which high dissolvedsolids concentrations have been found in wells between 15 and 90 m deep in previous studies (California State Water Resources Board, 1952, p. 34–38).

**Table 5.** Summary of general water chemistry in shallow ground water in rice areas in the Sacramento Valley, California [°C, degrees Celsius; CaCO<sub>3</sub>, calcium carbonate; μS/cm, microsiemens per centimeter at 25°C; mg/L, milligram per liter; SMCL, secondary maximum contaminant level; —, no value or standard available]

General Water Chemistry	Minimum	Median	Maximum	Drinking- water standard	Type of standard	Number of wells exceeding a drinking- water standard
Alkalinity, mg/L as CaCO <sub>3</sub>	110	370	580	_	_	
Dissolved oxygen, mg/L	0.2	0.4	6.6	_	_	_
Dissolved solids, mg/L, residue on evaporation at 180°C	168	532	8,730	500	SMCL <sup>1</sup>	16
Hardness, total, mg/L as CaCO <sub>3</sub>	110 (moderately hard)	340 (very hard)	4,000 (very hard)	_	_	_
pH, standard units	6.7	7.4	7.8	6.5-8.5	$SMCL^1$	0
Specific conductance, µS/cm	267	854	13,600	900	$SMCL^2$	12
Water temperature, °C	17.5	19.0	22.5	_	_	_

<sup>&</sup>lt;sup>1</sup> U.S. Environmental Protection Agency, 2000.

<sup>&</sup>lt;sup>2</sup> California Department of Water Resources, 1997.

#### **Major Inorganic Constituents**

The major inorganic constituents detected in this study are listed in table 6. Drinking-water standards were exceeded for chloride and sulfate. Four out of twenty-eight wells (14 percent) exceeded the MCL for sulfate, 500 mg/L (U.S. Environmental Protection Agency, 2000). Two out of twenty-eight wells (7 percent) exceeded the SMCL for chloride, 250 mg/L (U.S. Environmental Protection Agency, 2000).

The major water types found in this study (fig. 5) were magnesium and calcium bicarbonate waters with some wells having more sodium sulfate water types. Wells located on the eastern alluvial plain have the more magnesium-calcium-bicarbonate water, while wells located on the western alluvial plain have the more sodium-sulfate water types; wells in the central flood basins were intermediate between the two. One well, located south of Sutter Buttes in the central flood basins, yields sodium-calcium chloride water, distinctly different from the other wells sampled in this study; this is the same well discussed above, with the highest dissolved-solids concentration measured in this study.

#### **Trace Inorganic Constituents**

The trace inorganic constituents detected in this study are given in table 7. Trace elements analyzed for but not detected in this study were antimony, beryllium, lead, and silver. Aluminum was not detected above the concentration range of quality-control blanks, indicating possible contamination from the nitric acid preservative.

Drinking-water standards were exceeded for barium, boron, cadmium, manganese, and molybdenum. The MCL for barium, 1 mg/L (California Department of Water Resources, 1997), was exceeded in 1 out of 28 wells (4 percent). The HAL for boron, 0.6 mg/L (U.S. Environmental Protection Agency, 2000), as well as the water quality criterion for boron in irrigation water, 0.75 mg/L (National Academy of Sciences and National Academy of Engineering, 1972), was exceeded in 5 out of 28 wells (18 percent). The MCL for cadmium, 0.005 mg/L (U.S. Environmental Protection Agency, 2000), was exceeded in 3 out of 28 wells (11 percent). The SMCL for manganese, 0.05 mg/L (U.S. Environmental Protection Agency, 2000), was exceeded in 21 out of 28 wells (75 percent). The HAL for molybdenum, 0.04 mg/L (U.S. Environmental Protection Agency, 2000), was exceeded in 1 out of 28 wells (4 percent).

None of the wells sampled in this study exceeded the current MCL for arsenic, 0.05 mg/L (U.S. Environmental Protection Agency, 1996). Lower MCLs for arsenic have been proposed (0.005 mg/L [U.S. Environmental Protection Agency, 2000]; 0.010 mg/L [U.S. Environmental Protection Agency, 2001a]); however, those MCLs are being withdrawn and a new MCL is under review (U.S. Environmental Protection Agency, 2001b). The EPA also has an HAL for arsenic of 0.002 mg/L (U.S. Environmental Protection Agency, 2000); 16 out of 28 wells (57 percent) have an arsenic concentration over the HAL.

**Table 6.** Summary of major inorganic constituents detected in shallow ground water in rice areas in the Sacramento Valley, California [All detections and drinking-water standards are shown in milligrams per liter. SMCL, secondary maximum contaminant level; —, no value or standard available]

Constituent	Number of detections/number of samples	Minimum detection	Median detection	Maximum detection	Drinking- water standard	Type of standard	Number of wells exceeding a drinking-water standard
Bicarbonate, as HCO <sub>3</sub>	28/28	140	460	710	_	_	
Calcium, as Ca	28/28	22	62	810	_	_	_
Chloride, as Cl	28/28	2.3	12	4,800	250	$SMCL^1$	2
Magnesium, as Mg	28/28	13	46	480	_	_	_
Potassium, as K	28/28	0.5	1	9	_	_	_
Silica, as SiO <sub>2</sub>	28/28	16	40	70	_	_	_
Sodium, as Na	28/28	12	50	1,300	_	_	_
Sulfate, as SO <sub>4</sub>	27/28	5.0	42	1,500	250	$SMCL^1$	5

<sup>&</sup>lt;sup>1</sup> U.S. Environmental Protection Agency, 2000.

#### **Nutrient Constituents**

Nutrient constituents detected in this study included ammonia, nitrate, nitrite, and phosphorus (table 8). No nutrients were detected at levels above any drinking-water standards. Ammonia was detected in 10 out of 28 wells (36 percent), but in all but one well, ammonia concentrations were within the range of blank sample detections and may be the result of sample contamination. Ammonia plus organic nitrogen was detected in 3 out of 28 wells (11 percent). Nitrate concentrations ranged from 0.08 to 6.2 mg/L. Three out of twenty-eight wells (11 percent) had nitrate concentrations over 3 mg/L, a level that may indicate an impact from human activities (Hull, 1984, p. 19; Madison and Brunett, 1984). Nitrite was detected in 11 out of 28 wells (39 percent); detected concentrations ranged from

0.01 to 0.1 mg/L, with a median of 0.01 mg/L. The median concentration of nitrate plus nitrite in this study (0.58 mg/L) was less than the National NAWQA median of 2 mg/L measured in shallow ground water in other studies (Gilliom and others, 1998, p. 17). The lower nitrate concentrations may be attributable to low dissolved oxygen conditions, which would allow for the chemical reduction of nitrate to nitrogen gas.

#### **Dissolved Organic Carbon**

Dissolved organic carbon was detected in all 28 wells (100 percent) (table 8). The median concentration of DOC found in ground water in this study was 1.4 mg/L, which is higher than the median DOC concentration (0.7 mg/L) found in wells throughout the U.S. (Leenheer and others, 1974). Detections of

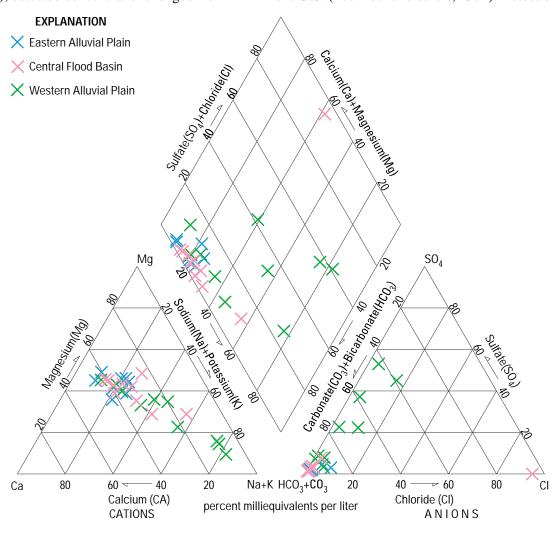


Figure 5. Trilinear diagram showing major-ion composition of shallow ground-water samples from rice areas in the Sacramento Valley, California.

**Table 7.** Summary of trace inorganic constituents detected in shallow ground water in rice areas in the Sacramento Valley, California [All detections and drinking-water standards are shown in milligrams per liter. HAL, health advisory level; MCL, maximum contaminant level; SMCL, secondary maximum contaminant level; —, no value available]

Constituent	Number of detections/ number of samples	Minimum detection	Median detection	Maximum detection	Drinking- water standard	Type of standard	Number of wells exceeding a drinking- water standard
Aluminum, as Al	27/28	0.002	0.004	0.010	1	MCL <sup>2</sup>	0
Arsenic, as As	28/28	0.001	0.0035	0.015	0.050	$MCL^3$	0
Barium, as Ba	28/28	0.01	0.063	5.05	1	MCL <sup>2</sup>	1
Boron, as B	28/28	0.02	0.2	1.8	0.6	$HAL^1$	5
Bromide, as Br	22/28	0.03	0.05	12	_	_	_
Cadmium, Cd	3/28	0.006	0.007	0.007	0.005	$MCL^1$	3
Chromium, as Cr	27/28	0.002	0.004	0.016	0.05	$MCL^2$	0
Cobalt, as Co	6/28	0.001	0.002	0.004	_	_	_
Copper, as Cu	13/28	0.001	0.003	0.009	1.3	$MCL^1$	0
Ferrous iron, as Fe <sup>+2</sup>	19/28	_	_	_	_		_
Fluoride, as F	22/28	0.1	0.25	1.8	4	$MCL^1$	0
Iron, as Fe	15/28	0.003	0.059	5.3	0.3	$SMCL^1$	3
Manganese, as Mn	27/28	0.002	0.1	3	0.05	$SMCL^1$	21
Molybdenum, as Mo	14/28	0.001	0.0045	0.051	0.04	$HAL^1$	1
Nickel, as Ni	19/28	0.001	0.002	0.009	0.1	$HAL^1$	0
Selenium, as Se	2/28	0.003	0.0125	0.022	0.05	$MCL^1$	0
Sulfide, as S <sup>-</sup>	14/28	_			_		
Uranium, as U	24/28	0.001	0.0035	0.023	2,000	$MCL^1$	0
Zinc, as Zn	12/28	0.001	0.002	0.017	2	$HAL^1$	0

<sup>&</sup>lt;sup>1</sup> U.S. Environmental Protection Agency, 2000.

**Table 8.** Summary of nutrient constituents and dissolved organic carbon detected in shallow ground water in rice areas in the Sacramento Valley, California

[All detections and drinking-water standards are shown in milligrams per liter. C, carbon; HAL, health advisory level; MCL, maximum contaminant level; N, nitrogen; P, phosphorus; —, no value available]

Constituent	Number of detections/ number of samples	Minimum detection	Median detection	Maximum detection	Drinking- water standard	Type of standard	Number of wells exceeding a drinking- water standard
Ammonia, as N	10/28	0.02	0.02	0.46	30	$HAL^1$	0
Ammonia + organic nitrogen, as N	3/28	0.3	0.4	0.7	30	$HAL^1$	0
Nitrate + Nitrite, as N	23/28	0.08	0.92	6.2	10	$MCL^1$	0
Nitrate, as N	23/28	0.08	0.58	6.2	10	$MCL^1$	0
Nitrite, as N	11/28	0.01	0.01	0.10	1	$MCL^1$	0
Orthophosphorus, as P	27/28	0.01	0.07	0.36	_	_	_
Phosphorus, as P	28/28	0.030	0.060	0.362	_	_	_
Dissolved organic carbon, as C	28/28	0.3	1.4	6.8	_	_	_

<sup>&</sup>lt;sup>1</sup> U.S. Environmental Protection Agency, 2000.

<sup>&</sup>lt;sup>2</sup> California Department of Water Resources, 1997.

<sup>&</sup>lt;sup>3</sup> U.S. Environmental Protection Agency, 1996.

DOC in field blanks indicate that ground-water sample concentrations measured below 1.8 mg/L in this study may be partly or entirely due to sample contamination introduced during sample collection or analysis. DOC concentrations in ground water above this value ranged from 1.9 to 6.8 mg/L in 12 out of 28 wells (43 percent), with a median of 2.7 mg/L.

#### **Pesticides**

From one to eight pesticides were detected in 25 of 28 wells (89 percent) in this study (table 9). This frequency of detection is almost twice the median frequency of a pesticide detection in shallow ground water (45.9 percent) from other NAWQA studies between 1992 and 1995 (Gilliom and others, 1998, p. 17). Eleven pesticides and one pesticide degradation product were detected in this study, indicating that human activities have affected shallow ground-water quality in the study area. Pesticides that were analyzed for but not detected are listed in table 10. All pesticide concentrations detected in this study were below state and federal 2000 drinking-water standards. The frequency of detection for all pesticides detected in this study except diuron was higher than the national

median frequency for their detections in shallow ground water in agricultural areas (U.S. Geological Survey Pesticide National Synthesis Project, 1998).

Pesticide use information reported in the Sacramento Valley area is shown in table 11 and was taken from California Department of Pesticide Regulation (1997) and California Department of Food and Agriculture (1989). The pesticides bentazon and dichlorprop are not currently used in the Sacramento Valley and have not been since the late 1980s. Four of the pesticides detected in this study have been used on rice crops: bentazon, carbofuran, molinate, and thiobencarb. From one to four rice pesticides were detected in 23 out of 28 wells (82 percent). Five of the pesticides detected in shallow ground water in this study have been used for agricultural crops other than rice: atrazine, carbofuran, diuron, methyl azinphos, and simazine. Five of the pesticides detected in shallow ground water have been used for nonagricultural purposes: atrazine, dichlorprop, diuron, simazine, and tebuthiuron.

Of the rice pesticides detected in this study, only bentazon has been detected in previous studies and determined to be from a nonpoint source. Bentazon was banned for use on rice in California in 1989

Table 9. Summary of pesticides detected in shallow ground water in rice areas in the Sacramento Valley, California

[All detections and drinking-water standards are shown in micrograms per liter. E, estimated value because compound was detected at a concentration outside of instrument calibration range; HAL, health advisory level; MCL, maximum contaminant level; —, no value available]

Pesticide	Number of detections/ number of samples	Minimum detection	Median detection	Maximum detection	Drinking- water standard	Type of standard	Number of wells exceeding a drinking- water standard
Atrazine	10/28	E 0.002	E 0.003	0.026	3	MCL <sup>1</sup>	0
Bentazon	20/28	0.06	0.935	E 7.8	18	$MCL^2$	0
Bromacil	1/28	0.19	_	_	90	$HAL^1$	0
Carbofuran	4/28	0.016	0.050	0.8	18	MCL $^2$	0
Desethyl atrazine	7/28	E 0.001	E 0.003	E 0.005	_	_	_
Dichlorprop	1/28	E 0.1	_	_	_	_	_
Diuron	2/28	0.04	0.06	0.09	10	$HAL^1$	0
Azinphos-methyl	1/28	E 0.014	_	_	_	_	_
Molinate	7/28	E 0.002	0.005	0.056	20	MCL $^2$	0
Simazine	10/28	E 0.002	E 0.003	0.027	4	$MCL^1$	0
Tebuthiuron	1/28	E 0.006	_	_	500	$HAL^1$	0
Thiobencarb	3/28	0.006	0.014	0.025	70	MCL <sup>2</sup>	0

<sup>&</sup>lt;sup>1</sup> U.S. Environmental Protection Agency, 2000.

<sup>&</sup>lt;sup>2</sup> California Department of Water Resources, 1997.

**Table 10.** Pesticides and degradation products not detected in shallow ground water in rice areas in the Sacramento Valley, California

2,4-D 2,4-DB Alachlor Aldicarb Benfluralin Bromoxynil Carbaryl Chloramben Cis-Permethrin Cyanazine Diazinon Diasulfoton Ethoprop EPTC Disulfoton Ethoprop Enforce Edman-HCH Linuron Malathion MCPA Methiocarb Methomyl Methomyl Methomyl Methomyl Methomyl Nordurazon Oryzalin Nordurazon Oryzalin Nordurazon Pronamide Poroace Pronamide Poropoxur Trippanm Propeoxur Trifluralin Propoxur Trifluralin Not detected and not applied: 2,4,5-T Chloropyr Trifluralin Acetochlor Butylate Clopyralid Dinoseb Dacthal (mono-acid) Dichloralin Doropalid Dinoseb Dacthal (mono-acid) Dichloralin Ethalfluralin Fenuron Fenuron Fenuron Fluometuron MCPB Methiocarb Neburon McPB Neburon Propachlor Propachlor Propachlor Propachlor Aldicarb sulfore Aldicarb sulfone Aldicarb sulfone Phorate Phorate Aldicarb sulfoxide 3-Hydroxycarbofuran	Not detected and applied:	Propargite
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cis-PermethrinAcetochlorCyanazineAcifluorfenDiazinonAlpha-HCHDicambaButylateDichlobenilClopyralidDinosebDacthal (mono-acid)DisulfotonDCPAEPTCDieldrinEthopropDNOCFonofosEsfenvalerateGamma-HCHEthalfluralinLinuronFenuronMalathionFluometuronMCPAMCPBMethiocarbNeburonMethomylp,p'-DDEMethyl parathionPebulateMetolachlorPropachlorMetribuzinPropyzamideNapropamideSilvex (2,4,5-TP)NorflurazonTerbufosOryzalinTriallateOxamylParathionPendimethalineAldicarb sulfonePhorateAldicarb sulfoxidePicloram3-Hydroxycarbofuran		
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Phorate Aldicarb sulfoxide Picloram 3-Hydroxycarbofuran Prometon	Parathion	Degradation products not detected:
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Prometon	Phorate	Aldicarb sulfoxide
	Picloram	3-Hydroxycarbofuran
Pronamide	Prometon	
	Pronamide	

because of detections in water wells, but it continues to be detected in ground water in the Sacramento Valley (Miller-Maes and others, 1993; Bartkowiak and others, 1998). In 1989, samples were collected by the California Department of Food and Agriculture and analyzed for bentazon from domestic wells in the

rice growing counties in California. Of the total number of wells sampled in that study, 134 were located in the USGS 1997 rice land-use study area; bentazon was detected in 56 of those wells, giving a detection frequency of 42 percent (Sitts, 1989). Well depth information was not available for all of the wells sampled in 1989, but the available information showed that well depths ranged from about 12 to 90 m (Bartkowiak and others, 1998), which are typical depths for domestic wells in the Sacramento Valley. Bentazon was detected in 68 percent of the shallow (less than 15 m deep) wells sampled by the USGS in 1997 at concentrations above the detection limit used in the 1989 study. Previous detections of molinate reported in the California Department of Pesticide Regulation ground-water database (Bartkowiak and others, 1998) either were determined to be from a point source or were a result of poor well construction. No detections of thiobencarb or carbofuran were reported in Bartkowiak and others (1998). The higher detection frequencies of bentazon, carbofuran, molinate, and thiobencarb in the 1997 study relative to previous studies are possibly due to the lower detection limits and shallower sampling depths used by the USGS.

#### **Ground-Water Redox Condition**

Hull (1984) demonstrated that reducing conditions in the fine-grained sediments in flood basin areas are a major factor influencing the ground water chemstry of the Sacramento Valley. The oxidationreduction (redox) state of water can affect what constituents are present. Water with chemistry indicating oxidizing chemical conditions is referred to as oxic; water with chemistry indicating reducing chemical conditions is referred to as anoxic. Anoxic conditions are divided into post-oxic (reactions involving reduction of nitrate, iron, and manganese) and sulfidic (reactions involving reduction of sulfate to sulfide). As it is very easy to introduce oxygen into ground water during the sampling process, we based our classification of ground water as oxic or anoxic on the concentrations of several constituents that are sensitive to dissolved-oxygen concentration (such as nitrate, iron, manganese, and sulfate), rather than basing the classification solely on dissolved-oxygen concentrations. The classification of ground-water redox conditions in this study was based on the classifications used in Saad and Thorstenson (1998).

Table 11. Reported uses of pesticides detected in rice areas in the Sacramento Valley, California

Pesticide detected in this study	Years pesticide used in the Sacramento Valley <sup>1</sup>	Major reported use <sup>2,3</sup>	Other reported uses <sup>2,3</sup>		
Atrazine	1974–present	Right-of-way weed control and other non- agricultural uses	Sorghum, corn, sudangrass		
Bentazon	1978–1989	Rice	Beans, corn		
Bromacil	1968–present	Right-of-way weed control and other non- agricultural uses	Citrus		
Carbofuran	1974-present	Rice	Alfalfa		
Dichlorprop	1980–1988	Right-of-way weed control and other non- agricultural uses	Ornamental trees, turf		
Diuron	1971-present	Right-of-way weed control and other non- agricultural uses	Alfalfa		
Azinphos-methyl	1975-present	Fruit and nut orchards	Row crops		
Molinate	1966-present	Rice	none		
Simazine	1963–present	Right-of-way weed control and other non- agricultural uses; fruit and nut orchards	Grapes		
Tebuthiuron	1974-present	Right-of-way weed control and other non- agricultural uses	none		
Thiobencarb	1982-present	Rice	none		

<sup>&</sup>lt;sup>1</sup>California Department of Pesticide Regulation, 1999.

Measurements of dissolved oxygen, nitrate, nitrite, iron, manganese, sulfate, and sulfide during this study indicated that post-oxic and sulfidic conditions exist at shallow depths beneath almost all of the rice areas in the Sacramento Valley. Wells that contained relatively high concentrations of dissolved oxygen (greater than 2.0 mg/L), nitrogen present as nitrate (no nitrite or ammonia), sulfur present as sulfate (no sulfides), and very low concentrations of manganese and iron (less than 0.002 mg/L) were classified as oxic. Wells that contained relatively low concentra-tions of dissolved oxygen (less than 2.0 mg/L); the presence of nitrite, ammonia, iron, or manganese; and sulfur as sulfate (no sulfides) were classified as post-oxic. Wells having the presence of sulfide, along with the other characteristics of postoxic water, were classified as sulfidic. Only 2 of 28 wells (7 percent) in this study have chemistry indicating oxic conditions; 12 out of 28 wells (43 percent) have chemistry indicating post-oxic conditions; and 14 out of 28 wells (50 percent) have chemistry indicating sulfidic conditions (fig. 6). The distribution of redox conditions is not significantly

different between geomorphic units. Relations between dissolved-oxygen concentrations and pesticide and nitrate occurrence in ground water have been found in other studies (Barbash and Resek, 1996; Rupert, 1997; Burow and others, 1998); however, in this study no correlations were found between (a) nitrate concentration, the number of pesticide detections, or pesticide concentrations, and (b) either dissolved-oxygen concentrations or redox condition.

#### ANALYSES OF GROUND-WATER QUALITY DATA

#### Statistical Analyses

Ground-water chemistry and other data from this study were used to evaluate possible sources and controlling factors of ground-water quality (inorganic, nutrient, and pesticide constituents) in shallow ground water beneath rice areas in the Sacramento Valley. The relation of ground-water quality to natural processes was tested by comparing water chemistry to geomorphic unit, depth to ground water, and depth to

<sup>&</sup>lt;sup>2</sup> California Department of Pesticide Regulation,1997.

<sup>&</sup>lt;sup>3</sup> California Department of Food and Agriculture, 1989.

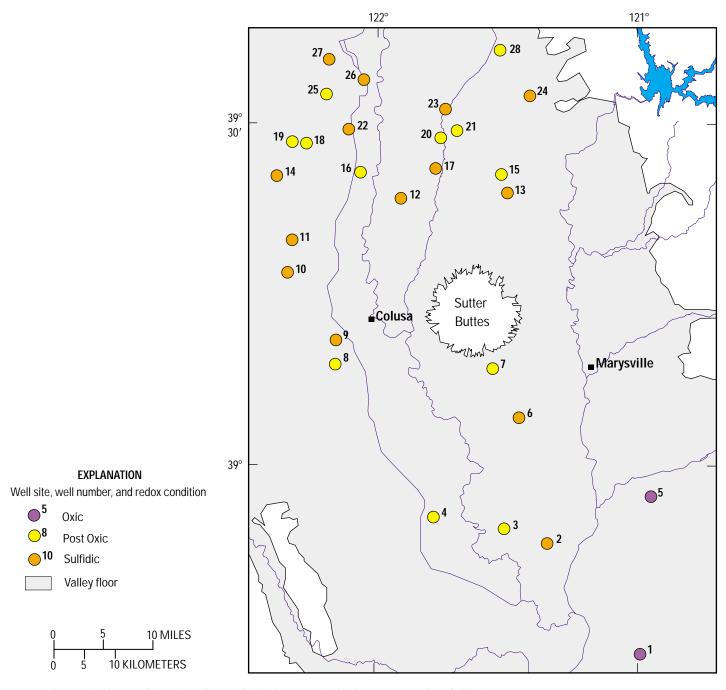


Figure 6. Redox conditions in wells sampled in rice areas in the Sacramento Valley, California.

top of well screen from land surface. The relation of ground-water quality to human activities was evaluated by comparing water chemistry to the number of pesticides detected in each well and to the type of land use within 500 m of the well (rice field, house or farm yard, road right-of-way). A relation between ground-water quality and rice land-use practices was evaluated by comparing water chemistry with the number of rice pesticides detected and the

concentration of bentazon in each well and the percentage of rice within 500 m of the well in 1998. Interpretations based on correlations with bentazon would apply only to the period since the late 1970s when bentazon was first used.

The following methods were used for statistical testing. To test ground-water chemistry for significant differences when grouped by geomorphic unit or by land use type, the Kruskal–Wallis test was used on the

ranks of the chemical data to determine difference among the geomorphic units or land use types; the rank-sum test was then used to determine which geomorphic groups of chemical data were significantly higher or lower. The Spearman rank correlation was used to determine whether there were significant correlations between ground-water chemistry and depth to ground water, depth to top of well screen, percentage of rice, number of pesticides and rice pesticides detected per well, and concentrations of nitrate and bentazon.

## Correlations Between Shallow Ground-Water Quality and Geomorphic Unit

Concentrations of arsenic, boron, chloride, dissolved solids, fluoride, molybdenum, nitrate, phosphorus, potassium, silica, sodium, sulfate, and zinc were found to be statistically different with 95 percent confidence when grouped by geomorphic unit (fig. 7). Concentrations of silica were significantly higher in wells on the eastern alluvial plain. Concentrations of potassium were significantly lower on the western alluvial plain. Concentrations of arsenic and phosphorus were significantly higher in wells in the central flood basins. Concentrations of nitrate were significantly lower in the central flood basins. Concentrations of boron, chloride, dissolved solids, fluoride, molybdenum, sodium, sulfate, and zinc were significantly higher in wells on the western alluvial plain.

The differences in inorganic constituent concentrations are thought to be related to the differences in recharge-water chemistry, which reflects differences in geology between the east and west sides of the Sacramento River Basin, and to the anoxic conditions in the center of the Sacramento Valley; these relations between inorganic constituents and location also were found in Hull (1984). No significant differences were found by geomorphic unit for the number of pesticides or rice pesticides detected, for bentazon concentration, or for depth to ground water or top of well screen. The inorganic chemistry in shallow ground water in the eastern alluvial plain (higher concentrations of silica, potassium, and, when compared to the western alluvial plain, arsenic, and lower concentrations of dissolved solids) reflects the recharge water chemistry influenced by the rock types in the Sierra Nevada and Cascade Mountains, particularly volcanic and granitic rocks. The shallow ground water chemistry (less nitrate and more arsenic) in the central flood basins is

thought to reflect anoxic conditions. The higher concentrations of many inorganic constituents and dissolved solids in wells on the western alluvial plain are thought to reflect recharge water chemistry influenced by the sedimentary rock types of the Coast Ranges.

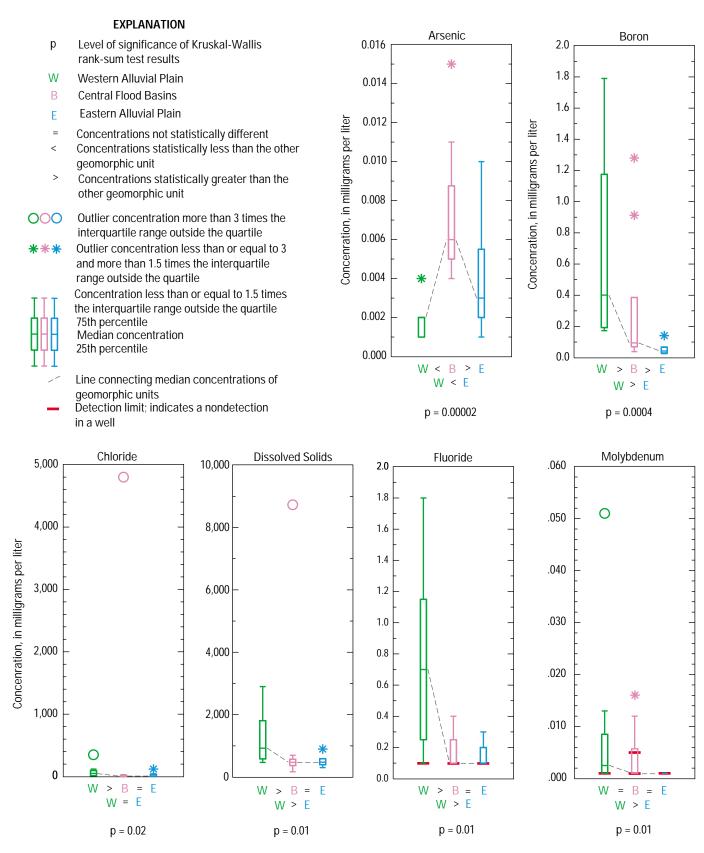
## Correlations Between Shallow Ground-Water Quality and Depth to Ground Water and Top of Well Screen

Even though the wells sampled in this study have a small range in depth to ground water (6.4 m) and to the top of the well screen (7.6 m), correlations were found between these two factors and the number of pesticides and rice pesticides detected, and the concentrations of nitrite and some inorganic constituents (fig. 8). The number of rice pesticides detected in each well was negatively correlated with the depth to ground water (fig. 8A). Concentrations of cobalt, manganese, and nickel were negatively correlated with depth to ground water (figs. 8B, 8C, and 8D, respectively). Concentrations of nitrite, which could be due to fertilizer use, also were negatively correlated with depth to ground water (fig. 8E). The number of pesticides detected in each well was negatively correlated with the depth to top of well screen (fig. 8F). No correlation was found between depth and bentazon concentration. Concentrations of molybdenum and sulfate were negatively correlated with depth to top of well screen (fig. 8G and 8H, respectively).

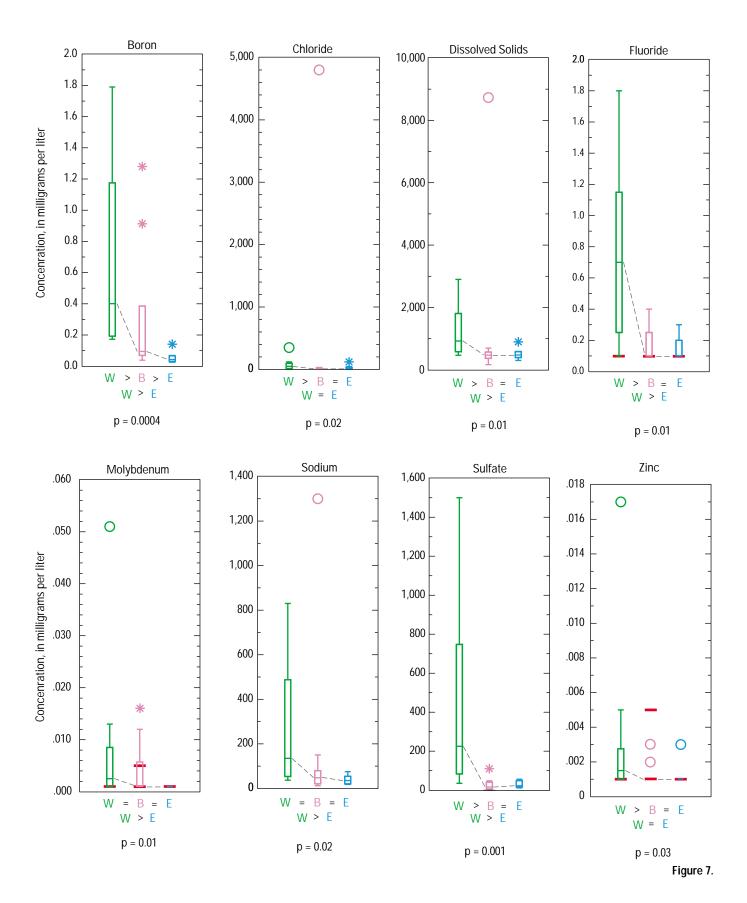
Reasons for the correlations between the inorganic constituents and depths to ground water or top of well screen are not known, but the correlation suggests a source of these constituents near land surface, and could be a result of human activities or of natural processes occurring near land surface. The correlations between pesticide detections and shallower depths to top of well screen and between nitrite concentrations and shallower depths to ground water are interpreted in this report as a relation to human and rice land-use activities (pesticide and fertilizer application) at land surface.

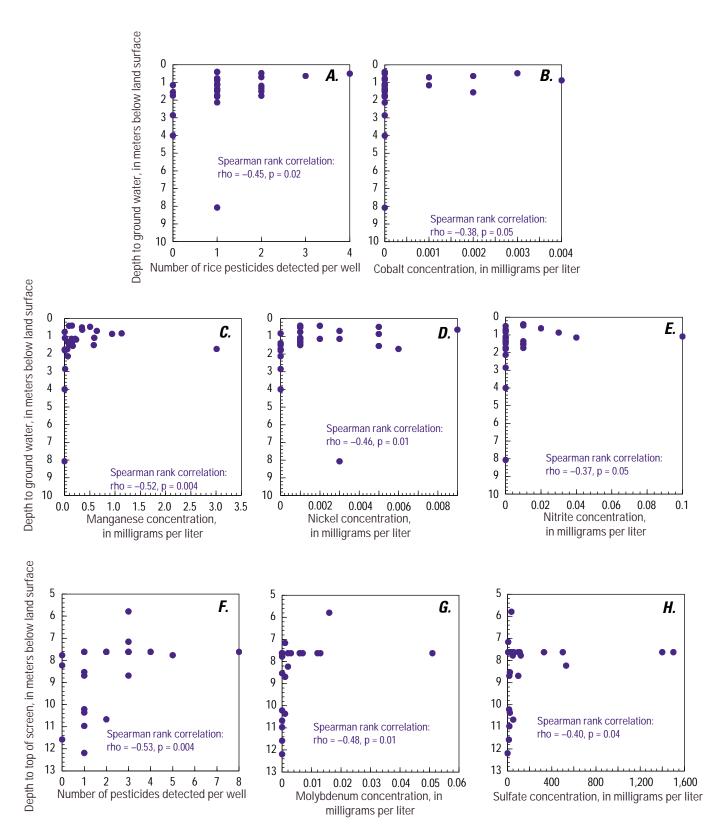
### Correlations Between Inorganic Constituents, Land Use, and Pesticides

No correlations were found between the concentrations of inorganic or nutrient constituents and the number of pesticides detected in each well, the percentage of rice within 500 m of each well, or the type of land use within 500 m of each well. No correlation



**Figure 7.** Concentrations of arsenic, boron, chloride, dissolved solids, fluoride, molybdenum, nitrate, phosphorus, potassium, silica, sodium, sulfate, and zinc detected in shallow ground water in rice areas in relation to well location and geomorphic unit, Sacramento Valley, California.





**Figure 8.** Correlations between depth to ground water and (*A*) number of rice pesticides detected per well, (*B*) cobalt, (*C*) manganese, (*D*) nickel, and (*E*) nitrite concentrations; and correlations between depth to top of screen and (*F*) number of pesticides detected per well, (*G*) molybdenum, and (*H*) sulfate concentrations in wells sampled in rice areas in the Sacramento Valley, California. p is the actual computed value of the level of significance of the test statistic.

was found between nitrate concentration and the number of pesticides, the number of rice pesticides, or the bentazon concentration of each well. No correlation was found between dissolved-solids concentration and the number of pesticides or rice pesticides detected in each well or bentazon concentration. Concentrations of tritium were correlated to concentrations of bentazon (fig. 9A); this correlation is an indication that bentazon concentration possibly is related to the recharge age of shallow ground water. Concentrations of boron and sodium were correlated to the number of rice pesticides detected in each well (figs. 9B and 9C, respectively). The correlations between boron, and sodium concentrations and either the number of rice pesticides or bentazon concentrations could be interpreted as a relation to rice land-use activities; however, the correlations of boron and sodium with geomorphic unit were higher than their correlations with the number of rice pesticides and were interpreted as an indication that the occurrence of rice pesticides, sodium, and boron is associated with similar geochemical conditions in the shallow ground water.

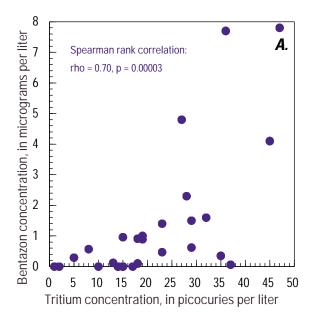
## Tritium Concentration, Pesticide Use, and Age of Shallow Ground-Water Recharge

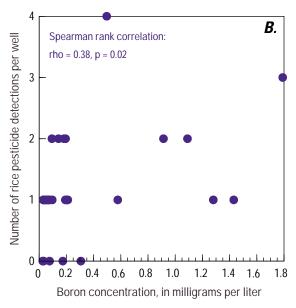
Tritium was detected in all wells sampled in this study, at concentrations ranging from 1 to 47 pCi/ L, with a median of 18.5 pCi/L (table 12). No tritium concentrations exceeded the MCL of 20,000 pCi/L (California Department of Water Resources, 1997). Tritium, a naturally occurring and manmade radioactive isotope of hydrogen with a half-life of 12.43 years, can be used to determine whether ground water has been recharged since the early 1950s when atmospheric hydrogen bomb testing began, producing tritium levels up to 3 orders of magnitude higher than natural concentrations (Michel, 1989, p. 2). Ground water that originated as precipitation and recharged before the 1950s should have a tritium concentration of about 1 pCi/L in 1997 (Plummer and others, 1993). Current tritium concen-trations in rainfall are about 44 pCi/L (1989–1993 average in rainfall at Menlo Park, California [Inter-national Atomic Energy Agency/World Meteoro-logical Organization, 1998]). Tritium concentrations measured in this study indicate that all but one of the wells sampled in this study yield ground water that was at least partially recharged since 1950.

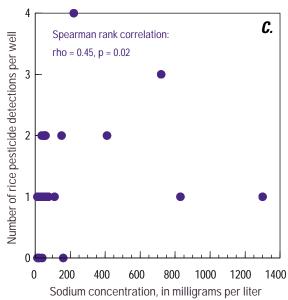
To further define a range of possible dates for recharge of the sampled ground water, the years of use of pesticides detected in shallow ground water were used (table 11) (California Department of Pesticide Regulation, 1999). Some of the pesticides used in the Sacramento Valley were not used until the late 1970s or 1980s, and if these pesticides are detected in the ground water, the conclusion is that at least part of the ground water was recharged since these pesticides were first used. For each of the 25 wells with pesticide detections, the detected pesticide chosen to further restrict the dates for recharge was the one with the most recent "first-use" date. For 18 of the wells sampled, this pesticide is bentazon, which was first used in the Sacramento Valley in 1978. For three wells, the pesticide used to define the recharge data is thiobencarb, first used in 1982. Pesticide detections in two wells indicated some recharge since 1974 (first use of atrazine and carbofuran). Pesticide detections in one well indicated some recharge since 1971 (first use of diuron), and in another well indicated some recharge since 1966 (first use of simazine). A recharge age since the late 1970s indicated in most of the wells sampled for this study suggests that an additional factor in the frequency of detection of pesticides in this study may be the changes in rice-field irrigation water management begun in the 1983 to protect surface water quality (Hill and others, 1997a; Scardaci and others, 1999). The holding of rice-field irrigation water after applications of molinate and thiobencarb may be allowing more recharge containing pesticides to reach shallow ground water.

## Stable Isotopes and Possible Sources of Shallow Ground Water

Stable isotopes of hydrogen and oxygen in water molecules can be used to determine potential sources of ground water, or to aid in the determination of ground-water flow paths. There are two stable isotopes of hydrogen ( $^{1}$ H and  $^{2}$ H) and two stable isotopes of oxygen ( $^{16}$ O and  $^{18}$ O). In this report, the delta notation is used for isotope measurements. The delta ( $\delta$ ) notation, expressed in per mil (parts per thousand), is the relation of the abundance of a particular isotope in a sample to that of a standard. The stable isotope  $^{2}$ H ranged from values of  $\delta$  –42.8 to –81.7 per mil (table 12). The stable isotope  $^{18}$ O ranged in values between –4.93 and –11.46 per mil (table 12). Figure 10 shows a plot of the  $\delta^{2}$ H and  $\delta^{18}$ O







**Figure 9.** Correlations between (*A*) concentrations of bentazon and tritium, and correlations between number of rice pesticides detected per well and concentrations of (*B*) boron and (*C*) sodium detected in shallow ground water in rice areas in the Sacramento Valley, California. p is the actual computed value of the level of significance of the test statistic.

**Table 12.** Summary of isotopes measured in shallow ground water in rice areas in the Sacramento Valley, California  $[\delta, \text{delta}; {}^2\text{H}, \text{deuterium}; {}^{18}\text{O}, \text{oxygen-}18; \text{MCL}, \text{maximum contaminant level}]$ 

Constituent	Units	Number of detections/ number of samples	Minimum detection	Median detection	Maximum detection	Drinking- water standard	Type of standard	Number of wells exceeding a drinking- water standard
$\delta^2$ H	Ratio per mil	28/28	-81.7	-61.5	-42.8	_	_	_
$\delta^{18}{ m O}$	Ratio per mil	28/28	-11.46	-8.20	-4.93	_	_	_
Tritium	Picocuries per liter	28/28	1	18.5	47	20,000	$MCL^1$	0

<sup>&</sup>lt;sup>1</sup> California Department of Water Resources, 1997.

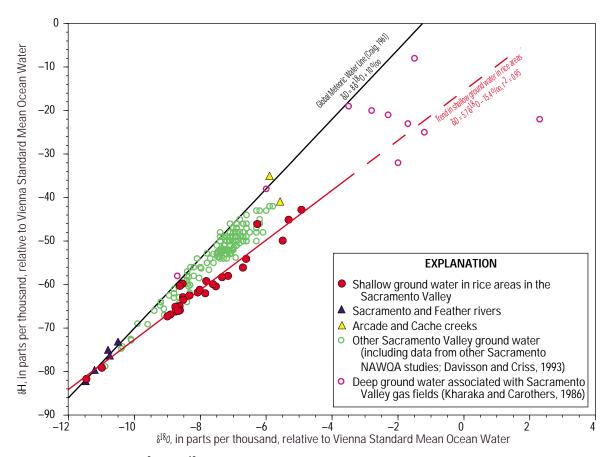


Figure 10. Relation between  $\delta^2$ H and  $\delta^{18}$ O in ground water and surface water in parts of the Sacramento Valley, California.

measured in shallow ground water in rice areas along with values measured in surface water and southeastern Sacramento Valley ground water for the Sacramento NAWQA Program, and values measured in ground water in previous studies (Davisson and Criss, 1993; Kharaka and Carothers, 1986). The Sacramento and Feather rivers that originate in the mountains to the north and east carry large amounts of precipitation and snowmelt (from higher elevations) that are isotopically lighter, plotted as blue triangles toward the lower left corner of the graph along the Global Meteoric Water Line (GMWL) (Craig, 1961). Smaller streams originating in the Coast Ranges to the west (Cache Creek) and eastern alluvial fans (Arcade Creek) carry rainfall that is isotopically heavier, plotted as yellow triangles along the GMWL toward the upper right corner of the graph. Stable isotope values measured in other parts of the ground water in the Sacramento Valley (including the southeastern side of the valley less than 90 m deep and in the Davis area on the southwestern side of the valley less than

600 m deep [Davisson and Criss, 1993]) plotted as green circles just below and along the GMWL, spanning the gap between the two groups of surfacewater values. Stable isotope values measured in very deep ground water associated with natural gas deposits in the Sacramento Valley generally plotted as purple circles further toward the upper right corner of the graph and to the right of the GMWL; these waters have been interpreted in previous studies (Kharaka and Carothers, 1986) as a mixture of meteoric waters and connate water that has been squeezed from shales and siltstones, and have high dissolved-solids concentrations and  $\delta^{18}$ O values.

While some of the ground-water data points (red circles, fig. 10) from shallow ground water in rice areas plot with the surface water along the GMWL, most plot in a group whose trend has a lower slope than the GMWL and is below the other ground-water data. Both  $\delta^2 H$  and  $\delta^{18} O$  are statistically different in the shallow ground water in rice areas than in other ground water in the Sacramento Valley aquifer

(rank-sum test:  $p \le 0.0001$  and p = 0.0015, respectively; p is the actual computed value of the level of significance of the test statistic). The trend of the stable isotopes in shallow ground water intersects the GMWL in the group of data points for the Feather and Sacramento rivers, suggesting that they are one source of recharge water. This agrees with information in Hill and others (1997a) that most of the irrigation water used for rice is surface water. Although stable isotopes in surface water show a separation between eastside and westside streams, and stable isotopes in other ground water in the Sacramento valley show a statistical difference with geomorphic unit (Kruskal-Wallis test:  $p \le 0.0001$  for both  $\delta^2 H$  and  $\delta^{18}O$ ), no difference was found in stable isotopes in shallow ground water from rice areas when grouped by geomorphic unit (Kruskal–Wallis test: p = 0.12 for  $\delta^2$ H and p = 0.23 for  $\delta^{18}$ O). The trend of the shallow ground-water data points away from the GWML; the surface-water values and the other ground-water values suggest that there are additional sources of water to the shallow ground water in the center of the Sacramento Valley.

The slope of the linear trend of the shallow ground-water group, 5.7 (fig. 10), indicates that evaporated water is one possible source to shallow ground water (Coplen, 1993, p. 235). Evaporation occurs in rivers, wetlands, vernal pool areas, rice fields, and other irrigated lands in the valley, especially during the summer months when precipitation and relative humidity are very low. It is possible that the increase in the heavier stable isotopes and the high concentrations in dissolved solids in the shallow ground water may be partly due to evaporation that occurred at land surface. In a study located in the Davis, California, area to the southwest of the rice land-use study area, the increase in  $\delta^{18}$ O in ground water was attributed to recharge of evaporated irrigation water and to evaporation in the vadose zone based on correlations between  $\delta^{18}$ O and dissolved-solids and nitrate concentration; dissolved-solids concentrations attributed to evaporation in the Davis area ground water were between 500 and 1,300 mg/L (Davisson and Criss, 1993). A study of salinity effects on rice production conducted from 1993 to 1995 on the west side of the Sacramento Valley reported specific-conductance measurements (which are directly related to dissolved-solids concentration) in rice-field water, irrigation-source and drain waters. The salinity study showed that values for both

water and soil in rice fields were generally between 500 and 1,500  $\mu S/cm$ , and were measured as high as 3,500  $\mu S/cm$  in some fields for brief periods of time when irrigation water was held in the fields (Scardaci and others, 1996). The median values for both dissolved-solids concentration (532 mg/L) and specific conductance (854  $\mu S/cm)$  measured in shallow ground in rice areas (table 5) are in the range of values measured in both the evaporated ground water in the Davis area and rice-field water and soil on the west side of the Sacramento Valley, suggesting that the elevated dissolved-solids concentrations in the shallow ground water are at least partly due to evaporation.

Contrary to these data on  $\delta^{18}O$  and dissolved solids, in the 1997 USGS rice land-use study, no correlation was found between  $\delta^{18}O$  and dissolved-solids concentration (Spearman rank correlation: rho = 0.17, p = 0.39), suggesting that simple evaporation is not the only process affecting the stable isotope and dissolved-solids composition of shallow ground water. A more complex relation between  $\delta^{18}O$  and dissolvedsolids concentration was found in this study (fig. 11) than the curvilinear relation found in the Davis-area ground water (Davisson and Criss, 1993, p. 242). Three of the wells sampled in the rice areas had dissolved-solids concentrations (2,880, 2,900, and 8,730 mg/L) or specific-conductance measurements (4,060, 4,480, and 13,600 µS/cm) that were higher than those measured in ground water in Davisson and Criss (1993) or in irrigation sources or rice-field water in Scardaci and others (1996). The stable isotope and dissolved-solids data suggest the following possible sources to shallow ground water in rice areas in the Sacramento Valley:

- Sacramento and Feather river water (isotopically light with dissolved-solids concentrations less than 100 mg/L).
- Sacramento Valley precipitation (isotopically variable with dissolved-solids concentrations less than 100 mg/L).
- Coast Ranges and Sacramento Valley surface waters (isotopically heavier with dissolvedsolids concentrations between 100 and 400 mg/L).
- Evaporated surface water and irrigation water (isotopically variable with dissolved-solids concentrations up to about 1,500 mg/L).

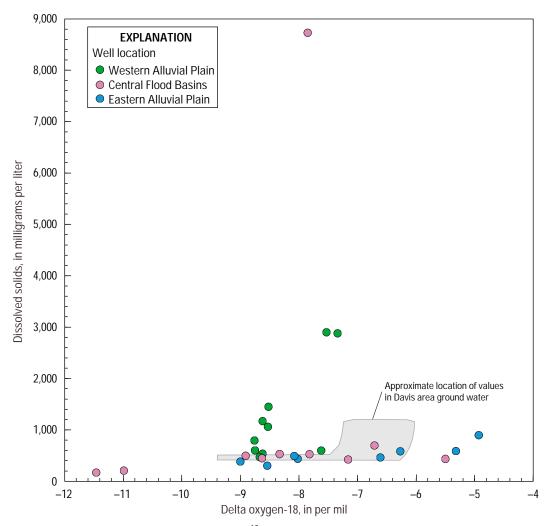


Figure 11. Relation between dissolved solids concentration and  $\delta^{18}$ O in shallow ground water in rice areas in the Sacramento Valley, California.

- Other Sacramento Valley ground water (isotopically variable with dissolved-solids concentrations up to about 1,500 mg/L).
- An unknown source (isotopically heavier with dissolved-solids concentrations greater than 1,500 mg/L).

The intersection of the shallow-ground-water stable isotope trend with the group of data points from the deep ground water associated with Sacramento gas fields (fig. 10) suggests that deep, high-dissolved-solids ground water could be another possible source to the shallow ground water beneath rice areas. This possibility has been mentioned in previous studies that discuss high dissolved-solids concentrations in the central Sacramento Valley (Hull, 1984; Olmsted and Davis, 1961; California State Water Resources Board,

1952), but there is insufficient data to thoroughly evaluate this possible contribution to shallow ground water in rice areas in the Sacramento Valley.

#### SUMMARY AND CONCLUSIONS

In 1997, the USGS installed and sampled 28 monitoring wells in rice areas in the Sacramento Valley, California, as part of the NAWQA Program. Maximum contaminant levels (barium or cadmium) and lifetime health advisory levels (boron or molybdenum) were exceeded in 7 out of 28 wells (25 percent); at least one secondary maximum contaminant level (chloride, sulfate, dissolved solids, iron, manganese, or specific conductance) was

exceeded in 22 out of 28 wells (79 percent). Median dissolved-solids concentrations and pesticide detection frequencies were higher, and median nitrate concentrations were lower in this study than those found nationally in similar NAWQA studies from 1993 to 1995 (Gilliom and others, 1998). Groundwater redox conditions were anoxic in 26 out of 28 wells (93 percent) sampled. Low nitrate concentrations were probably due to these reducing chemical conditions; in the two oxic wells, the nitrate concentrations were in the range that suggests an effect from human activities. Evidence of the effects of human activities was found in 25 of 28 wells (89 percent) sampled in this study, as a pesticide detection or a nitrate concentration over 3 mg/L.

Pesticides were detected in 89 percent of the wells sampled, and rice pesticides were detected in 82 percent of the wells sampled. All pesticides detected in this study were in use in the Sacramento Valley in the 1980s; however, use of two of these pesticides (bentazon and dichlorprop) was discontinued after 1989. Four of the detected pesticides (bentazon, carbofuran, molinate, and thiobencarb) have been used on rice crops; of these, only bentazon has been detected in previous studies and determined to be from a nonpoint source. In a study conducted in 1989, before the use of bentazon was halted in California, bentazon was detected in 42 percent of domestic wells sampled in the 1997 rice land-use study area; the bentazon detection frequency in shallow monitoring wells in 1997, when screened at the detection limit used in the 1989 study, was 68 percent. The increase in detection frequency of rice pesticides in this 1997 study compared with the 1989 study is possibly due to the lower detection limits and shallower sampling depths used in 1997.

The relation of the ground-water-quality components to natural processes and human activities was examined using statistical methods (Spearman rank correlation, Kruskal–Wallis, and rank-sum tests) to determine whether an influence from human activities could be found in addition to the presence of pesticides. Total dissolved solids and the inorganic constituent concentrations that exceed state and federal 2000 drinking-water standards show a statistical relation to geomorphic unit; this is interpreted as a relation to natural process and variations in geology in the Sacramento River Basin. No correlation was found between nitrate concentration and pesticide occurrence, indicating that an absence of high nitrate

concentrations is not a predictor of an absence of pesticide contamination in reducing ground-water conditions in the Sacramento Valley.

Tritium concentrations indicate that all wells sampled in this study with one exception yield ground water that was at least partially recharged since the 1950s. The years of use for pesticides detected in most of the wells sampled suggest that a part of the shallow ground water beneath rice areas in the Sacramento Valley was recharged since the late 1970s. An additional factor in the detection frequency of pesticides in this study may be the change in rice-field irrigation water management enacted in the 1980s to protect surface water quality. The holding of rice-field irrigation water after applications of molinate and thiobencarb may be allowing more recharge to shallow ground water of water containing pesticides.

Stable isotope, tritium, major anion, and dissolved-solids concentrations suggest that sources to shallow ground water in the rice areas of the Sacramento Valley may be a mix of recently recharged, partially evaporated water that contains pesticides and nitrate, and whose inorganic chemistry reflects well location (eastern alluvial plain, central flood basins, or western alluvial plain), and another source or mixture of sources that contain high concentrations of dissolved solids and some inorganic constituents. The water chemistry of the ground-water system in the Sacramento Valley aquifer and the effects of irrigation and ground-water pumping are extremely complex, and not thoroughly understood. More work needs to be done to understand the connections between the land surface, shallow ground water, deep ground water, and the sources of drinking water in the Sacramento Valley.

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