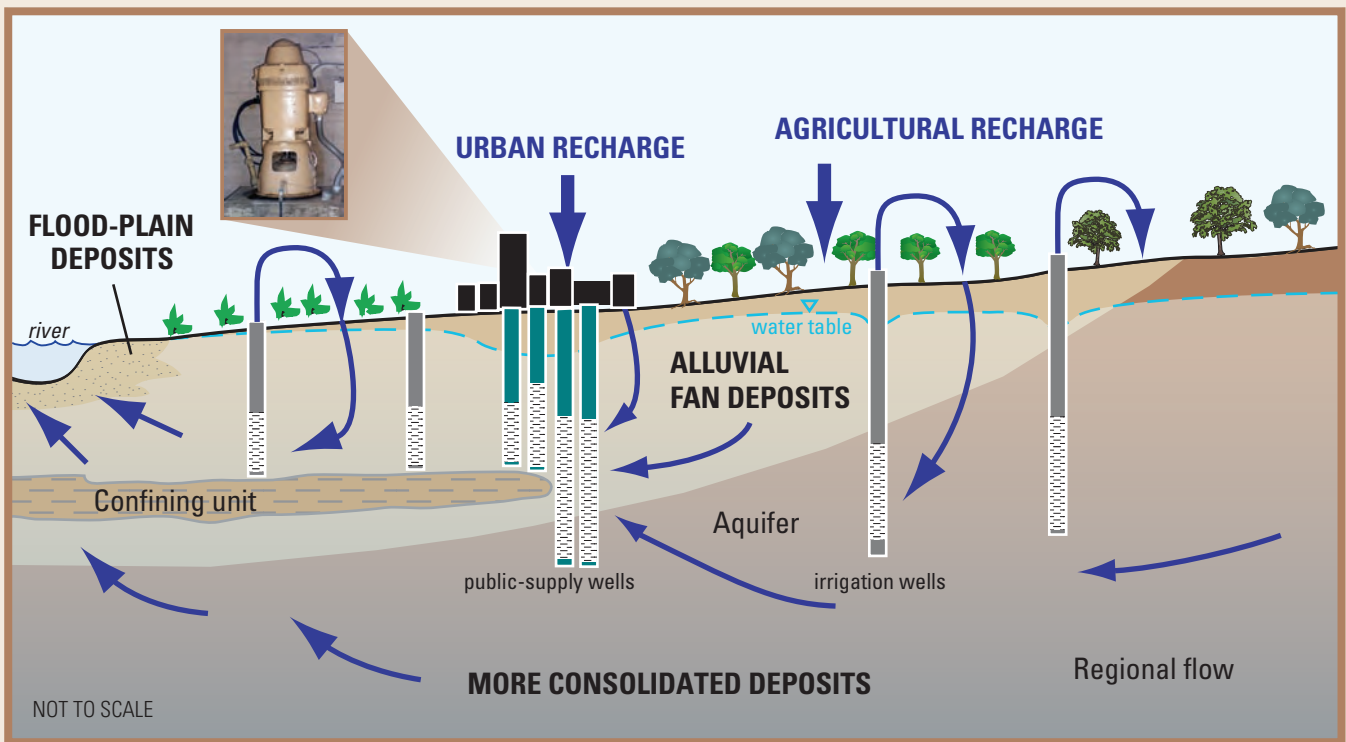


**National Water-Quality Assessment Program  
Transport of Anthropogenic and Natural  
Contaminants (TANC) to Public-Supply Wells**

# **Hydrogeology, Water Chemistry, and Factors Affecting the Transport of Contaminants in the Zone of Contribution of a Public-Supply Well in Modesto, Eastern San Joaquin Valley, California**



Scientific Investigations Report 2008–5156



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By Bryant C. Jurgens, Karen R. Burow, Barbara A. Dalgish, and Jennifer L. Shelton

National Water-Quality Assessment Program

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to Public-Supply Wells

Scientific Investigations Report 2008–5156

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## Foreword

The U.S. Geological Survey (USGS) is committed to providing the Nation with credible scientific information that helps to enhance and protect the overall quality of life and that facilitates effective management of water, biological, energy, and mineral resources (<http://www.usgs.gov/>). Information on the Nation's water resources is critical to ensuring long-term availability of water that is safe for drinking and recreation and is suitable for industry, irrigation, and fish and wildlife. Population growth and increasing demands for water make the availability of that water, now measured in terms of quantity and quality, even more essential to the long-term sustainability of our communities and ecosystems.

The USGS implemented the National Water-Quality Assessment (NAWQA) Program in 1991 to support national, regional, State, and local information needs and decisions related to water-quality management and policy (<http://water.usgs.gov/nawqa>). The NAWQA Program is designed to answer: What is the condition of our Nation's streams and ground water? How are conditions changing over time? How do natural features and human activities affect the quality of streams and ground water, and where are those effects most pronounced? By combining information on water chemistry, physical characteristics, stream habitat, and aquatic life, the NAWQA Program aims to provide science-based insights for current and emerging water issues and priorities. From 1991–2001, the NAWQA Program completed interdisciplinary assessments and established a baseline understanding of water-quality conditions in 51 of the Nation's river basins and aquifers, referred to as Study Units (<http://water.usgs.gov/nawqa/studyu.html>).

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

The USGS aims to disseminate credible, timely, and relevant science information to address practical and effective water-resource management and strategies that protect and restore water quality. We hope this NAWQA publication will provide you with insights and information to meet your needs, and will foster increased citizen awareness and involvement in the protection and restoration of our Nation's waters.

The USGS recognizes that a national assessment by a single program cannot address all water-resource issues of interest. External coordination at all levels is critical for cost-effective management, regulation, and conservation of our Nation's water resources. The NAWQA Program, therefore, depends on advice and information from other agencies—Federal, State, regional, interstate, Tribal, and local—as well as nongovernmental organizations, industry, academia, and other stakeholder groups. Your assistance and suggestions are greatly appreciated.

Matthew C. Larsen  
Acting Associate Director for Water

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## Conversion Factors, Spatial Datums, Abbreviations, and Acronyms

### SI to Inch/Pound

Multiply	By	To obtain
Length		
micrometer ( $\mu\text{m}$ )	0.00003937	inch (in.)
millimeter (mm)	0.03937	inch (in.)
meter (m)	3.281	foot (ft)
kilometer (km)	0.6214	mile (mi)
Area		
square meter ( $\text{m}^2$ )	0.0002471	acre
square kilometer ( $\text{km}^2$ )	247.1	acre
Volume		
cubic centimeter ( $\text{cm}^3$ )	0.06102	cubic inch ( $\text{in}^3$ )
cubic kilometer ( $\text{km}^3$ )	0.2399	cubic mile ( $\text{mi}^3$ )
milliliter (mL)	0.00211	ounce, US, liquid
Flow rate		
cubic meter per day ( $\text{m}^3/\text{d}$ )	0.000264	million gallons per day (Mgal/d)
cubic meter per day ( $\text{m}^3/\text{d}$ )	35.31	cubic foot per day ( $\text{ft}^3/\text{d}$ )
cubic meter per minute ( $\text{m}^3/\text{min}$ )	264.2	gallon per minute (gal/min)
meter per day (m/d)	3.281	foot per day (ft/d)
meter per year (m/yr)	3.281	foot per year (ft/yr)
Mass		
gram (g)	0.03527	ounce, avoirdupois (oz)
kilogram (kg)	2.205	pound avoirdupois (lb)
Hydraulic gradient		
meter per kilometer (m/km)	5.27983	foot per mile (ft/mi)

Temperature in degrees Celsius ( $^{\circ}\text{C}$ ) may be converted to degrees Fahrenheit ( $^{\circ}\text{F}$ ) as follows:

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

### Spatial Datums

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

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

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

### Water-Quality Information

Concentrations of chemical constituents in water are given either in milligrams per liter (mg/L) or micrograms per liter ( $\mu\text{g}/\text{L}$ ). Specific conductance (SC) is given in microsiemens per centimeter at  $25^{\circ}\text{C}$  ( $\mu\text{S}/\text{cm}$ ). The activity concentration of uranium isotopes is given in picocuries per liter (pCi/L); 1 pCi is equivalent to 2.2 disintegrations per minute. The concentration of dissolved tritium is expressed in tritium units (TU); 1 TU is 1 tritium atom per 1,018 hydrogen atoms or is equivalent to 7.1 disintegrations per minute per liter.

The saturation index (SI = IAP/Ksp) is the ratio of the ion activity product (IAP) in solution and the solubility equilibrium constant (Ks) of a mineral. It is a measure of a mineral's tendency to dissolve or precipitate. A positive value indicates that the water is supersaturated with respect to the mineral considered and that the mineral would tend to precipitate. A negative value indicates that the water is undersaturated with respect to the mineral considered and that mineral, if present, would tend to dissolve.

## Abbreviations and Acronyms

Ar	argon
atm	atmosphere
bls	below land surface
°C	degree Celsius
CaCO <sub>3</sub>	calcium carbonate
CH <sub>4</sub>	methane
CIAT	2-Chloro-4-isopropylamino-6-amino- <i>s</i> -triazine
cm <sup>3</sup>	cubic centimeter
cm <sup>3</sup> @ STP/g of water	cubic centimeters at standard temperature and pressure per gram of water
CO <sub>2</sub>	carbon dioxide
CO <sub>2</sub> (aq)	aqueous carbon dioxide
CRA	contributing recharge area
DEA	deethylatrazine
DHS	Department of Health Services
DO	dissolved oxygen
DOC	dissolved organic carbon
EM	Electromagnetic
emm	exponential mixing model
epm	exponential-piston flow model
Fe	iron
ft	foot
gpm	gallons per minute
<sup>3</sup> H	tritium
<sup>3</sup> He	helium-3
<sup>3</sup> He <sub>trit</sub>	tritogenic helium-3
<sup>4</sup> He	helium-4
ICP-MS	inductively-coupled plasma–mass spectrometry
kg/ha	kilogram per hectare
mg/kg	milligram per kilogram
mg/L	milligram per liter
pCP <sub>2</sub> (g)	partial pressure of carbon dioxide gas
pmC	percent modern carbon
ppm	parts per million
pptv	parts per trillion by volume
CIAT	2-Chloro-4-isopropylamino-6-amino- <i>s</i> -triazine
CRA	contributing recharge area
DEA	deethylatrazine
DHS	Department of Health Services
DO	dissolved oxygen
DOC	dissolved organic carbon
EM	Electromagnetic
<sup>3</sup> H	tritium
MCL	U.S. Environmental Protection Agency maximum contaminant level
MCL-CA	California maximum contaminant level
MTBE	methyl <i>tert</i> -butyl ether
NAWQA	National Water-Quality Assessment
N	nitrogen
NURE	National Uranium Resource Evaluation
NWIS	National Water Information System
NWQL	National Water Quality Laboratory
O	oxygen

PCE	tetrachloroethene
PSW	public-supply well
PVC	polyvinyl chloride
QC	quality control
RSD	relative standard deviation
SC	specific conductance
SF <sub>6</sub>	sulfur hexafluoride
STP	standard temperature and pressure
TANC	transport of anthropogenic and natural contaminants
TU	tritium unit
USEPA	U.S. Environmental Protection Agency
VCDT	Vienna Canyon Diablo Troilite
VSMOW	Vienna Standard Mean Ocean Water
USGS	U.S. Geological Survey
U(VI)	hexavalent uranium, a stable valence of uranium
UAR	uranium activity ratio of uranium-234 to uranium-238
VOC	volatile organic compound
ZOC	zone of contribution
δD	delta deuterium
δ <sup>15</sup> N	delta nitrogen-15
δ <sup>18</sup> O	delta oxygen-18
δ <sup>34</sup> S	delta sulfur-34
µg/L	microgram per liter
µm	micrometer

# Hydrogeology, Water Chemistry, and Factors Affecting the Transport of Contaminants in the Zone of Contribution of a Public-Supply Well in Modesto, Eastern San Joaquin Valley, California

By Bryant C. Jurgens, Karen R. Burow, Barbara A. Dalgish, and Jennifer L. Shelton

## Abstract

Ground-water chemistry in the zone of contribution of a public-supply well in Modesto, California, was studied by the U.S. Geological Survey National Water Quality Assessment (NAWQA) Program's topical team for Transport of Anthropogenic and Natural Contaminants (TANC) to supply wells. Twenty-three monitoring wells were installed in Modesto to record baseline hydraulic information and to collect water-quality samples. The monitoring wells were divided into four categories that represent the chemistry of different depths and volumes of the aquifer: (1) *water-table* wells were screened between 8.5 and 11.7 m (meter) (28 and 38.5 ft [foot]) below land surface (bls) and were within 5 m (16 ft) of the water table; (2) *shallow* wells were screened between 29 and 35 m (95 and 115 ft) bls; (3) *intermediate* wells were screened between 50.6 and 65.5 m (166 and 215 ft) bls; and (4) *deep* wells are screened between 100 to 106 m (328 and 348 ft) bls. Inorganic, organic, isotope, and age-dating tracers were used to characterize the geochemical conditions in the aquifer and understand the mechanisms of mobilization and movement of selected constituents from source areas to a public-supply well.

The ground-water system within the study area has been significantly altered by human activities. Water levels in monitoring wells indicated that horizontal movement of ground water was generally from the agricultural areas in the northeast towards a regional water-level depression within the city in the southwest. However, intensive pumping and irrigation recharge in the study area has caused large quantities of ground water to move vertically downward within the regional and local flow systems.

Analysis of age tracers indicated that ground-water age varied from recent recharge at the water table to more than 1,000 years in the *deep* part of the aquifer. The mean age of *shallow* ground water was determined to be between 30

and 40 years. *Intermediate* ground water was determined to be a mixture of modern (post-1950) and old (pre-1950) ground water. As a result, concentrations of age tracers were detectable but diluted by older ground water. *Deep* ground water generally represented water that was recharged under natural conditions and therefore had much older ages. Ground water reaching the public-supply well was a mixture of older *intermediate* and *deep* ground water and young *shallow* ground water that has been anthropogenically-influenced to a greater extent than *intermediate* ground water.

Uranium and nitrate pose the most significant threat to the quality of water discharged from the public-supply well. Although pesticides and VOCs were present in ground water from the public-supply well and monitoring wells, currently concentrations of these contaminants are generally less than one-hundredth the concentration of drinking water standards. In contrast, both uranium and nitrate were above half the concentration of drinking water standards for public-supply well samples, and were above drinking water standards for several *water-table* and *shallow* monitoring wells. *Shallow* ground water contributes roughly 20 percent of the total flow to the public-supply well and was the entry point of most contaminants reaching the public-supply well.

Naturally-occurring uranium, which is commonly adsorbed to aquifer sediments, was mobilized by oxygen-rich, high-alkalinity water, causing concentrations in some monitoring wells to be above the drinking-water standard of 30  $\mu\text{g/L}$  (microgram per liter). Adsorption experiments, sediment extractions, and uranium isotopes indicated uranium in *water-table* and *shallow* ground water was leached from aquifer sediments. Uranium is strongly correlated to bicarbonate concentrations (as measured by alkalinity) in ground water. Bicarbonate can effectively limit uranium adsorption to sediments. As a result, continued downward movement of high-alkalinity, oxygen-rich ground water will likely lead to larger portions of the aquifer having elevated uranium.



Nitrate concentrations were above the drinking water standard of 10 mg/L (milligram per liter) in two *water-table* wells influenced by agricultural practices. In contrast, concentrations in most *water-table* wells influenced by urban practices were less than 5.0 mg/L. All three *shallow* monitoring wells which were located beneath urban land had nitrate concentrations above the drinking water standard. Co-occurrence of sulfate with nitrate indicated that agricultural practices mainly were responsible for high nitrate in ground water. Denitrification can occur in localized areas; however, attenuation of nitrate was not significant enough to decrease contaminant concentrations throughout the aquifer. As a result, nitrate concentrations in ground water were mostly influenced by nitrogen fertilizer application rates and dispersion processes.

The water chemistry of the public-supply well was strongly influenced by well-bore leakage. During static conditions, anthropogenically-influenced *shallow* ground water migrated down the gravel pack or through the well screen and down the well into the *deep* part of the aquifer where it was stored until pumping was resumed. Because *deep* ground water contributes approximately 25 percent of the total flow, the amount of *shallow* ground water which could contribute to the total flow could increase from about 20 percent to approximately 45 percent. The relative amount of shallow ground water would then decrease as migrated *shallow* ground water was pumped from the *deep* part of the aquifer. As a result, historical water-quality data shows seasonal fluctuations, with higher concentrations of nitrate and uranium during winter months. Increasing the amount pumped during the winter months may improve water-quality during these months; however, continued downward migration of uranium and nitrate will likely negatively affect the long-term sustainability of the local ground-water aquifer as a source of drinking water, as well as the public-supply well itself.

## Introduction

In 2000, ground water provided 37 percent of the public drinking-water supplies used by 242 million people nationwide (Hutson and others, 2004). Dependence on ground water for public supply has increased five fold over the last 50 years, causing increased concern about the quality of water pumped by public-supply wells. California provides more ground water for public supply than any other state in the Nation, serving more than 30 million people and accounting for 18 percent of the total ground water withdrawals for public supply in 2000 (Hutson and others, 2004).

Ground-water withdrawals from the Central Valley Principal aquifer are the second largest in the Nation, accounting for 13 percent of total withdrawals (Maupin and Barber, 2005). Most of the ground water use is in the eastern San Joaquin Valley where irrigation is the primary water use; however, the rapidly increasing population and periods of

drought are expected to increase reliance on ground water for drinking water. Both agricultural and urban practices have affected the quality of ground water in the eastern San Joaquin Valley. In shallow ground water beneath farmed land, pesticides were detected in 69 percent of domestic wells sampled during 1993–95, and nitrate concentrations were above the maximum contaminant level (MCL) of 10 mg/L (U.S. Environmental Protection Agency, 2003) in 24 percent of domestic wells (Dubrovsky and others, 1998). Low concentrations of volatile organic compounds (VOC) were detected in more than 70 percent of the public-supply wells sampled in Fresno and in more than 90 percent of the wells sampled in Modesto in 2001–2002 (Wright and others, 2004). In addition to contaminants derived from land-use practices, natural contaminants such as arsenic and uranium were frequently near the top of the list of inorganic and radionuclide contaminants that have the highest number of MCL exceedences in public-supply wells throughout the State (California Department of Public Health, 2006). In the Modesto and Turlock areas, arsenic concentrations greater than 10 µg/L were detected in 12 percent of the wells (Belitz and others, 2003) and uranium concentrations greater than 30 µg/L have caused the abandonment of at least 11 public-supply wells in the Modesto area (city of Modesto, written comm., 2003). Multiple sources of contaminants and the generally permeable soils throughout the eastern San Joaquin Valley present a difficult challenge to water managers trying to provide a reliable, clean source of drinking water to an expanding population.

To improve understanding of the relations between the sources of contaminants, their transport through hydrologic systems, and the effects of contaminants on the quality of drinking water, the U.S. Geological Survey's National Water-Quality Assessment (NAWQA) program began several water-quality investigations within representative aquifers and geographic areas across the Nation to study the transport of anthropogenic and natural contaminants (TANC) to public-supply wells (Wilber and Couch, 2002). The TANC studies investigate the transport of contaminants within that part of the aquifer that contributes water to public-supply wells at multiple scales in different hydrogeologic settings (Eberts and others, 2005). Seven regional studies (hundreds to thousands of square kilometers) were completed in a range of settings, using regional ground-water flow models and water-quality data from multiple public-supply wells (Paschke and others, 2007). Following the regional analysis, more detailed local-scale studies (less than 100 km<sup>2</sup>) were implemented in 4 of the 7 study areas: the Central Valley Aquifer in the eastern San Joaquin Valley near Modesto, California; the Floridian Aquifer near Tampa, Florida; the Pomperaug River Basin near Woodbury, Connecticut; and the High Plains Aquifer near Lincoln, Nebraska (Eberts and others, 2005). The local-scale studies were designed to enhance the understanding of specific physical and chemical processes affecting the vulnerability of public-supply wells in the regional aquifer.



The public-supply well that is the focus of this report is in the eastern San Joaquin Valley in Modesto, California, and typifies many public-supply wells throughout the eastern San Joaquin Valley that have both urban and agricultural land uses within the area contributing recharge. Therefore, a detailed analysis of the sources and processes that affect the vulnerability of this well will likely elucidate factors common to other wells that are susceptible to contamination throughout the eastern San Joaquin Valley.

## Purpose and Scope

This report is one of two reports that document the local-scale TANC investigations in the eastern San Joaquin Valley near Modesto, California. This report describes the hydrogeology, water chemistry, and factors affecting the transport of contaminants in the zone of contribution of a public-supply well in Modesto, California. This characterization was used to develop hypotheses regarding the long-term vulnerability of the public-supply well to nitrate and uranium concentrations. A local-scale ground-water flow and transport model was used to test the hypotheses. The second report (Burow and others, 2008) documents the local-scale ground-water flow model and presents results of the tests of the hypotheses related to the transport and fate of contaminants of interest outlined in this report. These reports serve as a foundation for future comparisons among the four local-scale TANC study areas.

This report describes the design of the local monitoring well network and documents the methods used to collect the hydrogeologic and water-quality data. Water chemistry data and tracers of ground-water age collected from the monitoring wells and sediment analyses collected during monitoring well installation were used to understand the sources, distribution and processes controlling the transport of contaminants within the zone of contribution of the public-supply well. Because ground-water samples collected at the well head of the public-supply well were a composite of water contributed from different parts of the aquifer, water chemistry and age tracers were collected at different depths within the pumping public-supply well in order to determine where contaminants enter the well. General water-chemistry characteristics such as dissolved ions, and oxidation-reduction conditions are described. Organic constituents and nitrate, which are mainly derived from anthropogenic sources, were used to identify the influence of different land-uses on the water-quality of the aquifer. Sediment extractions and adsorption experiments were used to identify sources and processes affecting the mobilization and occurrence of arsenic and uranium in ground water. Several isotopes were also used to determine possible sources of water, and contaminant sources and elemental transformations. The report describes the interpretative steps

in estimating ground-water ages using atmospheric tracers and describes the distribution of apparent ground-water ages. Also, the report describes construction and well-bore flow characteristics of the public-supply well and how operation of the well affects the chemistry of water discharging from the well head.

## Description of Study Area

The local-scale study area is in the northeastern part of the San Joaquin Valley ([fig. 1](#)). The San Joaquin Valley occupies the southern two-thirds of the Central Valley of California. The Central Valley is a large, northwest-trending, asymmetric structural trough filled with marine and continental sediments up to 10 km thick (Page, 1986; Gronberg and others, 1998). The San Joaquin Valley is a level depression more than 400 km long and 30 to 90 km wide. East of the Valley, the Sierra Nevada rise to an elevation of more than 4,200 m; west of the Valley are the Coast Ranges, a series of parallel ridges of moderate elevations (Mendenhall and others, 1916). Streams in the northern part of the San Joaquin Valley drain through the San Joaquin River northward to the San Francisco Bay; the southern part of the Valley is hydrologically closed.

The local-scale study area is in the north part of Modesto and occupies 50 km<sup>2</sup> ([fig. 1](#)). The study area is nested within the TANC regional study area. The TANC regional-scale study area is about 2,700 km<sup>2</sup>, and extends from the Stanislaus River on the north to the Merced River on the south and bounded on the east by the Sierra foothills and the west by the San Joaquin River (Phillips and others, 2007).

The land surface in the regional study area slopes downward from the Sierra Nevada foothills to the San Joaquin River; gradients range from about 5 m/km near the foothills to less than 1 m/km near the river. The climate is semiarid, characterized by hot summers and mild winters; rainfall averaged 315 mm annually from 1931 to 1997 and normally occurs during late fall through early spring (Western Regional Climate Center, 2008). Mean annual air temperature was 17 degrees Celsius between 1971 and 2000 (Western Regional Climate Center, 2008).

The San Joaquin River ([fig. 1](#)) is the central drainage for the northern San Joaquin Valley and is the only major surface-water outlet from the valley. The Stanislaus, Tuolumne, and Merced Rivers drain the Sierra Nevada and are tributaries to the San Joaquin River. All rivers in the study area have been significantly modified from natural conditions. Each has multiple reservoirs for irrigation and power generation, which delays discharge of large amounts of snowmelt runoff. Imprinted over this hydrology is an extensive network of canals used to deliver water for irrigation.

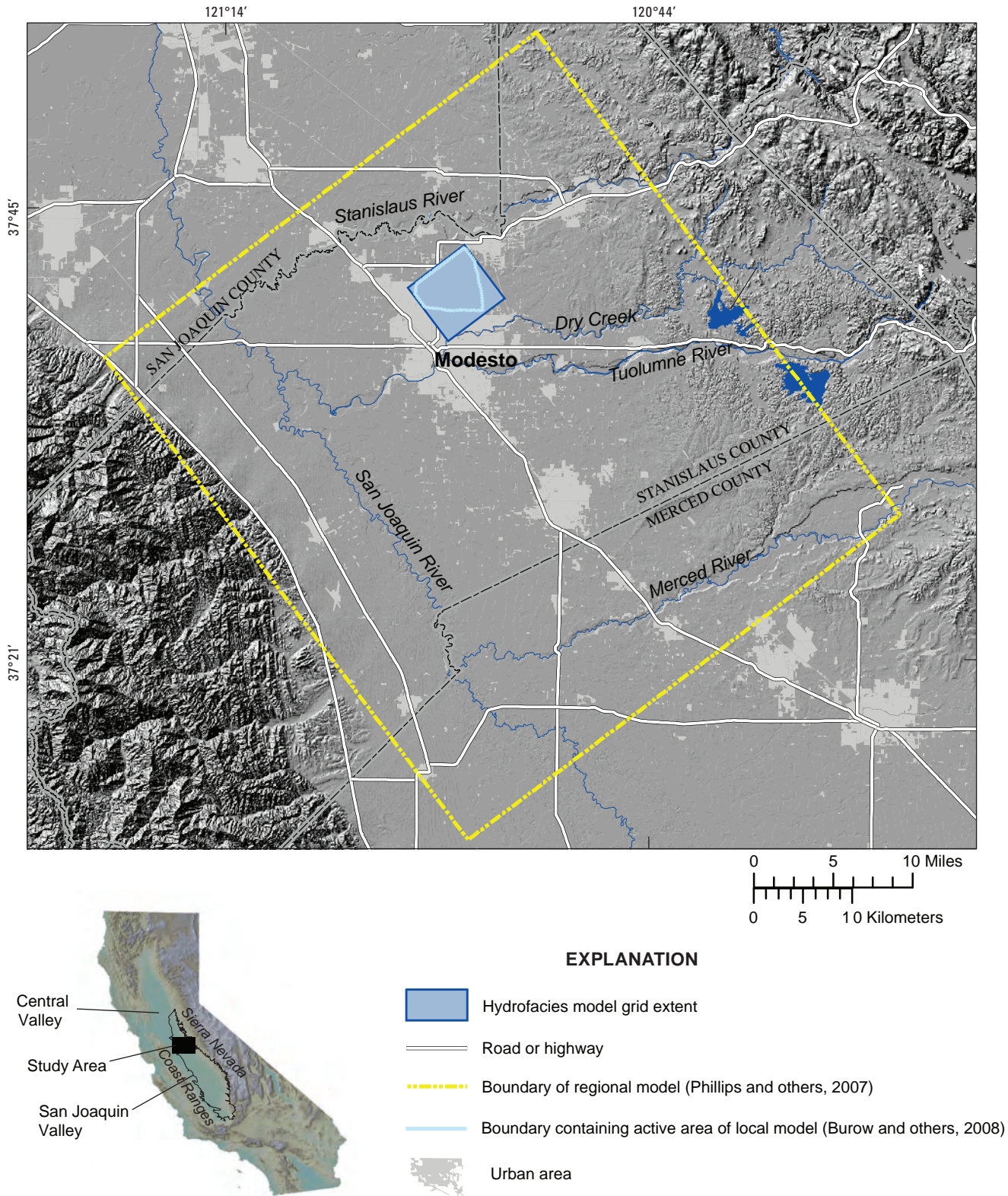


Figure 1. Study area near Modesto in the eastern San Joaquin Valley, California.



Dry wells have been used extensively throughout the regional study area since the 1950s as means to rapidly route and distribute storm water to the subsurface in agricultural and urban areas. In the Modesto urban area, dry wells were drilled using large-diameter bits (about 1 m) to depths of 15 to 25 m and were filled to the surface with rock aggregate. A perforated casing approximately 6 m long and 15 cm wide was placed in the center of the borehole for the first 6 m below land surface (bls) to promote infiltration (city of Modesto, oral commun. 2004). Adjacent to each dry well, a catch basin was constructed to capture surface runoff and deliver water to the dry well when the catch basin overflowed. Over 11,000 dry wells have been constructed in the Modesto incorporated area (city of Modesto, oral commun. 2004) and could affect the quality of shallow ground water in the local study area.

About 65 percent of the regional study area is planted in irrigated crops. Dominant crops include almonds, walnuts, peaches, grapes, grain, corn, pasture, and alfalfa (California Department of Water Resources, 2001). The local study area contains about 54 percent urban land and 46 percent agricultural land. During the last 4 decades, the urban area has expanded into the agricultural area as a result of increasing population. In Stanislaus County, the estimated population in 2005 was more than 500,000 people, an increase of more than 10 percent since 2000 (California Department of Finance, 2006).

Agricultural irrigation began in the regional study area in the early 1900s, and as of 2000, accounts for about 95 percent of the total water use (Burow and others, 2004). Surface-water supplies from the Stanislaus and Tuolumne Rivers are managed by irrigation districts and delivered to agricultural users through hundreds of kilometers of lined canals. Most irrigation districts and private agricultural users pump ground water for irrigation. Some districts also pump ground water to lower the water table in areas where it has risen too close to the land surface to support agriculture without active management. Private agricultural ground-water pumpage is not measured in the study area, but is estimated at about 32 percent of total agricultural water use in water year 2000 (Burow and others, 2004; Phillips and others, 2007).

Urban water demand is met by surface-water and ground-water supplies. Before 1995, drinking water for the city of Modesto was supplied by ground water only. In 1994, a surface-water treatment plant was completed, which now provides about half of Modesto's municipal and industrial water supply. In water year 2000, about 55 percent of the urban water requirement was met with ground water (Burow and others, 2004; Phillips and others, 2007).

The aquifer in the local study area is unconfined, although water-bearing layers of sand and gravel become semi-confined with depth owing to numerous, overlapping, discontinuous clay lenses. Before the ground-water basin was developed, most ground-water recharge occurred in the upper parts of the alluvial fans where streams entered the

basin. Ground water generally moved southwest, toward the axis of the San Joaquin Valley, and discharged primarily to the San Joaquin River and surrounding marshlands. However, diversion of surface water from streams and intensive pumping and recharge resulting from irrigated agriculture and urban growth have significantly altered the natural flow system. Following development of the ground-water basin, percolating irrigation water became the primary form of ground-water recharge, and irrigation pumping became the primary form of ground-water discharge (Davis and others, 1959; Page and Balding, 1973; Londquist, 1981). As a result, ground water has been driven vertically downward within the regional and local flow systems, and water moving laterally may be pumped and reapplied at the surface multiple times. In addition to irrigation pumping, focused ground-water pumping and lower recharge within the urban area have caused a water level depression within the city (Burow and others, 2004).

## Summary of Previous Water-Quality Studies

In general, previous studies found the quality of ground water in the regional study area to be good, although the chemistry of the water has been affected by agricultural and urban activities. Ground water in the unconfined system was typically a mixed cation-bicarbonate type water, and trends from a calcium-bicarbonate or calcium-magnesium-bicarbonate type water in the east to a calcium-sodium-bicarbonate or sodium-bicarbonate type water near the San Joaquin River, according to a study by Page and Balding (1973). Total dissolved solids and chloride concentrations varied laterally and vertically, but generally increased along the direction of regional ground-water flow from less than 200 mg/L and 20 mg/L east of Modesto to more than 500 mg/L and 100 mg/L near the San Joaquin River (Page and Balding, 1973).

Nitrate concentrations in public-supply wells sampled in Modesto in 2001 ranged from 0.23 to 9.5 mg/L as nitrogen; the median was 3.5 mg/L (Wright and others, 2004). Nitrate concentrations were elevated (greater than 3.5 mg/L as nitrogen) more frequently in public-supply wells that were within 500 m of agricultural or undeveloped areas than in wells surrounded by urban areas only (Wright and others, 2004). In the eastern San Joaquin Valley, nitrate concentrations in ground water from domestic wells were significantly higher beneath almond orchards than beneath corn, alfalfa, and vegetable crops and vineyards (Burow and others, 1998).

In contrast to nitrate, VOCs were related to urban land-use practices: at least one VOC was detected in 37 out of 40 public-supply wells in Modesto (Wright and others, 2004). The most frequently detected VOCs were disinfection byproducts, such as chloroform, and solvents, such as PCE, TCE, and dibromomethane; these VOCs were detected in more than 25 percent of the wells.

In addition to anthropogenic contaminants, naturally-occurring trace elements and radionuclides in ground water, such as arsenic and uranium, are of concern in the Modesto area. Arsenic concentrations commonly exceed 5 µg/L (Belitz and others, 2003) and uranium has exceeded the U.S. Environmental Protection Agency (USEPA) MCL of 30 µg/L in several public-supply wells, causing the operation of these wells for drinking water use to stop (city of Modesto, written commun. 2003). Because these naturally-occurring contaminants are ubiquitous in the alluvial sediments, identifying the processes which control their mobilization and transport could help water managers meet compliance standards.

## Study Design

To investigate the sources and processes affecting public-supply well vulnerability, hydrologic modeling and water chemistry data were used to select a single well from 60 public-supply wells. A monitoring well network was installed at multiple depths within the contributing recharge area (CRA) and the zone of contribution (ZOC) of the selected public-supply well. Hydrogeologic and water-quality data were collected during and after installation of monitoring wells and used to characterize the aquifer. Water-quality data were collected from the public-supply well and monitoring wells multiple times over the course of two and half years to determine seasonal variations in water chemistry.

## Public-Supply Well Selection

A regional ground-water flow model was used to simulate the ZOC and CRA for 60 public-supply wells (Phillips and others, 2007). The ZOC is the three-dimensional volumetric part of the aquifer through which ground water flows to the discharging well from the CRA (Alley, 2003). The CRA is defined as the surface area on the three-dimensional boundary of the ground-water system that delineates the location of water entering the ground-water system that eventually flows to the well from the aquifer. Particle tracking analysis was used to compute the extent and percentages of different land uses within the CRA of each well and to relate the occurrence of contaminants in the wells to each land use.

The public-supply well selected for this study is in northeast Modesto (fig. 2), and was selected from a subset of 15 wells that were sampled by the USGS in 2003 for a wide range of analytes. These 15 wells had annual pumpage that ranked in the top 25 percent of public-supply wells in Modesto for 2000, and most wells had longer screened intervals and a larger CRA than the other public-supply wells in the study area. The selected well was approximately 120 meters deep (391 ft), was screened from 27.7 (91 ft) to 111.6 m (366 ft) bls, and had an open bottom to a depth of about 115 m (377 ft) (table 1). This well withdrew water at an average rate of about 6.1 cubic meters per minute (1,600 gpm). The CRA

for the selected well had an areal extent of 4.2 km<sup>2</sup> (fig. 2, 3), consisting of about 65 percent agricultural land and 32 percent urban land.

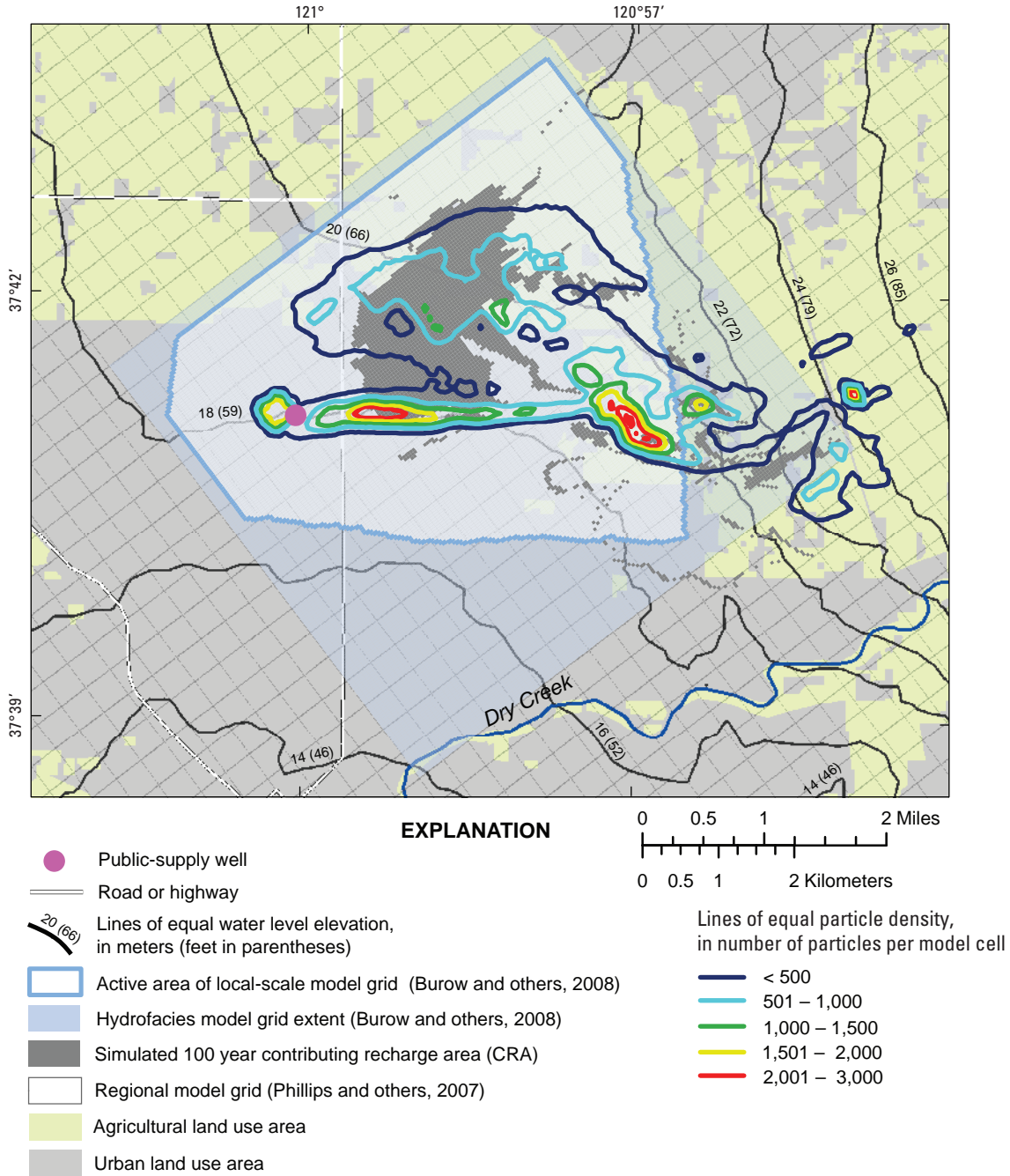
## Monitoring Well Network

Monitoring wells were constructed in the CRA and ZOC of the selected public-supply well and adjacent areas to define hydrologic boundaries and characterize chemical compounds present beneath the different land-use settings. Uncertainty in defining the areal extent of the CRA necessitated finding locations at the water table that were most likely to contribute recharge to the public-supply well. Therefore, a probabilistic method was used to create a particle density map (fig. 2) to reveal areas within the ZOC that were more likely to contribute recharge that would reach the public-supply well. A more detailed description of this method is outlined in the accompanying TANC model report (Burow and others, 2008). Candidate sites for monitoring wells were prioritized on the basis of their relative location within the CRA boundaries and on the particle density map; however, other factors, such as drilling permission, accessibility, and civilian and worker safety were also considered.

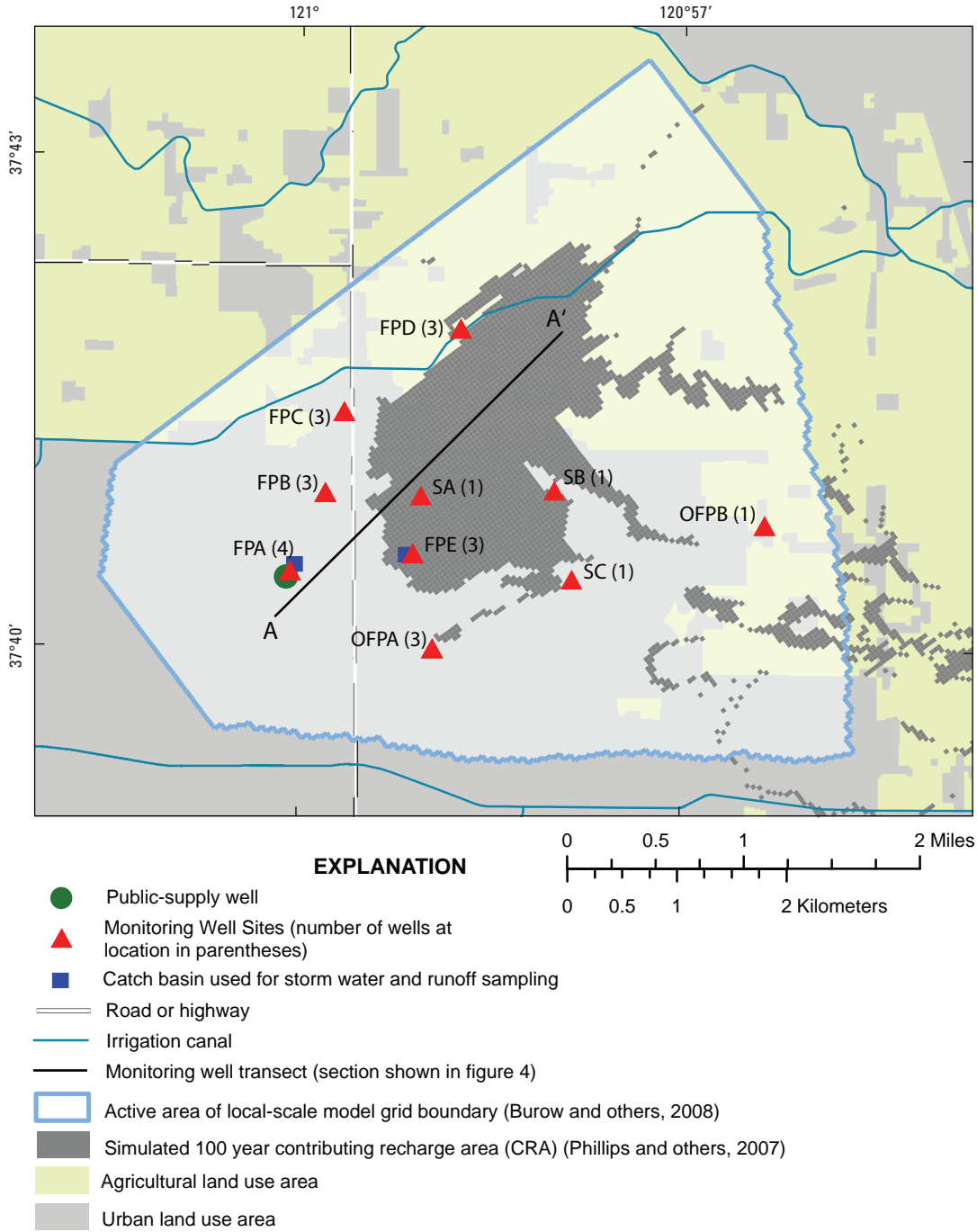
Monitoring wells were installed in two phases. During the first phase, thirteen wells were installed at four sites (FPA [4 wells], FPB [3 wells], FPC [3 wells], and FPD [3 wells]) during the summer of 2003 (fig. 3). During the second phase, 10 additional monitoring wells were installed between February and March 2004 at 6 sites (FPE [3 wells], OFPA [3 wells], OFPB [1 well], SA [1 well], SB [1 well], SC [1 well]) to target more probable recharge sites and specific depth zones within the aquifer. The wells were completed at depths ranging from within less than 5 m (16 ft) below the water table to more than 100 m (328 ft) bls (table 1). The screen length for each monitoring well was 1.5 m (5 ft).

The 23 monitoring wells installed during this study were divided into four categories that represent the chemistry of different depths and volumes of the aquifer: (1) *water-table* wells were screened between 8.5 and 11.7 m (28 and 38.5 ft) bls and were within 5 m (16.4 ft) of the water table; (2) *shallow* wells were screened between 29 and 35 m (95 and 115 ft) bls and represent the chemistry of ground water below the water-table and down to 50 m (164 ft) bls; (3) *intermediate* wells were screened between 50 and 65.5 m (166 and 215 ft) bls and represent the chemistry of ground water between 50 m and 70 m (164 and 230 ft) bls; and (4) *deep* wells are screened between 100 to 106 m (328 and 347 ft) bls and represent the chemistry of ground water below 70 m (230 ft) (table 1).

The wells were also assigned a land-use category on the basis of the surrounding land use. *Urban* land consisted primarily of residential land with commercial land along major streets. *Agricultural* land was farmed land growing primarily citrus and almond orchards. *Recently Urbanized* land was land that had been *agricultural* within the last 10 to 20 years, but has been or is being currently developed, mostly for residential housing. Some parts of this land may still be farmed.



**Figure 2.** Regional model simulation of 100-year contributing recharge area (CRA) and contours of areas of recharge with higher probabilities of reaching the public-supply well (Phillips and others, 2007). Water level elevation contours from spring 2000 water-level measurements.



**Figure 3.** Location of monitoring wells installed for a study of the Transport of Anthropogenic and Natural Contaminants (TANC) to a public-supply well in Modesto, eastern San Joaquin Valley, California.



**Table 1.** Construction characteristics and grouping variables for the installed well network in Modesto, eastern San Joaquin Valley, California.

[NAVD 1988, North American Vertical Datum 1988; no., number; PSW, public-supply well]

Well identification no.	Depth category/well type	Land-use setting	Altitude above mean sea level, NAVD 1988 (meter)	Depth below land surface to top of open interval (meter)	Depth below land surface to bottom of open interval (meter)	Well depth (meter)	Depth below land surface to water (meter)
FPA-1	<i>Water-table</i>	Urban	27.1	9.1	10.7	11.3	7.8
FPA-2	<i>Shallow</i>	Urban	27.1	35.1	36.6	37.2	7.9
FPA-3	<i>Intermediate</i>	Urban	27.1	65.5	67.1	67.7	10.1
FPA-4	<i>Deep</i>	Urban	27.1	104.6	106.1	106.7	10.5
FPB-1	<i>Water-table</i>	Urban	28.3	9.1	10.7	11.9	7.8
FPB-2	<i>Intermediate</i>	Urban	28.3	57.0	58.5	59.2	10.9
FPB-3	<i>Deep</i>	Urban	28.3	100.0	101.5	102.2	11.5
FPC-1	<i>Water-table</i>	Recently urbanized	29.6	11.7	13.3	13.9	8.5
FPC-2	<i>Intermediate</i>	Recently urbanized	29.6	61.9	63.4	64.1	11.8
FPC-3	<i>Deep</i>	Recently urbanized	29.6	105.8	107.3	108.0	12.2
FPD-1	<i>Water-table</i>	Agricultural	31.1	8.5	10.1	10.7	9.3
FPD-2	<i>Intermediate</i>	Agricultural	31.1	50.9	52.4	53.1	13.0
FPD-3	<i>Deep</i>	Agricultural	31.1	101.8	103.3	109.5	13.5
FPE-1	<i>Water-table</i>	Urban	28.7	9.1	10.7	11.7	8.8
FPE-2	<i>Shallow</i>	Urban	28.7	29.9	31.4	32.3	8.8
FPE-3	<i>Intermediate</i>	Urban	28.7	61.9	63.4	64.3	11.9
OFPA-1	<i>Water-table</i>	Urban	28.0	9.1	10.7	11.6	9.2
OFPA-2	<i>Shallow</i>	Urban	28.0	29.0	30.5	32.0	9.2
OFPA-3	<i>Intermediate</i>	Urban	28.0	57.3	58.8	60.8	11.9
OFPB-2	<i>Intermediate</i>	Agricultural	31.1	50.6	52.1	53.2	11.3
SA	<i>Water-table</i>	Urban	29.6	9.1	10.7	11.7	8.7
SB	<i>Water-table</i>	Urban	31.1	9.1	10.7	10.8	9.3
SC	<i>Water-table</i>	Urban	29.6	9.1	10.7	12.3	10.2
PSW	<i>PSW</i>	Urban	27.1	27.7	111.6	114.9	10.2

## Methods

### Drilling, Coring, and Well Installation

Two drilling methods were used to install the monitoring wells. Mud-rotary methods were used to install twenty of the 23 monitoring wells at seven sites (FPA, FPB, FPC, FPD, FPE, OFPA, OFPB); multiple 5.1-cm (2.0-in.) diameter monitoring wells were installed in a single borehole at each of these sites. Monitoring wells were constructed using schedule-80 polyvinyl chloride (PVC) with a sand pack that usually spanned 0.61 m (2 ft) below the screen to 0.61 m (2 ft) above the screen; the annular space between each well was sealed with bentonite and the well was finished flush with the land surface. Hollow-stem auger methods were used to install the three *water-table* wells (SA, SB, SC). Construction of the *water-table* wells was the same as that of wells installed

using the mud-rotary method, although only a single well was installed in each borehole. All drilling equipment was steam-cleaned or pressure-washed near each site before being moved to the next site.

Cuttings were rinsed and archived by 1.5-m (5 ft) depth intervals in order to determine approximate lithology in each borehole. Core samples were collected from various depths and boreholes to obtain representative vertical, lateral, and textural profiles of the aquifer material. The core collection procedures and analysis methods and results are detailed in [Appendix A](#) at the end of this report. Electromagnetic (EM) induction, resistivity, and natural-gamma geophysical logs were collected at each borehole and were correlated with the drill cuttings and core descriptions. The geophysical logs were used to help place monitoring well screens and help identify the formation boundaries and the textural categories from which the hydrofacies were determined.

## Sampling Periods and Collected Analytes

Wells were sampled between one and five times during the study (from October 2003 through June 2005), depending on the depth and the time each well was drilled and installed (table 2). Most wells were sampled once for an extensive list of constituents, including major ions and trace elements, radon and radionuclides, dissolved gases, age tracers, stable isotopes, volatile organic compounds, and pesticides (table 3). Some wells were screened near the water table so that contaminant sources could be characterized and temporal variability could be assessed. These wells and the public-supply well were sampled two or three additional times for an abbreviated list of analytes. To characterize the water-quality of different parts of the aquifer that contribute water to the public-supply well, samples were collected for an extensive list of analytes at multiple depths within the pumping public-supply well in August 2004 (tables 2, 3). Because of difficulty collecting depth-dependent samples, not all analytes were collected from the public-supply well in August 2004. The adjacent monitoring wells (at site FPA) also were sampled with a more limited schedule at that time.

“Dry wells” are underground structures that receive water from precipitation events during the winter and from landscape irrigation and other residential uses during the summer. Over 11,000 dry wells are located in the incorporated areas of Modesto and are an important pathway for recharge. To identify constituents contributed to the dry wells, urban runoff samples were collected during a winter storm and a summer sprinkler irrigation that produced enough runoff to permit sampling. Because of flow conditions, summer runoff samples were only collected for major ions, nutrients, and stable isotopes.

## Water Sample Collection

Ground-water samples were collected following methods developed by the NAWQA program to minimize contamination and to promote the collection of high-quality, consistent ground-water data among NAWQA study units (major hydrologic systems that are the focus of NAWQA studies) throughout the Nation (Koterba and others, 1995). Ground-water samples were collected using a submersible impeller pump connected to polytetrafluoroethylene (PTFE or “Teflon”) tubing to minimize cross-contamination between successive sampling locations. A minimum of 3 casing volumes was removed to purge each well, and water samples were collected after readings of pH, dissolved oxygen concentration (DO), specific conductance (SC), turbidity and temperature had become stable (as defined by Koterba and others, 1995). Water-quality samples from the public-supply well were collected near the well head using Teflon tubing connected to a stainless-steel ball valve that tapped the discharge pipe. Samples from the public-supply well were collected before chlorination or treatment. Sample-collection and preservation chambers were used to reduce airborne contamination. All equipment was cleaned following each sampling event with dilute phosphate-free liquid soap and methanol and rinsed repeatedly with de-ionized water.

Five depth-dependent and one composite sample was collected from the public-supply well in August 2004. Sampling the public-supply well at different depths required different sampling techniques and methods. One depth-dependent sample was collected at 45.7 m (150 ft) bls using the submersible impeller pump and methods described above; however, restrictions between the pump bowls and well casing prevented using this equipment at depths greater than 45.7 m.

**Table 2.** Water-quality sample periods and schedule of analytes collected from monitoring wells, the public-supply well, and surface-water sites in Modesto, eastern San Joaquin Valley, California, 2003–2005.

[DDS, depth-dependent sample. PSW, public-supply well. Dry wells are underground structures that receive water from precipitation events during the winter and from landscape irrigation and other residential uses during the summer]

Date	Seasonal category	Sites/wells	Depth levels	Schedule
<b>Ground water sampling</b>				
October–November 2003	Winter	FPA, FPB, FPC, FPD, PSW	All	Flow-path 1
June 2004	Summer	FPA, FPB, FPC, FPD, FPE, OFPA, SA, SB, SC, PSW	Water table only	Source
August 2004	Summer	FPA, PSW (DDS)	All	Flow-path 1
October–November 2004	Winter	FPA, FPB, FPC, FPD, PSW	Water table only	Source
October–November 2004	Winter	FPE, OFPA, OFPB, SA, SB, SC	All	Flow-path 2
June 2005	Summer	FPA, FPB, FPC, FPD, FPE, OFPA, SA, SB, SC, PSW	Water table only	Source
<b>Surface water sampling</b>				
February 2005	Winter	Surface urban runoff - FPA, FPE catch basin	2 sites	Dry well
June 2005	Summer	Surface urban runoff - FPE catch basin	1 site	Dry well



**Table 3.** List of analytes for schedules listed in [table 2](#).

[DO, dissolved oxygen concentration; SC, specific conductance. Dry wells are underground structures that receive water from precipitation events during the winter and from landscape irrigation and other residential uses during the summer]

Analyte	Sampling schedule of analytes			
	Flow-path 1	Flow-path 2	Source well	Dry well
Water-quality field measurements (Temperature, pH, turbidity, DO, SC, alkalinity)	X	X	X	X
Volatile organic compounds	X	X	X	X <sup>1</sup>
Gasoline oxygenates	X	X		X <sup>1</sup>
Pesticides	X	X		X <sup>1</sup>
Herbicide metabolites	X			
Major inorganic constituents	X	X	X	X
Trace elements	X	X		X
Nutrients	X	X	X	X
Arsenic speciation	X	X		
Dissolved organic carbon	X	X	X	
Ultra-violet absorbance	X	X	X	
Nitrogen and oxygen isotopes in dissolved nitrate	X	X		
Stable isotopes of water	X	X		X
Carbon isotopes	X			
Sulfur isotopes	X	X		
Uranium isotopes	X	X		
Radium isotopes	X	X		
Radon-222	X	X		
Gross alpha/gross beta radiation (72-hour/30-day)	X	X		
Gross alpha/gross beta radiation	X			
Dissolved gases	X	X		
Tritium <sup>2</sup>		X		
Tritium/helium-3 <sup>3</sup>	X			
Sulfur hexafluoride	X			

<sup>1</sup>February 2005 samples only.

<sup>2</sup>University of Miami, Tritium Laboratory.

<sup>3</sup>Lamont-Doherty Earth Observatory.

Below this depth, a modified small-diameter gas displacement pump, which is operated by repeated pressure and release cycles of compressed gas, was used to collect water-quality samples at 51.8, 57.9, 88.4, and 97.5 m bls (Izbicki, 2004). Because this type of sampler does not provide a continuous flow of sample water, samples were collected periodically in conjunction with water-quality samples after successive pressure cycles to monitor pH, SC, DO, and temperature to ensure sample consistency. The composite sample was collected by connecting teflon tubing to a ball-valve on the side of the well head.

Two dry wells at sites FPA and FPE were sampled during this study. Samples were collected from both sites in February 2005, and one sample was collected from site FPE in June 2005. Storm water and runoff from residential watering is

collected in catch basins in the street gutter, and overflow from the catch basins is routed to dry wells beneath the sidewalk. Dry wells were sampled at either the catch basin or within the dry well using a peristaltic pump with tygon tubing. VOCs were sampled directly from the peristaltic pump to avoid losing compounds to volatilization. Approximately three liters of water was retrieved and used to process filtered samples for pesticides, major ions, nutrients, and trace elements.

## Laboratory Analytical Methods

Samples collected for VOCs, gasoline oxygenates, pesticides, DOC, major ions, trace elements, nutrients, and radon-222 were analyzed by the USGS National Water Quality Laboratory (NWQL) in Lakewood, Colo. Gasoline oxygenates (NWQL schedule 4024) are VOCs added to gasoline to aid in the combustion of fuel (Rose and Sandstrom, 2003). Eight compounds are analyzed on this schedule and include the oxygenates themselves and their main degradates (Rose and Sandstrom, 2003). The VOCs referred to throughout this report are a set of 85 compounds that includes 5 of the compounds on the gasoline oxygenate schedule. Samples collected for VOCs, including gasoline oxygenates, were unfiltered and determined by gas chromatography and mass spectrometry using methods described by Connor and others (1998) and Rose and Sandstrom (2003). Pesticide samples were collected using a 0.7- $\mu$ m glass-fiber filter and analyzed by C-18 solid-phase extraction and capillary column gas chromatography and mass spectrometry (Zaugg and others, 1995; Lindley and others, 1996; Madsen and others, 2003; Sandstrom and others, 2001). Water samples collected for DOC were pushed through a 0.45- $\mu$ m glass-fiber filter using high-purity nitrogen gas and analyzed by ultra-violet-promoted persulfate oxidation and infrared spectrometry (Brenton and Arnett, 1993). Samples collected for major ions, trace elements, arsenic speciation, and nutrients were filtered through a 0.45- $\mu$ m capsule filter and analyzed using inductively-coupled plasma atomic emission spectrometry (ICP-AES), graphite furnace atomic absorption spectrometry, and ion-exchange chromatography and colorimetry equipment according to methods described by Fishman and Friedman (1989), Faires (1993), Fishman (1993), McLain (1993), Garbarino (1999), Garbarino and others, 2002, and Patton and Kryskalla (2003). Chemical concentrations in water are reported in milligrams per liter (mg/L) or micrograms per liter ( $\mu$ g/L). Samples to be analyzed for radon-222 were collected in a syringe before the water came into contact with the atmosphere and were injected into a mineral-oil-based scintillation solution in a 30-ml glass scintillation vial. The vial was tightly capped, shaken vigorously, and shipped within 24 hours of collection to the laboratory for analysis by liquid-scintillation counting (Prichard and Gesell, 1977); results are reported in picocuries per liter (pCi/L).

Ground-water samples collected for stable isotopes of hydrogen, oxygen, sulfur, and nitrogen and oxygen in dissolved nitrate were sent to the USGS Stable Isotope Laboratory in Reston, Virginia. Stable isotopes are reported as ratios of heavier elemental isotopes to their corresponding lighter elemental isotopes in per mil (‰ or per thousand) relative to defined isotopic standards. Delta-deuterium ( $\delta D$ ) and delta-oxygen-18 ( $\delta^{18}O$ ) in water were measured by a continuous-flow isotope ratio-mass spectrometer using hydrogen-gas/water equilibration and carbon-dioxide-gas/water equilibration techniques, respectively (Coplen and others, 1991; Epstein and Mayeda, 1953; Coplen, 1994). The results were reported relative to Vienna Standard Mean Ocean Water (VSMOW). Dissolved sulfate samples were collected and prepared for isotopic analysis using the methods of Carmody and others (1997), and the results were reported relative to the Vienna Canyon Diablo Troilite (VCDT). Isotopes of nitrogen and oxygen in nitrate samples were analyzed by bacterial conversion of nitrate to nitrous oxide and the results were reported relative to nitrogen gas in air for nitrogen and to the VSMOW for oxygen (Sigman and others, 2001; Casciotti and others, 2002; Coplen and others, 2004).

Ground-water samples were analyzed for radioactive isotopes of uranium and radium by Eberline Services in Richmond, California, and are reported in pCi/L. Eighteen ground-water samples were analyzed for uranium isotopes by standard methods using alpha spectrometry (ASTM D 3972). Radium-226 and radium-228 were measured by radon emanation and beta counting, respectively, following standard USEPA methods (EPA 903.1; EPA 904.0—modified). Gross alpha and gross beta in ground-water samples were determined after 72 hours and 30 days of sample collection. Gross alpha and gross beta were determined by evaporating an aliquot of sample water and counting alpha and beta emissions from the residue (EPA 900.0—modified).

Ground-water samples were analyzed for dissolved gases ( $N_2$ , Ar,  $CO_2$ ,  $CH_4$ ,  $O_2$ ) and sulfur hexafluoride ( $SF_6$ ) at the USGS Chlorofluorocarbon Laboratory in Reston, Virginia. Dissolved gases were measured by gas chromatography after being extracted from headspaces of glass samplers (Busenberg and others, 1998); sulfur hexafluoride was determined by methods described by Busenberg and Plummer (2000).

Samples collected for tritium and helium-3 were submitted to the Noble Gas Laboratory of Lahmont-Doherty Earth Observatory for analysis following methods described by Clark and others (1976) and Schlosser and others (1989). Tritium samples collected in October and November 2004 were analyzed at the University of Miami Tritium Laboratory in Miami, Florida. Tritium from these samples was determined by electrolytic enrichment and gas counting as described by Östlund, 1987.

Some organic compounds were analyzed more than once using different methods. Methyl *tert*-butyl ether and acetone were the only analytes detected in ground-water samples that

were analyzed by multiple methods. Only the results from preferred analytical methods are presented in this report.

## Quality-Control Sample-Collection Methods

Quality-control samples were collected to assess the validity of ground-water data used for interpretation, and to describe any bias and variability in data associated with sample collection, processing, transport, storage, and laboratory analysis. Three types of quality-control samples were collected in the field: blanks, replicates, and spikes.

### Blanks

All blanks were processed using nitrogen-purged “universal” blank water that was certified for use in collecting blanks for VOCs, pesticides, low-level nutrients, DOC, major ions, and trace elements. Three types of blanks were collected: equipment, field, and source-solution. Equipment blanks were used to determine if the sampling equipment, such as tubing, pumps, and fittings, used to collect ground-water samples had introduced contamination. Before ground-water samples were collected from monitoring well sites, equipment blanks were collected at the USGS Sacramento Field Office for two sets of ground-water sampling equipment. Field blanks were collected to determine if the methods used for sample collection, processing, transport, storage, and laboratory analysis had introduced contamination and to determine if the decontamination procedures used to clean the equipment between sampling sites were effective. Source-solution blanks were collected to verify that the universal blank water had no detectable concentrations of interest. Source-solution blanks were only collected for VOCs because they are volatile and ubiquitous and therefore can potentially contaminate the blank water used for quality-control samples. For this study, field blanks were collected for 10 percent of the samples.

### Replicates

Replicates were collected sequentially; that is, after all of the regular sample containers were filled (and processed, if necessary) for each type of analysis, a replicate set of sample containers was filled (and processed, if necessary) for that type of analysis, and so on for the different types of analyses, until all of the regular samples and corresponding replicates were collected for one site. For this study, approximately 15 percent of the samples had corresponding replicates.

### Spikes

Spikes included surrogates and matrix spikes. Surrogates are special performance-monitoring compounds that routinely are added to samples for certain types of analytical methods that involve extractions. Surrogate compounds are usually

deuterated or fluoridated analogs of the analytes of interest, but do not exist in the environment. For this study, surrogates were measured in all of the samples for VOCs and pesticides. Spike samples were replicate samples to which known concentrations of all of the analytes of interest for a method were added for the purpose of verifying analyte recoveries in the ground water being studied (after subtracting any amounts present in the corresponding environmental sample). For this study, about 5 percent of VOC and pesticide samples had corresponding matrix spikes.

## Quality-Control Summary

Analysis of the quality-control samples indicated that the quality of most data collected throughout this study is good. Detailed discussions of quality-control samples are presented at the back of this report in [Appendix B](#). Not all data collected for this study is presented or analyzed in this report. Data from this study can be retrieved online from the NAWQA Data Warehouse at <http://infotrek.er.usgs.gov/traverse/?p=NAWQA:HOME:2677137420746277>. Some water-quality results from this study not in the text of this report are given in [Appendix C](#) (major ions), [D](#) (VOCs), and [E](#) (pesticides).

Only one compound (toluene), out of 88 VOCs and gasoline oxygenates, had concentrations in water samples that could have been the result of contamination during sample handling or analysis. Consequently, toluene was not used in the data analysis of ground-water samples. Ground-water samples from FPC-1 and FPD-1 had concentrations of gasoline compounds (MTBE, *m*- and *p*-xylenes) that could have been the result of incidental contamination and therefore were removed from analysis. A “V” is marked next the values for the compounds from FPC-1 and FPD-1 ([Appendix D](#)), indicating the concentration could be the result of contamination. 2-Chloro-4-isopropylamino-6-amino-*s*-triazine (CIAT, a metabolite of atrazine, also known as deethylatrazine or DEA) had the lowest recovery of analytes in a spiked solution. The analytical method used to determine CIAT concentrations in samples has performed poorly, and therefore, CIAT concentrations are reported as estimated concentrations ([Appendix E](#)). Bromide, fluoride, and manganese were detected in blanks, which indicates that concentrations in ground-water samples could be partly due to contamination introduced during sampling or analysis. Fluoride was not frequently detected and was not used in the data analysis sections of this report. Bromide concentrations less than 0.031 mg/L (the mean blank concentrations plus three standard deviations) and manganese concentrations less than 4.3 µg/L (three standard deviations of the mean blank concentration) were removed from analysis. As a result, 1 bromide sample and 28 manganese samples were excluded. Zinc had an average relative standard deviation (RSD) greater than 60 percent within replicate pairs and was detected in field blanks at concentrations similar to environmental concentrations. Zinc was not included in the data analysis section of this

report. Radium-226 had an RSD greater than 20 percent but was not used in the data analysis section of this report.

## PHREEQC Calculations

Speciation of dissolved uranium and saturation indices of uranium minerals and calcite in ground water was determined using PHREEQC, version 2.12.5 (Parkhurst and Appelo, 1999). The Lawrence Livermore National Laboratory thermodynamic database, included with PHREEQC, was modified for speciation calculations. Formation constants for uranium complexes were updated using thermodynamic data reported by Grenthe and others (1992) and Langmuir (1997), and two uranium species ( $\text{Ca}_2\text{UO}_2(\text{CO}_3)_3^0$  and  $\text{CaUO}_2(\text{CO}_3)_3^{-2}$ ) reported by Bernhard and others (2001) were added to the database. Some species whose existence has been questioned were excluded or modified to represent a more likely species. The resulting thermodynamic database is consistent with uranium species and formation constants used by Davis and Curtis (2003).

## Hydrogeologic Setting

### Geology

The local-scale study area is on the belt of coalescing alluvial fans of low relief that lie between the dissected uplands to the east and the nearly flat surface of the valley trough (Burow and others, 2004). The aquifer in the local study area consists of approximately 120 meters of unconsolidated Pliocene-Pleistocene sediments overlying Tertiary sedimentary units. The sediments dip to the southwest, so progressively older units outcrop at the surface to the northeast. All wells in this study were completed in the Pliocene-Pleistocene sediments, although some wells in the Modesto area penetrate the water-bearing Tertiary Mehrten Formation.

The unconsolidated Pliocene-Pleistocene deposits are separated into four units: Laguna, Turlock Lake, Riverbank, and Modesto Formations. The Turlock Lake, Riverbank, and Modesto Formations form a sequence of overlapping terrace and alluvial fan systems (Davis and Hall, 1959; Marchand and Allwardt, 1981) indicating cycles of alluviation, soil formation, and channel incision that were influenced by climatic fluctuations and resultant glacial stages in the Sierra Nevada (Bartow, 1991; Weissmann and others, 2005). The sediments were deposited by the Stanislaus and Tuolumne Rivers as a heterogeneous mixture of unconsolidated, interlayered lenses of gravel, sand, silt, and clay (Marchand and Allwardt, 1981; Burow and others, 2004). The sediments of the Pleistocene formations are primarily derived from igneous intrusive rocks of the Sierra Nevada, with minor amounts of metavolcanic and metasedimentary rocks derived from the western metamorphic belt (Gronberg and others, 1998).



As part of the TANC study, sediments collected from drill cuttings and cores were characterized to depths greater than 110 m bls. The lithology of the cuttings and cores was primarily silt and clay, which comprises more than 60 percent of the sediments collected, although some boreholes contained more coarse materials than other boreholes. Optical mineralogy of coarse sediments (sands) primarily consisted of quartz, feldspar, and biotite, which is consistent with the x-ray diffraction results for core samples presented in [Appendix A](#). Iron- and manganese-oxide stains were on many surfaces of mineral grains, and sand grains were commonly weakly-cemented at depths greater than 70 m.

Recognition of buried soils, or paleosols, has been used to identify formation and sequence boundaries in the San Joaquin Valley and was used in this study to define approximate boundaries of formations and of units within formations ([fig. 4](#); Davis and Hall, 1959; Arkley, 1964; Marchand and Allwardt, 1981; Weissmann and others, 2002a). Between glacial episodes, long periods of landscape stability allowed the formation of mature, well-developed soils having distinct features that were often preserved after burial by successive glacial cycles. These paleosols are texturally clay-rich and have distinctive color and structure owing to intensive pedogenic alteration. Oxidation of iron during weathering of the soil when it was exposed at the surface results in a reddish color (Munsell hue 5YR-7.5YR) throughout the soil horizon, and evidence of clay translocation, a common pedogenic process, can be inferred from coatings on grains and ped surfaces (soil aggregates).

The Modesto Formation, of Pleistocene age, is the uppermost formation interpreted in the subsurface and is exposed at the surface across most of the local-scale study area. The formation is usually unsaturated and comprises approximately the top six meters of the subsurface, with moderately to poorly sorted unconsolidated arkosic sand, gravel, clay, and silt. The soils developed on these sediments are young and typically have a poorly defined B-horizon. As a result, infiltration is moderate to moderately rapid (Burow and others, 2004).

The Riverbank Formation, also of Pleistocene age, underlies the Modesto Formation in much of the local-scale study area, but is exposed at the surface to the east. Sediments are moderately sorted, comprised of unconsolidated arkosic sand, gravel, and silt, and less coarse-grained materials than underlying formations. Soils developed on the exposed portion of the formation are moderately developed with a clay-rich B-horizon that is commonly cemented (duripan) (Burow and others, 2004).

Locally, the Turlock Lake Formation is a relatively thick Pleistocene formation (up to 90 m thick in places) and is divided into lower and upper units by a distinct well-developed paleosol. Although the sediments of the Turlock Lake formation are commonly indistinguishable from those of the older Laguna Formation or of the younger Riverbank and Modesto Formations, the sediments are

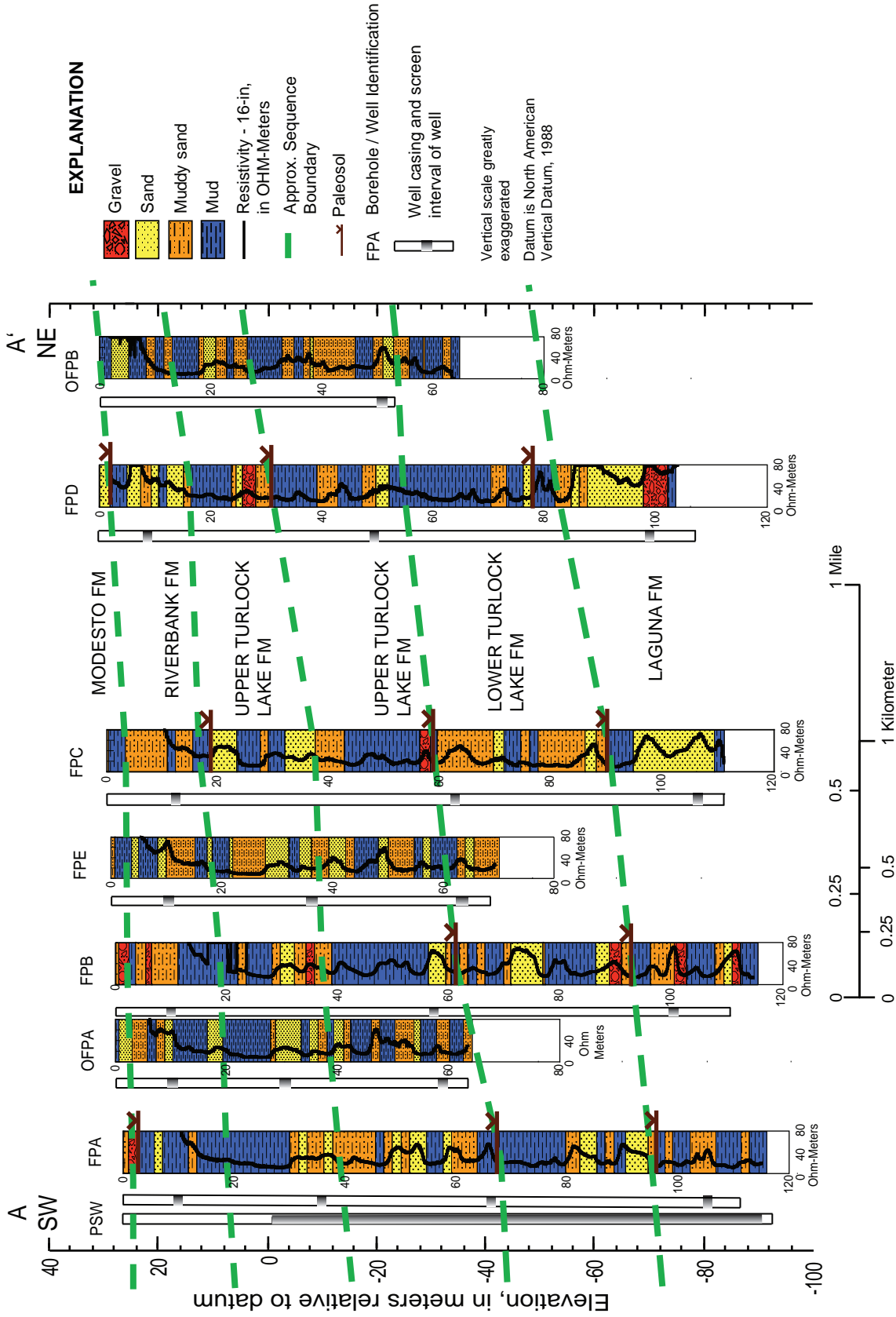
characterized by coarsening upward sequences of gravel and coarse sand overlying well sorted fine-grained sand, silt and clay.

The Laguna Formation consists of Pliocene age fluvial deposits of gravel, sand, silt, and clay that coarsen upwards. The sediments are primarily granitic in origin but have a higher mafic content in some deposits because of erosion and redeposition of volcanic sediments from the older Tertiary Mehrten Formation. Sediments from the Laguna Formation are more consolidated than those from the younger formations and sand grains are commonly cemented.

## Hydrofacies

Sediments were classified into hydrofacies units to facilitate development of a spatial correlation model of hydraulic conductivity used in the ground-water flow model (Burow and others, 2008). Hydrofacies are defined here as sediments having similar or predictable hydraulic properties on the basis of geologic attributes such as texture or depositional environment. The alluvial sediments in the study area consist primarily of interlayered lenses of gravel, sand, silt, and clay deposited by the Stanislaus and Tuolumne Rivers. The sediments were deposited in cyclic aggradation sequences linked to Pleistocene glacial episodes and the local base level of the San Joaquin River (Davis and Hall, 1959; Weissmann and others, 2002a; Burow and others, 2004; Weissmann and others, 2005).

For this study, sediments were classified into four hydrofacies categories: *gravel*, *sand*, *muddy sand*, and *mud* ([fig. 4](#)). The occurrence and distribution of these four hydrofacies for each well site was projected along a ground-water transect. The *gravel* hydrofacies was characterized as cobbles and pebbles in a coarse sand matrix, representing channel lag deposits. The *gravel* hydrofacies was expected to have the highest hydraulic conductivity. The *sand* hydrofacies was characterized as moderately well sorted medium to coarse sand, representing primary channels of the Stanislaus or Tuolumne Rivers or secondary tributary channels. The *muddy sand* hydrofacies was characterized as finely laminated fine-grained sand in a matrix of clay and silt, typically representing floodplain deposits near channels. The *mud* hydrofacies was characterized as massive to laminated silt and mud, representing floodplain deposits more distal than the *muddy sand* hydrofacies. The term mud is defined here as undifferentiated silt and (or) clay. The *mud* hydrofacies was expected to have the lowest hydraulic conductivity. A more detailed discussion of hydraulic properties of the hydrofacies presented in this report is given in the companion report by Burow and others (2008).



**Figure 4.** Distribution of hydrofacies and approximate location of formation boundaries from boreholes drilled for a study of the Transport of Anthropogenic and Natural Contaminants to a public-supply well in Modesto, eastern San Joaquin Valley, California. Locations of the well sites were projected onto the plane of the transect and do not represent the true distances between neighboring sites.

## Ground-Water Occurrence and Movement

Locally, ground water flows from the northeast, beneath agricultural land, towards the urban area to the southwest (fig. 5), although a large component of ground-water flow is downward. Seasonal fluctuations in pumping and recharge caused the water-table elevation to vary between 0.5 and 0.7 m (1.5 to 2.3 ft) between winter (January 2004) and summer (June 2005). The water-table elevation beneath urban land (FPA-1) was lowest during peak pumping season (August–September), approximately 18.9 m (62 ft) above sea level, and was highest during the winter when pumping was at a minimum, approximately 19.8 m (65 ft) (fig. 6). Similar patterns of maximum and minimum water-table elevation changes were expected in the agricultural area. Only one *agricultural* well (FPD-1) had continuous recorders in this study. This well is located near an irrigation canal that was filled with water between March and October each year. As a result of irrigation and possibly seepage from the canal, the water table at site FPD was highest during the summer irrigation season, approximately 22.5 m (74 ft) in 2004, and lowest during the winter, approximately 21.3 m (70 ft). Continuous water-level monitoring of *deep* monitoring wells (FPA-4 and FPD-3) indicated a significant response to cyclic and seasonal pumping, which created strong vertical gradients during the summer months (fig. 6). Vertical gradients in the study area ranged from 0.009 to 0.04 during the winter to 0.01 to 0.11 during the summer of 2004. Steep vertical gradients were caused by inter-bedded lenses of clays and silts and pumping stress, resulting in semiconfined conditions at depths greater than 50 meters (164 feet) bls. Horizontal movement of *deep* ground water was primarily the same direction as that of the unconfined aquifer, and typical horizontal gradients were about 0.0006.

## Public-Supply Well Construction and Well-Bore Flow Characteristics

The public-supply well in this study was drilled in 1961 to a depth of approximately 115 m (377 ft) bls. It is perforated from 27.7 m (91 ft) to 111.6 m (366 ft) bls and has an open bottom. On the basis of the monitoring well data and the long open interval, it was determined that the water discharged from the well was a mixture of water from the three depth zones identified in this report: *shallow*, *intermediate*, and *deep*.

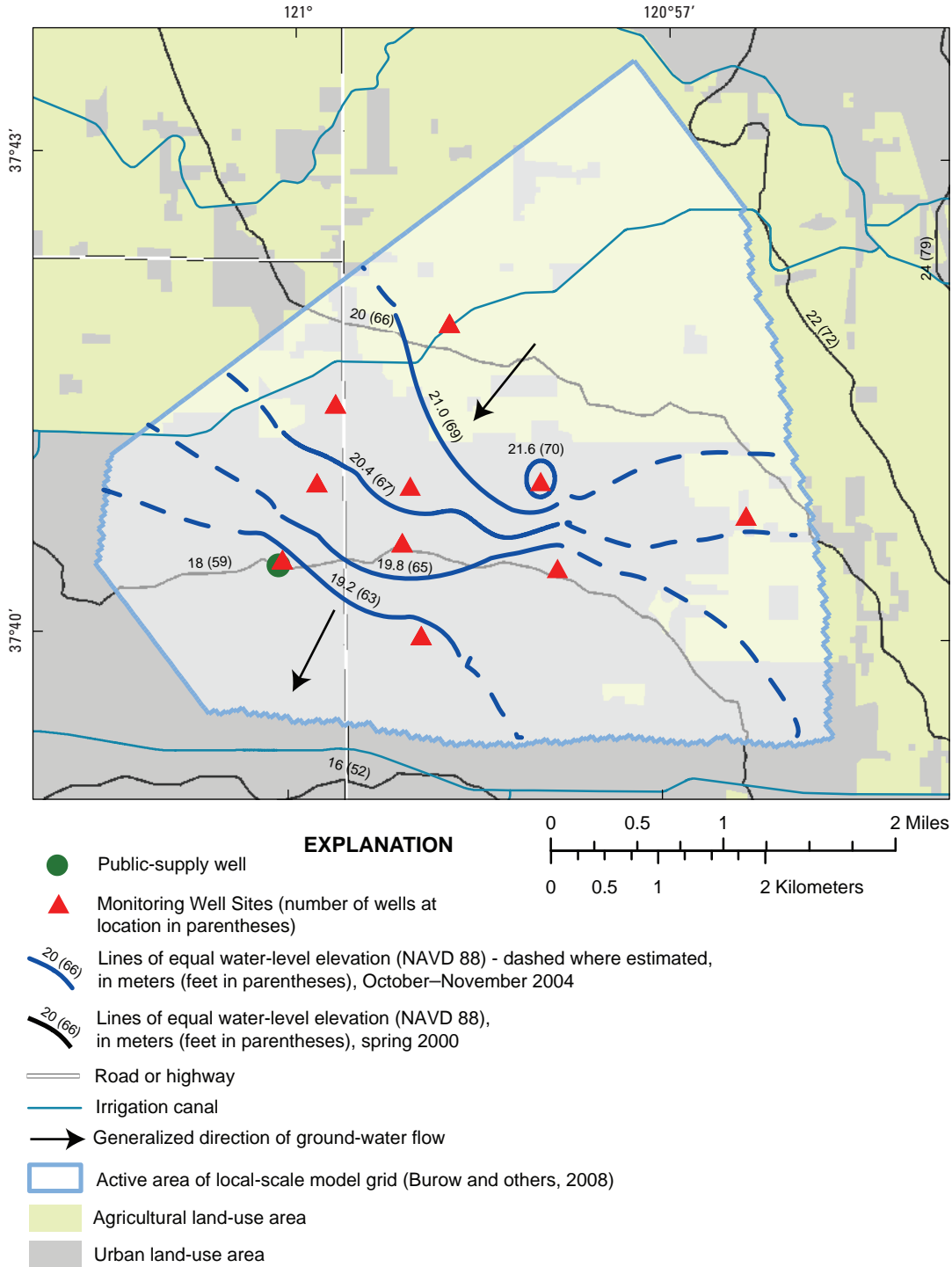
Well-bore flow at different depths within the pumping public-supply well was calculated from two sets of tracer-injection data in order to quantify the proportion of water contributed to the well-bore from each zone (fig. 7). Tracer injections were done every 20 ft and each set of tracer

injections were offset by 3 m (10 ft) to provide greater detail in the vertical direction. Less than 20 percent of the flow was from the *shallow* zone, about 55 percent was from the *intermediate* zone, and 25 percent was from the *deep* zone. Because the pump intake was located at approximately 47 m (155 ft) bls, water entering the well above this depth flowed downward, while water below the pump intake flowed upward (fig. 7). Although perforations started at 27.7 m (91 feet) bls, the velocity profile showed that most of the *shallow* ground water did not enter the well until a depth of 39.6 m (130 ft) bls. A review of a television log of the well provided by the city of Modesto showed the well casing was encrusted with mineral deposits, which likely decreased the ability of the perforations less than 39.6 m (130 ft) to transmit water from the aquifer. Most of the mineral deposit likely consisted of calcite, which is supersaturated in shallow ground water; discussed later in this report.

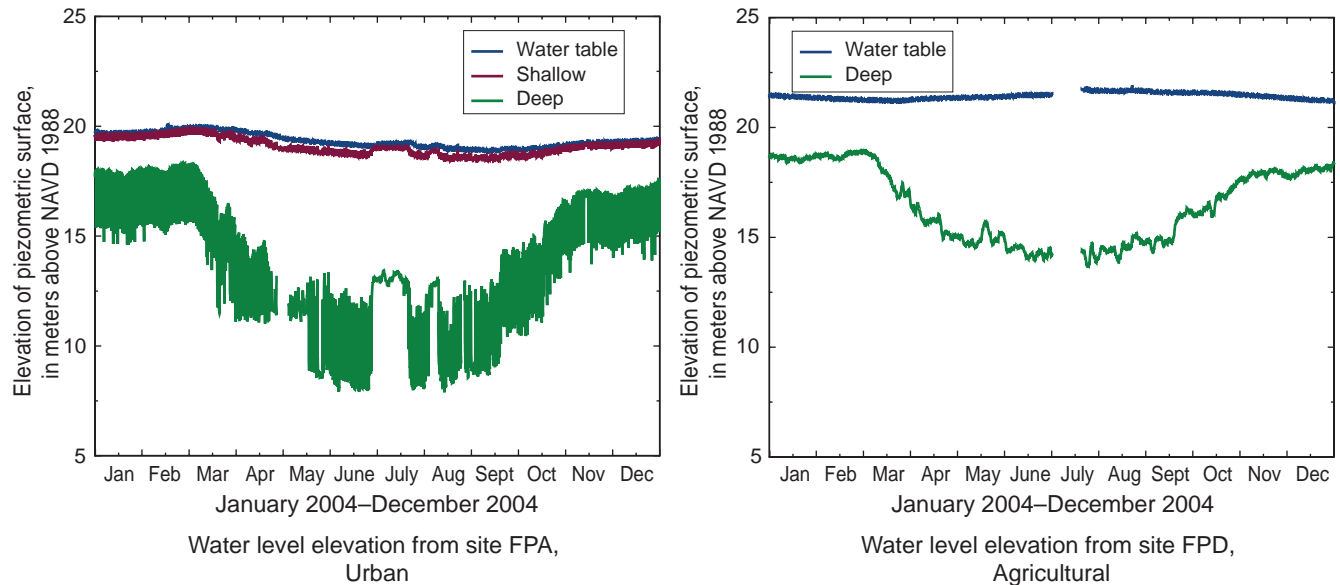
## Ground-Water Age

The age of ground water is often estimated in order to characterize ground-water flow paths and determine susceptibility of an aquifer to contamination. The age of ground water is the time elapsed since a water mass was isolated from the atmosphere. Water that enters an unsaturated zone moves downward to the water table as “recharge” to the ground-water flow system. As additional recharge continues to enter the ground-water flow system, older recharge is pushed deeper by the newer recharge, resulting in a trend of increasing ground-water age with depth. This trend can be perturbed locally in areas of ground-water pumping or artificial recharge, in areas of above-average hydraulic conductivity, and at sites where well-bore leakage can cause hydraulic short-circuiting, or as a combination of any or all of these factors.

In this study, ground-water ages were determined by measuring tritium, helium-3, sulfur hexafluoride and carbon-14 in ground water. Not all constituents were measured at all wells. Each tracer has a timescale for which the age of ground water can be determined. Tritium, its decay product helium-3, and sulfur hexafluoride are tracers of “modern” (less than 50 years) ground water because their concentrations in the atmosphere increased within the last four or five decades as a result of human activities. Sulfur hexafluoride has a more recent datable time period than tritium. Carbon-14 is usually used to identify ground water that was recharged more than 1,000 years ago, although carbon-14 concentrations increased in the atmosphere within the last 50 years, also as a result of nuclear bomb testing. In this study, carbon-14 was collected only at *deep* wells and was used as an indicator of old ground water.



**Figure 5.** Water-level elevations in water-table wells in October–November 2004 in Modesto, eastern San Joaquin Valley, California.



**Figure 6.** Water-level elevation in monitoring wells at an urban and agricultural land-use setting in Modesto, eastern San Joaquin Valley, California.

Wells located beneath agricultural land are at the head of the flow path while the urban wells are at the toe of the flow path.

## Carbon-14

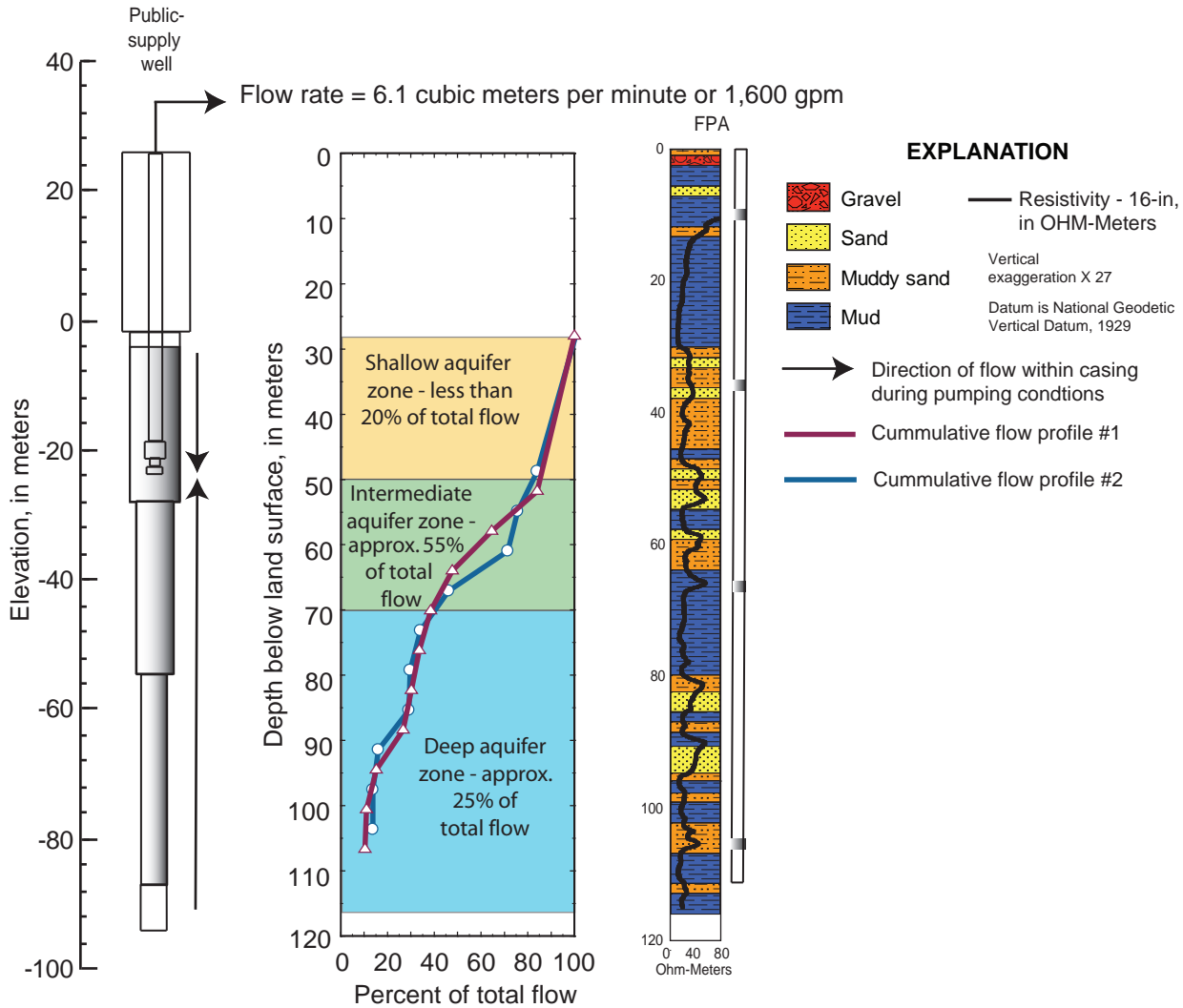
Carbon-14 is a naturally occurring radioactive isotope of carbon having a half-life of 5,730 years. Because of its long half-life, carbon-14 can be used to estimate mean ground-water ages ranging from 1,000 to less than 30,000 years before present (Clarke and Fritz, 1997). Carbon-14 dating or radiocarbon dating is considered to be an interpretive age-dating tool because carbon-14 is measured from dissolved carbon in ground water and is not part of the water molecule; therefore, one must infer the source of carbon to the ground water. For age-dating purposes, the source of carbon was presumed to be solely the recharge water that entered the ground-water flow system, assuming negligible contribution from old organic carbon that might have been in the sediment. Radiocarbon dating is based on measuring the loss of the parent radionuclide carbon-14 in a given sample, assuming the initial carbon-14 concentration is known and that losses or gains of carbon-14 are minimal or can be quantified (Clarke and Fritz, 1997). The activity of carbon-14 in a sample is reported in percent modern carbon (pmC), which indicates the carbon-14 activity of the sample relative to that of modern carbon, defined as 95 percent of the carbon-14 activity of the National Bureau of Standards oxalic acid in 1950 (Clarke and Fritz, 1997).

Carbon-14 activities for the four *deep* wells in order of lowest to highest were 32, 37, 43, and 58 pmC (table 4); the highest carbon-14 activity was from FPA-4, which was determined to be influenced by *shallow* water that migrated

through the public-supply well to deep parts of the aquifer during static conditions (discussed later in this report). As a result, the FPA-4 sample represents a mixture of young and old ground water and does not accurately reflect native carbon-14 activities of the *deep* aquifer zone. Excluding this sample, the carbon activities corresponded to a median carbon-14 age of approximately 8,300 years (table 4). The ages of water from wells FPD-3, FPC-3, and FPB-3 increase from north to south, suggesting the source of recharge of old ground water could be from the Stanislaus River. Sodium concentrations also increased along this transect indicating that cation exchange processes may be causing sodium concentrations to increase as ground-water ages.

The carbon-14 ages presented here assume minimal dilution from water and rock interactions. Dissolution and precipitation of carbonate and oxidation of old organic carbon within the aquifer causes dilution of dissolved carbon-14 in ground water. Carbon-14 ages that do not account for sources of carbon-14 are older than the true carbon-14 age. The extent of these reactions have not been rigorously analyzed for this report, but water chemistry data indicate these processes are probably not significant enough to affect carbon-14 activities by more than about 10 percent modern carbon. As a result, the calculated carbon-14 ages are interpretive and subject to considerable uncertainty, but indicate that the age of the deep ground water is thousands of years old.





**Figure 7.** Percentage of cumulative flow at 6.1-meter (20-foot) intervals and approximate distribution of flow contributed from the shallow, intermediate, and deep aquifer zones to a public-supply well in Modesto, eastern San Joaquin Valley, California.

### Tritium

Tritium ( $^3\text{H}$ ) is a radioactive isotope of hydrogen having a half-life of 12.3 years (Lucas and Unterweger, 2000). Tritium is produced naturally in the upper atmosphere as a result of cosmogenic radiation and in the subsurface from the neutron bombardment of lithium-6, although the amount of tritium produced from this reaction is often negligible (Clark and Fritz, 1997). Large quantities of tritium were introduced into the atmosphere from above-ground nuclear bomb testing between 1952 and the early 1960s (Michel, 1989). As a result, concentrations of tritium in precipitation since 1952 were substantially elevated and reached a peak in 1963. Since that time tritium in precipitation has been gradually declining. Because tritium is a radioactive isotope, tritium concentrations measured in ground water in 2004 would be

lower than the concentration would have been at the moment when that water first precipitated from the atmosphere. As a result, tritium concentrations in ground water were compared with the concentration of tritium in precipitation minus the amount of tritium that would have decayed between the time of precipitation and time of sampling (fig. 8).

Approximate ages of ground water can be inferred from concentrations of tritium using the following criteria: (1) ground water containing tritium concentrations less than 1 tritium unit (TU) is considered to have been recharged before 1950; (2) ground water containing tritium concentrations greater than 1 TU is considered to have been recharged after 1950. High concentrations of tritium (>10 TU) indicate post-1950s ground water that was likely recharged around the time of the 1963-bomb peak.

**Table 4.** Carbon-14, tritium/helium-3, and sulfur hexafluoride measurements and interpreted ages of ground water collected from monitoring wells in October and November of 2003 and 2004 and in August 2004 in Modesto, eastern San Joaquin Valley, California.

[DDS-X, depth-dependent sample and depth below land surface; emm, exponential mixing model; epm, exponential piston-flow model; <sup>3</sup>H, hydrogen-3; <sup>3</sup>He, helium-3; pptv, parts per trillion by volume; SF<sub>6</sub>, sulfur hexafluoride; STP standard temperature and pressure; TU, tritium units. cm<sup>3</sup>, cubic centimeter; g, gram; na, not applicable; nc, not collected; no., number. <, less than; —, not detected]

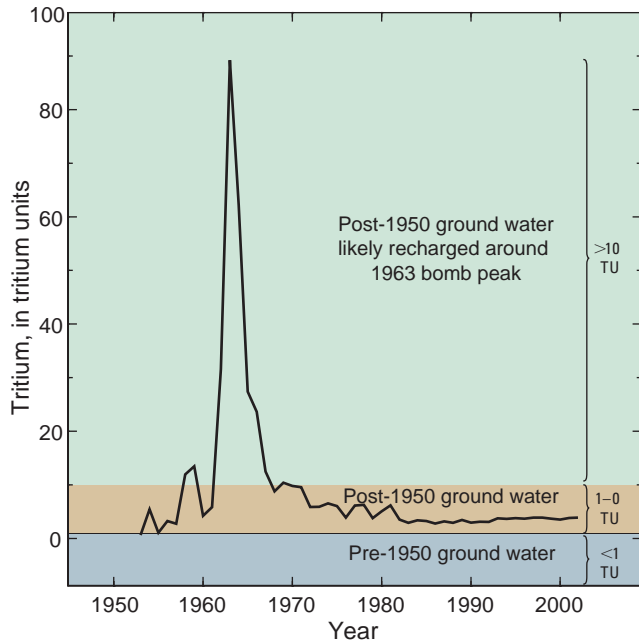
Well identification no.	Depth category	Sample date	Carbon-14 dating			Tritium and tritium/helium-3 dating				
			Carbon-14, water, filtered, percent modern	Uncorrected carbon-14 age (years)	Counting error (± years)	Tritium (TU)	Tritium age category	[ <sup>3</sup> He] <sub>tritogenic</sub> (TU)	Terrigenous helium-4 (x 10 <sup>-8</sup> cm <sup>3</sup> @ STP/g of water)	[ <sup>3</sup> H]/[ <sup>3</sup> He] <sub>tritogenic</sub> apparent piston-flow age (years)
FPA-1	Water-table	10/29/2003	nc	na	na	3.3	Post-1950	—	—	Not datable
FPB-1	Water-table	11/19/2003	nc	na	na	2.5	Post-1950	—	—	Not datable
FPC-1	Water-table	10/20/2003	nc	na	na	4.7	Post-1950	—	2.5	Not datable
FPD-1	Water-table	10/21/2003	nc	na	na	4.6	Post-1950	—	—	Not datable
FPE-1	Water-table	10/27/2004	nc	na	na	2.6	Post-1950	nc	na	na
OFPA-1	Water-table	11/03/2004	nc	na	na	3.4	Post-1950	nc	na	na
FPA-2	Shallow	11/04/2003	nc	na	na	17.3	Circa 1963	115	—	36.6
FPE-2	Shallow	10/27/2004	nc	na	na	11.2	Circa 1963	nc	na	na
OFPA-2	Shallow	11/03/2004	nc	na	na	5.2	Post-1950	nc	na	na
FPA-3	Intermediate	11/05/2003	nc	na	na	4.0	Post-1950	40.2	8.1	43.1
FPB-2	Intermediate	11/18/2003	nc	na	na	8.3	Post-1950	68.5	0.5	40.2
FPC-2	Intermediate	11/12/2003	nc	na	na	7.7	Post-1950	44.1	0.3	34.3
FPD-2	Intermediate	11/13/2003	nc	na	na	0.9	Post-1950	7.8	0.2	40.2
FPE-3	Intermediate	10/27/2004	nc	na	na	2.5	Post-1950	nc	na	na
OFPA-3	Intermediate	11/03/2004	nc	na	na	1.1	Post-1950	nc	na	na
OFPB-2	Intermediate	11/02/2004	nc	na	na	14.2	Circa 1963	nc	na	na
FPA-4	Deep	11/06/2003	57.6	4,600	100	<sup>1</sup> 1.1	Pre-1950	—	101.6	Pre-1950
FPB-3	Deep	11/18/2003	32.3	9,300	100	0.5	Pre-1950	—	—	Pre-1950
FPC-3	Deep	11/12/2003	36.7	8,300	100	<0.1	Pre-1950	—	20.1	Pre-1950
FPD-3	Deep	11/17/2003	42.6	7,100	100	0.4	Pre-1950	—	15.5	Pre-1950
PSW	Flowpath	11/13/2003	98.6	<100	100	6.9	Post-1950	41.4	4.6	34.9
PSW	DDS-Composite	08/17/2004	nc	na	na	4.6	Post-1950	32.7	37.0	37.6
PSW	DDS-45.7	08/17/2004	nc	na	na	8.5	Post-1950	56.6	—	36.6
PSW	DDS-51.8	08/24/2004	nc	na	na	2.5	Post-1950	nc	na	Not datable
PSW	DDS-57.9	08/25/2004	nc	na	na	1.4	Post-1950	nc	na	Not datable
PSW	DDS-88.4	08/23/2004	56.7	4,700	100	<sup>1</sup> 2.7	Pre-1950	nc	na	Not datable
PSW	DDS-97.5	08/19/2004	59.4	4,300	100	<sup>1</sup> 1.5	Pre-1950	nc	na	Not datable

**Table 4.** Carbon-14, tritium/helium-3, and sulfur hexafluoride measurements and interpreted ages of ground water collected from monitoring wells in October and November of 2003 and 2004 and in August 2004 in Modesto, eastern San Joaquin Valley, California.—Continued

[DDS-X, depth-dependent sample and depth below land surface; emm, exponential mixing model; epm, exponential piston-flow model;  $^3\text{H}$ , hydrogen-3;  $^3\text{He}$ , helium-3; pptv, parts per trillion by volume;  $\text{SF}_6$ , sulfur hexafluoride; STP standard temperature and pressure; TU, tritium units.  $\text{cm}^3$ , cubic centimeter; g, grams; na, not applicable; nc, not collected; no., number. <, less than; —, not detected]

Well identification no.	Depth category	Sample date	$\text{SF}_6$ dating		Combined tritium/helium-3 and $\text{SF}_6$ dating	
			$\text{SF}_6$ (pptv)	$\text{SF}_6$ apparent piston-flow age (years)	Lumped-parameter model used for interpreted mean age	Combined $[\text{}^3\text{H}]/[\text{}^3\text{He}]^{\text{tritogenic}}$ and $\text{SF}_6$ interpreted mean age (year)
FPA-1	Water-table	10/29/2003	3.92	7.5	$\text{SF}_6$ , $^3\text{H}$ epm	6
FPB-1	Water-table	11/19/2003	3.43	9.25	$\text{SF}_6$ , $^3\text{H}$ epm	10
FPC-1	Water-table	10/20/2003	2.47	13.5	$\text{SF}_6$ , $^3\text{H}$ epm	15
FPD-1	Water-table	10/21/2003	2.82	12	$\text{SF}_6$ , $^3\text{H}$ epm	12
FPE-1	Water-table	10/27/2004	nc	na	na	na
OFPA-1	Water-table	11/03/2004	nc	na	na	na
FPA-2	Shallow	11/04/2003	1.09	22	$\text{SF}_6$ , $^3\text{H}/^3\text{He}$ epm	32
FPE-2	Shallow	10/27/2004	nc	na	na	na
OFPA-2	Shallow	11/03/2004	nc	na	na	na
FPA-3	Intermediate	11/05/2003	nc	na	$^3\text{H}/^3\text{He}$ epm	81
FPB-2	Intermediate	11/18/2003	0.51	27.75	$^3\text{H}/^3\text{He}$ epm	53
FPC-2	Intermediate	11/12/2003	1.10	22	$^3\text{H}/^3\text{He}$ epm	32
FPD-2	Intermediate	11/13/2003	0.75	25	$\text{SF}_6$ , $^3\text{H}/^3\text{He}$ emm	90
FPE-3	Intermediate	10/27/2004	nc	na	na	na
OFPA-3	Intermediate	11/03/2004	nc	na	na	na
OFPB-2	Intermediate	11/02/2004	nc	na	na	na
FPA-4	Deep	11/06/2003	nc	na	na	na
FPB-3	Deep	11/18/2003	nc	na	na	na
FPC-3	Deep	11/12/2003	nc	na	na	na
FPD-3	Deep	11/17/2003	nc	na	na	na
PSW	Flowpath	11/13/2003	nc	na	$^3\text{H}/^3\text{He}$ epm	35
PSW	DDS-Composite	08/17/2004	0.73	25	$^3\text{H}/^3\text{He}$ epm	55
PSW	DDS-45.7	08/17/2004	1.73	17.5	$^3\text{H}/^3\text{He}$ epm	35
PSW	DDS-51.8	08/24/2004	0.48	28	$\text{SF}_6$ , $^3\text{H}$ epm	38
PSW	DDS-57.9	08/25/2004	0.48	28	$\text{SF}_6$ , $^3\text{H}$ epm	38
PSW	DDS-88.4	08/23/2004	nc	na	na	na
PSW	DDS-97.5	08/19/2004	nc	na	na	na

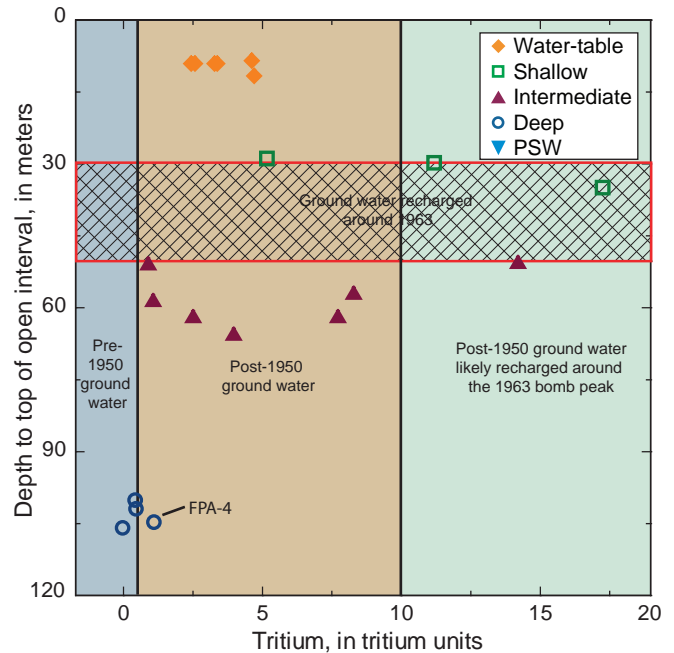
<sup>1</sup>Native ground water was generally pre-1950, but samples are, at times, influenced by wellbore flow and storage of water from the shallow part of the aquifer to the deep part of the aquifer during non-pumping periods of the public-supply well.



**Figure 8.** Tritium concentrations expected in Modesto area ground water in 2004 that originated as precipitation between 1953 and 2003.

Expected concentrations were calculated by subtracting the amount of tritium that decayed between the time precipitation fell and the time ground water was sampled from the original tritium in precipitation. Modified and updated from Michel, 1989.

Tritium concentrations in ground water in the study area varied with depth (fig. 9), but generally resembled a diluted “piston-flow” profile (simple aging of the ground water as it moves along a flow path, without mixing or preferential flow), mirroring the tritium atmospheric source curve with increasing depth below the water table. Water-table wells had concentrations of tritium ranging from 2.5 to 4.7 TU and a median of 3.4 TU (table 4, fig. 9). These concentrations are consistent with recent tritium concentrations in precipitation (fig. 8). The well having the highest tritium concentration at each site was either the *shallow* or the *intermediate* well, which suggests that the tritium bomb peak in the aquifer was between 30 and 50 m (about 95 and 165 ft) bls (fig. 9). However, tritium concentrations in this zone were not as high as bomb-peak concentrations (fig. 8). The concentrations predicted in ground water were based on the assumption of piston-flow transport with no mixing or dispersion of the concentration front. Under this assumption, tritium concentrations in ground water (fig. 9) would be similar to, but not less than, the recharge input shown in figure 8. The lower-than-expected concentrations observed in ground water was likely caused by mixing and dispersion within the aquifer. It is also likely that the wells were not screened in the precise depth intervals that would capture the maximum of the tritium peak.



**Figure 9.** Relation between tritium concentrations in ground-water samples collected during October and November of 2003 and 2004 and depth to the top perforated interval of monitoring wells in Modesto, eastern San Joaquin Valley, California.

The concentrations of tritium in intermediate wells varied widely, from less than 1 TU to more than 14 TU. Some *intermediate* wells containing tritium greater than 3 TU were perforated in deeper sediments than wells with less than 3 TU, indicating that heterogeneous aquifer materials have affected the vertical migration of water and led to earlier arrival of the tritium pulse in the more vertically connected parts of the aquifer. In other parts of the aquifer, clays and more-flow-restrictive units likely hindered the vertical movement of the tritium pulse.

The concentration of tritium in deep monitoring wells was generally less than 1 TU and suggests that water was recharged before 1950, which is consistent with carbon-14 age results. One deep well, FPA-4, had concentrations higher than 1 TU (fig. 9), but does not represent concentrations of the deep aquifer zone since the sample was affected by shallow water that flowed through the public-supply well to the deep aquifer zone during static conditions (discussed later in this report). As a result, this sample is labeled “pre-1950” ground water.

### Tritium/Helium-3

Tritium decays to the stable isotope helium-3 ( $^3\text{He}$ ). If helium-3 is measured in a ground-water sample along with its parent radionuclide,  $^3\text{H}$ , then, assuming closed-system behavior, the time ( $t$ ) elapsed since recharge is determined by (Plummer and others, 1993)

$$t = (t_{1/2}/\ln(2)) \ln[1 + {}^3\text{He}_{\text{trit}} / {}^3\text{H}], \quad (1)$$

where

$t$  is the apparent ground-water age in years before time of sampling,

$t_{1/2}$  is the half-life of tritium (12.3 years),

${}^3\text{He}_{\text{trit}}$  is the tritiogenic concentration of helium-3 in the sample (in tritium units), and

${}^3\text{H}$  is the sample tritium concentration in tritium units

Although this calculation is straightforward, determining the concentration of helium-3 that directly resulted from the radioactive decay of tritium, or the “tritiogenic” concentration of helium-3 ( ${}^3\text{He}_{\text{trit}}$ ), can be complicated because helium in ground water can have several sources. Helium concentrations in ground water often exceed the concentration predicted from air-water equilibrium. Most of the additional helium is usually from excess air. Excess air is introduced to ground water when entrapped air bubbles dissolve during fluctuations of the water table. In older ground water, helium concentrations also can exceed concentrations from air-water equilibrium and excess air. This additional component of helium is termed “terrigenic helium” because the source of the helium is generated from geologic sources in the subsurface. Terrigenic helium is comprised of helium generated from the decay of uranium and thorium in subsurface sediments or from the introduction of mantle helium into the ground-water system either by mineral weathering of volcanic sediments or from mantle fluid migration along faults. Since there are no known faults in the study area, mantle fluid migration is not thought to occur in the study area. In order to derive an equation for  ${}^3\text{He}_{\text{trit}}$  (1), a mass-balance equation for helium-3 is needed.

$${}^3\text{He}_{\text{trit}} = {}^3\text{He}_{\text{tot}} - {}^3\text{He}_{\text{eq}} - {}^3\text{He}_{\text{exc}} - {}^3\text{He}_{\text{terr}} \quad (2)$$

where,

${}^3\text{He}_{\text{tot}}$  is the total helium-3 concentration in the sample,

${}^3\text{He}_{\text{eq}}$  is the air-water equilibrium (see below) concentration of helium-3 in water,

${}^3\text{He}_{\text{exc}}$  is the concentration of helium-3 from the entrainment of excess air during recharge, and

${}^3\text{He}_{\text{terr}}$  is the concentration of helium-3 from terrigenic sources, such as mantle derived helium-3, or from the decay of lithium-6 (Schlosser and others, 1989).

In this study, helium concentrations are reported in cubic centimeters at standard temperature and pressure per gram of water ( $\text{cm}^3$  @ STP/g of water). Helium-3 was analyzed using isotopic methods and is reported in delta notation as the ratio of helium-3 to helium-4 in the sample ( $R_s$ ) relative to the ratio of helium-3 to helium-4 in the atmosphere ( $R_{\text{atm}}$ ;  $1.384 \times 10^{-6}$ ; [Clarke and others, 1976]):

$$\delta^3\text{He} = (R_s/R_{\text{atm}} - 1) \cdot 100 \quad (3)$$

In order to obtain the tritiogenic concentration of helium-3 ( ${}^3\text{He}_{\text{trit}}$ ), the isotope ratios for other sources of helium and the concentration of helium-4 must be known. This requires a mass-balance equation for helium-4:

$${}^4\text{He}_{\text{tot}} = {}^4\text{He}_{\text{eq}} + {}^4\text{He}_{\text{exc}} + {}^4\text{He}_{\text{terr}} \quad (4)$$

where,

${}^4\text{He}_{\text{tot}}$  is the total helium-4 concentration in the sample,

${}^4\text{He}_{\text{eq}}$  is the concentration of helium-4 in water at equilibrium with the atmosphere,

${}^4\text{He}_{\text{exc}}$  is the concentration of helium-4 from the entrainment of excess air during recharge, and

${}^4\text{He}_{\text{terr}}$  is the concentration of helium-4 from terrigenic sources, such as mantle derived helium-4, or from radioactive decay of uranium-thorium series elements (Schlosser and others, 1989).

Finally, equations 2, 3, and 4 were used to derive the concentration of tritiogenic helium-3 ( ${}^3\text{He}_{\text{trit}}$ ):

$${}^3\text{He}_{\text{trit}} = {}^4\text{He}_{\text{tot}} \times R_s - {}^4\text{He}_{\text{tot}} \times {}^4\text{He}_{\text{tot}} \times R_{\text{atm}} + {}^4\text{He}_{\text{terr}} \times R_{\text{atm}} + {}^4\text{He}_{\text{eq}} \times R_{\text{atm}} (1 - \alpha) - {}^4\text{He}_{\text{terr}} \times R_{\text{terr}} \quad (5)$$

where

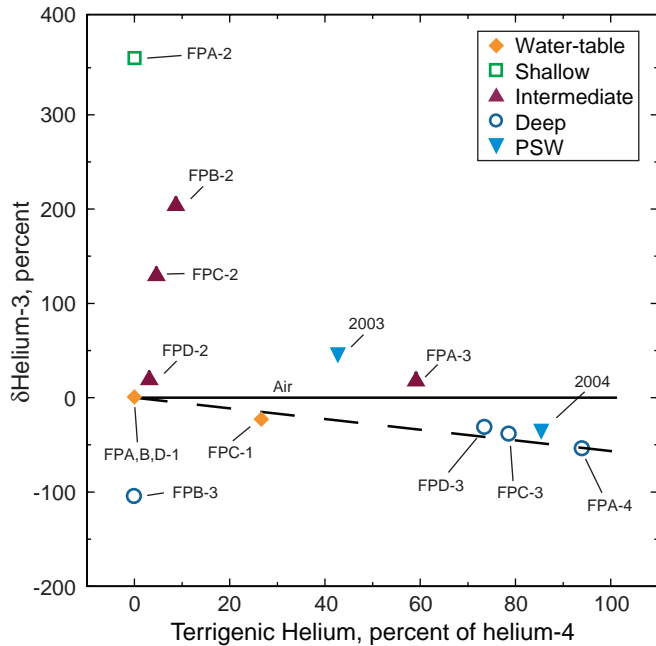
$\alpha$  is the  ${}^3\text{He}/{}^4\text{He}$  isotope fractionation between air and water (0.983) and

$R_{\text{terr}}$  is the ratio of helium-3 to helium-4 of terrigenic helium ( ${}^3\text{He}_{\text{terr}}/{}^4\text{He}_{\text{terr}}$ ) (Schlosser and others, 1989).

Calculations of concentrations of tritiogenic helium-3 ( ${}^3\text{He}_{\text{trit}}$ ) were evaluated for two potential sources of error associated with  ${}^4\text{He}_{\text{eq}}$  and  ${}^4\text{He}_{\text{terr}}$ . The air-water equilibrium concentration of helium-4 ( ${}^4\text{He}_{\text{eq}}$ ) was determined from neon concentrations in the sample to correct for helium-4 concentrations from excess air ( ${}^4\text{He}_{\text{exc}}$ ). The neon concentration in the atmosphere was calculated using recharge temperatures determined from argon and nitrogen concentrations in ground water. The mean recharge temperature determined from argon and nitrogen concentrations in ground-water samples was 16.5 degrees Celsius, which is similar to the mean annual air temperature of 17 degrees Celsius, suggesting minimal error in  ${}^4\text{He}_{\text{eq}}$ .

Ground water containing terrigenic helium ( ${}^4\text{He}_{\text{terr}}$ ) that is greater than 10 percent of the total dissolved helium-4 ( ${}^4\text{He}_{\text{tot}}$ ) complicates the determination of age because the  $R_{\text{terr}}$  must be known to calculate the age accurately (Plummer and others, 2000). The percentage of terrigenic helium in total dissolved helium was more than 3 percent in ten of the fifteen samples





**Figure 10.** Relation between  $\delta^3\text{He}$  (delta helium-3) and percentage of terrigenous helium in ground-water samples from Modesto, eastern San Joaquin Valley, California. The dashed line, which diverges from the solubility of helium in water at 16.5 degrees Celsius and 33 meters in elevation, corresponds to the addition of excess helium with  $^3\text{He}/^4\text{He}$  of  $6.0 \times 10^{-7}$ . The solid line for air corresponds to the addition of helium with a  $^3\text{He}/^4\text{He}$  ratio of  $1.384 \times 10^{-6}$ .

and more than 20 percent in seven of the fifteen (table 4). Ground-water samples that had less than 10 percent terrigenous helium were insensitive to changes in the terrigenous helium-3 to helium-4 ratio ( $R_{\text{terr}}$ ), while samples that had the largest percentage of terrigenous helium-4 were most sensitive. Ages for samples having greater than 10 percent were calculated using an  $R_{\text{terr}}$  value of  $6.0 \times 10^{-7}$  (fig. 10) and indicates a small amount of mantle helium (~5 percent) is present in ground water. The source of mantle helium is likely from the weathering of volcanic sediments associated with the Mehrten formation. Varying the value of  $R_{\text{terr}}$  by  $\pm 2.0 \times 10^{-7}$  caused ages to differ by as much as 20 years. Helium could not be measured in samples from FPB-3 and in depth-dependent samples deeper than 50 meters bls; these samples were “not datable” (table 4).

Of the 13 monitoring wells where samples for tritium/helium-3 dating were collected, only five wells could be dated using the tritium/helium-3 method (FPA-2, FPA-3, FPB-2, FPC-2, FPD-2: table 4). In addition, the composite sample from August 2004, the flow-path sample from October 2003,

and the shallowest depth-dependent sample (August 2004) from the public-water-supply (PSW) well were datable (table 4; fig. 10). Four tritium/helium-3 samples collected from monitoring wells screened near the water table could not be dated because the tritiogenic component of helium-3 could not be computed. Young waters require very accurate determinations of excess air and helium-3 because the helium-3 produced from tritium decay is such a small part of the total helium-3 in ground water. Diffusion of helium-3 across the water table could also prevent the determination of age using the tritium/helium-3 method. Three of the four deep monitoring wells (FPB-3, FPC-3, FPD-3) had tritium concentrations below 1 TU and contained terrigenous helium in excess of 70 percent (fig. 10); helium could not be determined from FPB-3, indicating the ground water from these wells was recharged before atomic weapons tests. The samples from these wells are categorized as “pre-1950” on table 4. This finding is consistent with carbon-14 results that suggested deep ground water was recharged prior to nuclear bomb testing. The deep monitoring well at FPA-4 had tritium slightly above 1 TU (1.1 TU); however, this sample was influenced by chemistry of shallow ground water that migrated through the public-supply well and recharged the deep aquifer during static conditions. This finding and the data for the other deep monitoring wells were interpreted as indicating that the native ground water at FPA-4 was recharged before 1950.

The spatial variability in calculated apparent tritium/helium-3 ages indicate that aquifer heterogeneity may be important in controlling the transport of dissolved species. The apparent age of the sample from shallow well FPA-2 was 37 years as of 2004 or the apparent year of recharge was 1967 (table 4). Apparent ages of samples from the four intermediate wells ranged from 34 to 43 years. The youngest sample was from the deepest intermediate well, FPC-2 and was younger than ground water at FPA-2, whose screen was about 25 m shallower. This suggests that the vertical movement of water is not uniform throughout the study area. At some sites, the vertical connection of highly permeable hydrofacies (fig. 4) permits faster migration of dissolved species to deeper parts of the aquifer. In addition, most of these intermediate samples contained water that was recharged near the time of the 1963 bomb-peak, but tritium plus tritiogenic helium-3 concentrations in these samples were much less than would be expected from a piston-flow input of the tritium in precipitation (fig. 11). This suggests that dispersion and mixing with pre-1950 water diluted the concentrations of the atmospheric age tracers.

## Sulfur Hexafluoride

Sulfur hexafluoride ( $\text{SF}_6$ ) is a colorless, odorless, nonflammable, nontoxic, stable gas that is used as an electrical insulator in high-voltage switches and transformers, and as a blanket gas in the melting operations of magnesium metal production (Busenberg and Plummer, 2000).  $\text{SF}_6$  in the atmosphere has increased from nearly zero before  $\text{SF}_6$ -filled electrical switches were introduced in 1953 to more than 85,700 tons in 1995 (Busenberg and Plummer, 2000). Because of its high rate of increase in the atmosphere, its known atmospheric history, and its apparent resistance to biodegradation and adsorption onto sediments and organic matter,  $\text{SF}_6$  can be used as a conservative tracer of ground-water age where sediments and rocks do not contribute significant natural background concentrations (Busenberg and Plummer, 2000). The use of  $\text{SF}_6$  as a tracer of ground-water age has a practical dating limit from the present to 1973, when atmospheric concentrations were 3 times the natural background concentration and the age uncertainty for waters recharged in that year was less than  $\pm 3$  years (Busenberg and Plummer, 2000).

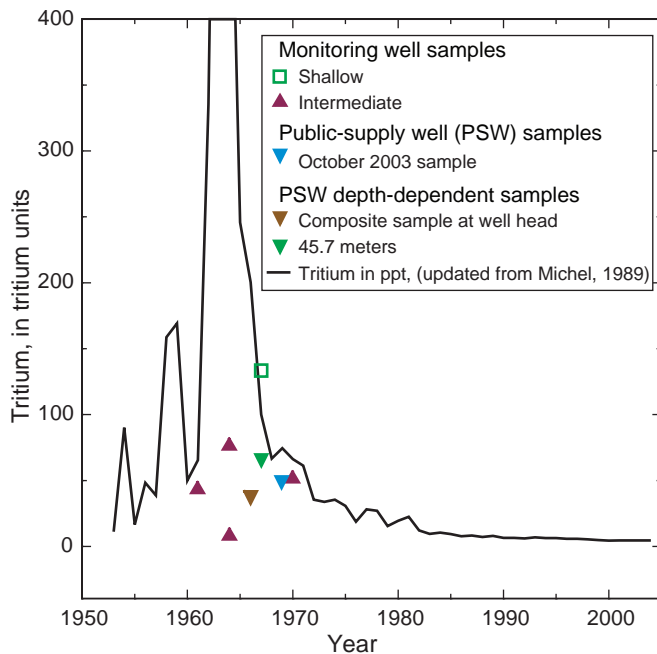
In the absence of terrigenous sources,  $\text{SF}_6$  concentrations in ground water result from the solubility of  $\text{SF}_6$  in water at the time of recharge and from the entrainment of excess air. Uncertainty in  $\text{SF}_6$  concentrations in ground-water results from estimations of solubility conditions at the time of recharge, such as recharge temperature, elevation, salinity, and the amount of excess air in ground water. However, an uncertainty of  $\pm 1$  to  $2^\circ\text{C}$  in the recharge temperature or  $\pm 100$  m in the

recharge elevation usually results in errors of less than one year in the estimated age (Busenberg and Plummer, 2000). Salinity was not considered a source of error in samples from the study area, since specific conductance was less than 2,000 microsiemens per centimeter ( $\mu\text{S}/\text{cm}$ ). Higher uncertainty can result from underestimating excess air, which can cause the ground-water age to be underestimated by 1 to 2 years for waters recharged between 1973 and 1990, and by 1 to 2.5 years for waters recharged after 1990 (Busenberg and Plummer, 2000). For this study, recharge temperature and excess air were determined from dissolved argon and nitrogen concentrations in ground-water samples using an average recharge elevation of 30.5 m (100 ft) above sea level (North American Vertical Datum, 1988).

Granitic rocks can contain  $\text{SF}_6$  in amounts large enough to preclude the use of  $\text{SF}_6$  as a dating tool (Busenberg and Plummer, 2000) in certain ground-water systems. For example, ground-water samples collected from wells perforated in pre-Cambrian granitic sediments in the Middle Rio Grande Basin, New Mexico, contained  $\text{SF}_6$  concentrations in excess of modern concentrations in the atmosphere, which prevented the use of  $\text{SF}_6$  to date ground water in that study area (Busenberg and Plummer, 2000). The study area in this report contains sediments derived mainly from granitic rocks of the Sierra Nevada. Concentrations of  $\text{SF}_6$  in some ground-water samples were higher than would be indicated by tritium/helium-3 apparent ages but far below concentrations found in other granitic settings. Consequently, granitic rocks in the study area were not considered a source of  $\text{SF}_6$  in samples.

Concentrations of  $\text{SF}_6$  in eight monitoring wells ranged from 0.51 to 3.4 pptv (parts per trillion by volume); they were highest at the water table and generally decreased with depth.  $\text{SF}_6$  samples were not collected from the *deep* wells since it was expected that the water from these wells were recharged before the introduction of  $\text{SF}_6$  in the atmosphere (table 4).  $\text{SF}_6$  concentrations in *water-table* wells corresponded to an apparent age range of 7.5 to 13.5 years and a median apparent age of 10.5 years. Ground-water samples from *shallow* and *intermediate* wells had apparent ages ranging from 22 to 28 years. FPA-2 and FPC-2 had the youngest apparent age (22 years) of the four deeper samples; the apparent ages for FPB-2 and FPD-2 were 28 and 25 years, respectively. As the tritium/helium-3 age dates indicate, vertical ground-water velocities are not uniform in space and vertically connected pathways can allow contaminants to migrate locally to deeper parts of the aquifer.

$\text{SF}_6$  samples from the public-supply well indicate that some ground water reaching the well first entered the ground-water system less than 30 years before sampling. The composite public-supply well sample indicated that ground water discharging from the well has an apparent age of 25 years. The apparent ages of depth-dependent samples are less than 18 years for the shallowest sample at 45.7 m bls and 28 years for samples from *intermediate* depths of 51.8 and 57.9 m bls (table 4).



**Figure 11.** Relation between total tritium (tritium plus tritiogenic helium-3) in ground-water samples and public-supply well samples in Modesto, eastern San Joaquin Valley, California.

## Combined Tritium/Helium-3 and SF<sub>6</sub> Interpreted Ages

The interpretation of ground-water ages from tracer concentrations given above is based on an assumption of piston-flow, whereby little dispersion or mixing of water having different tracer concentrations (or ages) has taken place within the aquifer or well. This assumption allows the direct computation of time elapsed since the water was isolated from the atmosphere, as if the water has a single age. Although this assumption may be valid in certain instances, dispersion and mixing is often significant enough to affect the mean age of the ground water in wells, even in wells that are screened over short intervals (<1.5 m), such as the monitoring wells installed for this study (Weissmann and others, 2002b). This leads to deviations of the apparent tracer-derived age and the true mean age. Inconsistencies between the apparent age of a water sample interpreted using different environmental tracers can indicate that the sampled ground water represents a mixture of water with different ages. The use of multiple tracers, therefore, can help account for effects of dispersion and mixing on apparent mean ground-water age and can provide some insight into the distribution of ages in a ground-water sample.

For this TANC study, the apparent ages calculated using the tritium/helium-3 method did not agree well with those apparent ages calculated using the sulfur hexafluoride method in those samples where both tritium/helium-3 and sulfur hexafluoride were collected (table 4). The tritium/helium-3 ages for FPA-2, FPB-2, FPC-2, and FPD-2 were on average about 14 years older than the ages based on SF<sub>6</sub> concentrations. In addition, the combined tritium and tritiogenic helium-3 (<sup>3</sup>He<sub>trit</sub>) concentrations in at least two of the *intermediate* wells were lower than expected for water affected by fallout from the 1963 bomb-peak, which suggests the tritium was diluted with pre-1950 water (fig. 11). Because of these inconsistencies, several lumped parameter models, which are simple mathematical functions that describe age distributions for various combinations of recharge area and aquifer geometry (Maloszewski and Zuber, 1982; Zuber, 1986), were tested as alternatives to account for the age distributions represented by the ground-water samples.

Mean ages of ground-water samples were determined from an age distribution described by the exponential-piston flow model using software developed by Böhlke (2006). This software permits comparison of tracer concentrations with predicted concentrations for a variety of lumped parameter models. The *epm* calculation is a fractional summation of the exponential mixing and piston-flow model. As a result, the *epm* distribution varies for different fractions of exponential mixing and piston-flow. The fractions are usually expressed

as a ratio of piston-flow to exponential (xP/xE). The *epm* used to determine mean ages for monitoring wells had equal fractions of piston-flow and exponential mixing (xP/xE = 0.5/0.5 = 1). A ratio of 0.20 (xP/xE = 0.17/0.83 = 0.20) was used for public-supply well samples. Generally, these model distributions best represented the tracer concentrations in this study.

Exponential-piston flow (*epm*) mean ages for four *water-table* wells was based on tritium and SF<sub>6</sub> concentrations. Ground water from *deep* monitoring wells was excluded from this analysis because the water was more than 1,000 years old and did not contain tritium from atomic weapons testing.

Mean ages estimated by the exponential-piston flow model for *water-table* wells ranged from 6 to 15 years and were very close to the piston-flow ages calculated from SF<sub>6</sub> concentrations (table 4). The deeper (*shallow* and *intermediate*) wells had mean ages that ranged from 32 to 90 years and were either between the tritium/helium-3 and SF<sub>6</sub> apparent ages or older than both of these ages. The sample from FPD-2 had the oldest mean age of those from the monitoring wells containing young tracer concentrations. A large portion of the water in this well and in FPA-3 was from water recharged before the 1950s. Therefore, the modern-water tracer concentrations were diluted and the mean ages of the well samples were greater.

The public-supply well withdraws water from a large volume of aquifer and captures water that varies in age from less than 30 years old near the top of the well screen to more than 1,000 years old near the bottom. The concentrations of tracers of ground-water age in composite samples from 2003 and 2004 were affected by well-bore leakage and (or) the mixture of young and very old ground water within the borehole. The mean ages of the public-supply well samples was 35 years in 2003 and 55 years in 2004. These ages show that the age of ground water pumped from the public-supply well depended on the time of year, pumping history, and hydrologic conditions. The younger mean age was influenced by wellbore leakage, whereas the older mean age in 2004 more accurately reflects the influence of older ground water contributed to the well under normal operation during the summer. Identifying the amount and influence of old ground water in the public-supply well is an important factor affecting the vulnerability of the well to anthropogenic and perhaps natural contaminants. While modern tracers are appropriate for identifying the most vulnerable water entering the well, wells containing a significant amount of older water can dilute contaminants contained within the young fraction.



### Aquifer and Public-Supply Well Vulnerability

The mean ages and carbon-14 ages were used to delineate approximate ages of ground water within the aquifer (fig. 12) and identify parts of the aquifer that are vulnerable to anthropogenic contaminants. Both urban and agricultural land-use activities are potential sources of contaminants within the study area. Consequently, parts of the aquifer recharged within the last 50 years are particularly susceptible to contaminants such as nitrate and volatile organic compounds because the use of these compounds has increased since their introduction into the environment. It was expected that contaminants associated with agricultural activities would be more prevalent in ground water located in the northeast, whereas urban contaminants would be more prevalent in ground water near the public-supply well in the southwest.

The contributing recharge area of the public-supply well encompasses urban and agricultural land-use settings. The proportion of water within the public-supply well that is less than 50 years is at least 20 percent. As a result, the water

chemistry discharging from this well is expected to contain anthropogenic contaminants.

### Water Chemistry

The chemical composition of ground water in the study area reflects chemical reactions with sediment, directions and rates of ground-water flow, and natural and anthropogenic constituent sources. On the basis of chemical analyses of aquifer material and water sampled within the study area, the sections below include (1) a description of ground-water and surface-water chemistry, (2) a description of constituents of special interest, and (3) an interpretation of water chemistry data together with ground-water flow data to help indicate ground-water flow patterns and pathways. This characterization allows for improved understanding of ground-water chemistry in different parts of the aquifer system and chemical transport to the public-supply well.

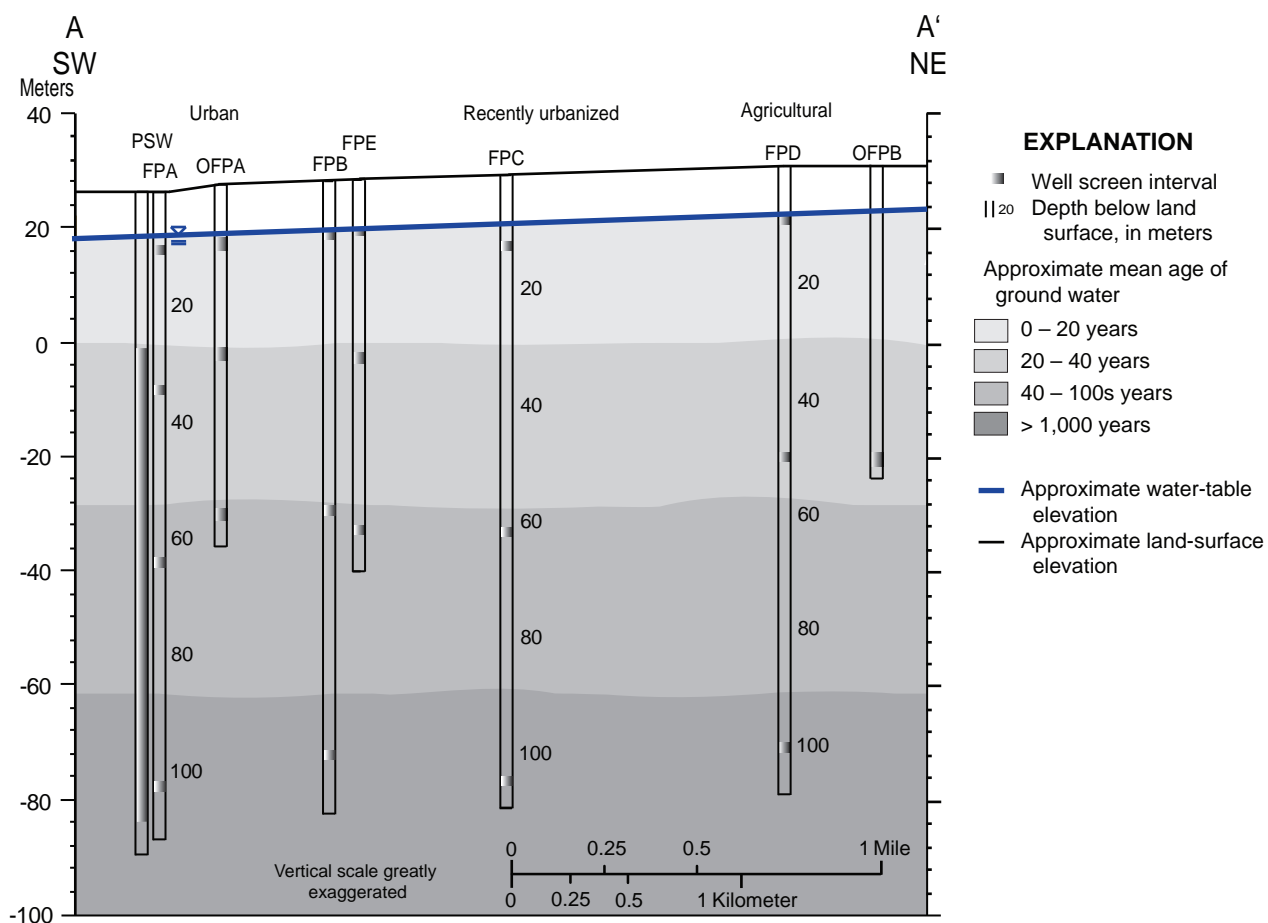


Figure 12. Estimated mean age of ground water in the local study area in Modesto, eastern San Joaquin Valley, California.

## Field Measurements

Specific conductance, alkalinity, and pH at different well depths indicate the water chemistry of the aquifer is vertically stratified (table 5). Specific conductance, which is related to the total dissolved ions in solution, was highest near the water table (median = 886  $\mu\text{S}/\text{cm}$ ) and decreased with depth to a median value of 201  $\mu\text{S}/\text{cm}$  in *deep* monitoring wells. Similarly, alkalinity (reported as calcium carbonate;  $\text{CaCO}_3$ ) exceeded 450 mg/L near the water table and decreased with depth to a minimum of 79 mg/L in *deep* monitoring wells. pH ranged from 6.8 near the water table to a maximum of 8.1 in *deep* monitoring wells and was inversely related to alkalinity (Spearman's  $\rho = -0.63$ ,  $p$ -value  $<0.001$ ) and specific conductance (Spearman's  $\rho = -0.61$ ,  $p$ -value  $<0.001$ ).

Field measurements of pH, specific conductance, and alkalinity of one deep well, FPA-4, were distinctly different from those of other deep wells (table 5). The water chemistry of this well, which is less than 30 m away from the public-supply well, was affected by inter-borehole flow within the public-supply well during a prolonged period of non-operation. During static conditions, strong downward vertical gradients allowed ground water from the *shallow* part of the aquifer to travel through the public-supply well and recharge the surrounding *deep* portion of the aquifer. Well FPA-4 likely received some this water. This effect, which was recognized after sampling was completed, influenced the chemistry of all water samples collected from FPA-4 during October 2003, and details of this process are presented later in the Well Construction and Operation Effects on Water-Quality section.

Hydraulic gradients, along with the stratified water chemistry, suggest ground water from the water table moved downward to depths of at least 35 meters (tables 1, 4). Below 50 m, specific conductance measurements of *intermediate* wells (334  $\mu\text{S}/\text{cm}$ ) suggest the vertical movement of the overlying shallow ground water may be hindered by fine-grained strata. However, some *intermediate* wells have higher specific conductance values, indicating the presence of more vertically connected pathways that allow water to migrate to deeper parts of the aquifer. The lower specific conductance values of *deep* wells likely reflects the chemistry of recharge before the area was developed. Recharge prior to development was primarily from precipitation and seepage from streams near the mountain front. These sources of recharge would likely yield low specific conductance water to the ground-water system.

Dissolved ions in ground water originate from the recharge source itself (for example, precipitation) and from the geochemical reactions that release additional ions as the water infiltrates down through the soil and unsaturated zone to the water table. The primary geochemical reactions in the soil are mineral dissolution and cation exchange. The concentration of dissolved ions in water reaching the water table can be increased by evaporation, transpiration, and application of fertilizers or soil amendments during infiltration.

Dissolved ion concentrations in ground water were strongly correlated to alkalinity measurements; Spearman's  $\rho = 0.94$ ,  $p$ -value  $<0.001$ ). Alkalinity is a measure of the capacity of water to resist changes in pH. The principal source of alkalinity in the study area is bicarbonate, which is the primary product of mineral dissolution. Mineral dissolution is enhanced by biological activity in the unsaturated zone. The partial pressure of carbon dioxide gas ( $\text{pCO}_2$  (g)) can be as much as two-orders of magnitude higher in soils than in the atmosphere because of plant root respiration and microbial respiration from the decomposition of organic matter. The acidity derived from carbon dioxide gas dissolution to form aqueous carbon dioxide,  $\text{CO}_2$  (aq), is buffered by mineral dissolution causing the release of ions and the formation of bicarbonate in solution. Neglecting processes that tend to increase or concentrate dissolved ions, mineral dissolution is the primary process affecting the ion composition of water reaching the water table.

The calculated  $\text{pCO}_2$  (g) of ground water from *water-table* and *shallow* wells averaged about  $10^{-1.6}$  atm, indicating recharge water is strongly affected by biological activity beneath both urban and agricultural land (Appendix C). Concentrations of carbon dioxide in all ground water in the study area were higher than concentrations in the atmosphere, but generally decreased with depth. As ground water moves below the water table, the fluid loses contact with atmospheric gases and with time (hundreds to thousands of years), the dissolution of primary minerals will cause the  $\text{pCO}_2$  (g) to increase and the pH to increase in ground water. The chemistry of ground water in *deep* wells likely reflects this process.

## Reduction/Oxidation Conditions

Reduction/oxidation (redox) conditions in ground water were evaluated using field measurements of dissolved oxygen and laboratory measurements of nitrate, manganese, iron, and sulfate according to the redox classification methodology described by Paschke and others (2007). All ground-water samples were consistent with an oxygen-reducing environment. Dissolved oxygen concentrations ranged from 1.8 to 6.6 mg/L; the median concentration was 4.7 mg/L (table 5).

Dissolved oxygen concentrations measured in *water-table* wells varied more than those in deeper wells. This is likely because organic carbon content varies with sediment texture, and some *water-table* wells may have been screened in more fine-grained strata. The *water-table* well FPA-1 showed some indication of reducing conditions where concentrations of manganese and iron were close to significant levels used in the redox classification. This well also had the lowest dissolved oxygen concentration (1.8 mg/L), but nitrate concentration was greater than 0.5 mg/L, indicating this well is likely a mixture of water from different redox environments.

**Table 5.** Summary of well characteristics and water chemistry field measurements of depth categories for monitoring wells sampled from October through November of 2003 and 2004, for the public-supply well sampled from October 2003 through June 2005, and for surface-water sites sampled in February and June 2005, in Modesto, eastern San Joaquin Valley, California.

[Values reported as ranges with median values in parentheses unless specified otherwise. CaCO<sub>3</sub>, calcium carbonate; mg/L, milligrams per liter; °C, degrees Celsius; µS/cm, microsiemens per centimeter; PSW, public supply well; na, not applicable]

Site type or depth category	Depth to top of screened interval (screen length) (meter)	Water-level elevation at time of sampling (meter)	Number of wells/samples	Temperature, °C	Specific conductance, µS/cm @ 25°C	Dissolved oxygen, mg/L	pH, standard units	Alkalinity, dissolved, mg/L as CaCO <sub>3</sub>
<b>Surface-water chemistry</b>								
Catch basin	surface sample	surface sample	3	12–13 (13)	54–463 (59)	4.9–10.2 (8.4)	7.0–7.6 (7.0)	17–110 (22)
<b>Ground-water chemistry</b>								
<i>Water-table</i>	8.5–11.7 (1.5)	18.9–21.8 (20.5)	9/9	19.8–23.2 (22.4)	529–1060 (886)	1.8–6.6 (4.8)	6.8–7.4 (7.1)	208–477 (418)
<i>Shallow</i>	29.0–35.1 (1.5)	18.8–19.8 (19.2)	3/3	20.3–21.0 (20.8)	704–1080 (784)	3.6–5.0 (3.9)	7.1–7.4 (7.4)	285–384 (298)
<i>Intermediate</i>	50.6–65.5 (1.5)	16.1–19.8 (17.5)	7/7	20.6–22.4 (21.6)	288–492 (334)	3.4–5.4 (5.0)	7.4–7.8 (7.6)	110–187 (133)
<i>Deep</i>	100.0–105.8 (1.5)	16.6–17.6 (17.1)	4/4	22.7–23.0 (23.0)	175–329 (201)	2.2–3.0 (2.7)	7.4–8.1 (8.1)	79–139 (84)
PSW	27.7 (91.4)	na	1/4	19.4–21.2 (20.2)	414–667 (500)	4.4–5.1 (4.6)	7.1–7.5 (7.4)	171–288 (204)

In general, *deep* ground water was consistently lower in dissolved oxygen than ground water from *shallow* and *intermediate* depths. Although the aquifer is primarily oxic, reducing microenvironments within aquifer material may cause localized declines in oxygen concentrations over long time scales.

## Stable Isotopes of Hydrogen and Oxygen

Stable isotopes of hydrogen and oxygen were used to characterize the isotopic composition of local ground water, to identify sources and mixtures of water, and to characterize fractionation processes that affect ground-water chemistry. The isotopic composition of ground water is usually similar to the mean isotopic composition of recharge water from precipitation, streamflow, or other sources that infiltrate into the ground and the unsaturated zone to reach the water table (Kendall and McDonnell, 1998). Precipitation is formed from water vapor from the atmosphere that condenses as a result of adiabatic cooling (cooling due to decreased pressure) of the air mass. Precipitation that condenses at colder temperatures, such as snow in the Sierra Nevada, is enriched in the lighter isotopes compared with precipitation in the Valley, which condenses at warmer temperatures. The Global Meteoric Water Line (GMWL), which defines the relation between  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$  in worldwide fresh surface waters (as determined by Rozanski and others, 1993), was used as a reference line to compare with local ground-water and surface-water trends (fig. 13).

Ground water from FPD-1 and surface water from the Stanislaus and Tuolumne Rivers and the canal near FPD-1 had the lightest isotopic composition of water in the study area (fig. 13). The isotope values reflected values for precipitation and runoff from the Sierra Nevada, which is collected behind dams and distributed through a network of canals for use as irrigation water during the summer growing season. The isotopic composition of ground water from FPD-1 was similar to the canal and other surface-water compositions (fig. 13), indicating water from this well originated from canal leakage or surface water used for irrigation.

Most of the ground water sites in the study area had heavier isotopic compositions than the surface-water sites (fig. 13). However, three samples (from FPA-2, FPC-2, FPE-2) had isotope values between those of the surface water and most ground water, indicating a mixture of native ground water with surface water. Ground water from OFPA-2 and FPB-2 could also have been affected by irrigation with local surface water, although to a lesser extent.

The isotopic composition of ground water from *deep* wells, except from FPA-4, generally varied less than that of ground water from shallower depths. Isotope values for FPA-4 were lighter than those for the other deep wells because some ground water from the *shallow* zone, which was isotopically lighter, recharged the *deep* zone through the public-supply well during static (non-pumping) conditions.

Water used for agricultural and residential irrigation in the summer can be partially evaporated during infiltration. Evaporation of water fractionates the isotopes of hydrogen and oxygen and increases the concentration of dissolved ions in solution. Fractionation of the isotopes during evaporation is highly dependent on the relative humidity (Clark and Fritz, 1997). If the relative humidity is 100 percent, values for the isotopic composition of water during evaporation forms a line having a slope of about 8, similar to the slope of 8.17 that characterizes the GMWL. If relative humidity is less than 100 percent, evaporation forms a line having a slope less than 8, which plots to the right of the GMWL. Previous investigations in the San Joaquin Valley found slopes between 4.1 and 5.7 for evaporated ground water (Fujii and Swain, 1995).

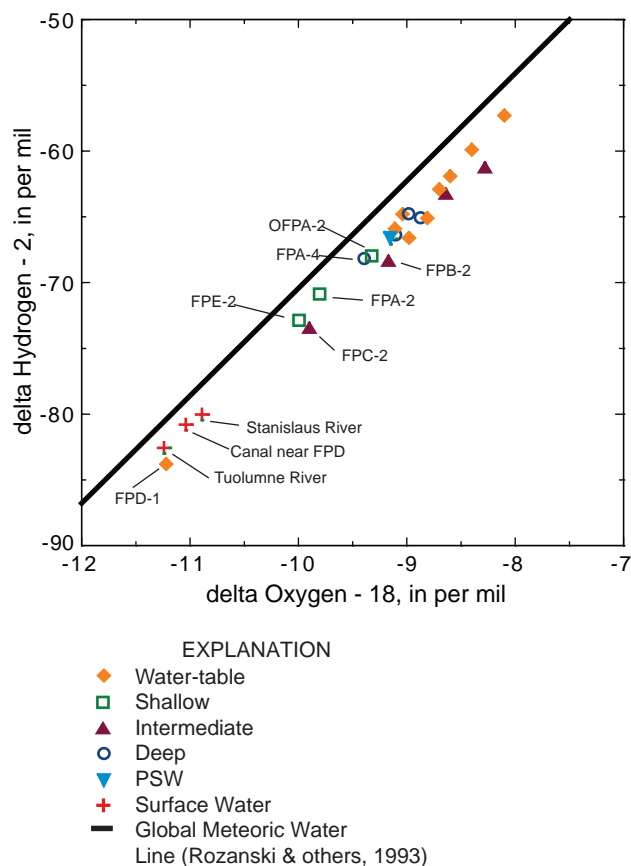
The isotopic composition of ground water in the study area indicates that evaporation did not have a major effect on ground-water quality. Consequently, higher concentrations of dissolved ions the shallow aquifer were not the result of significant evaporative concentration. However, plant transpiration can also concentrate solutes in the subsurface while leaving the residual water isotopically unchanged (Clark and Fritz, 1997). Using ground water for irrigation could also increase the concentrations of dissolved ions, but its affect on ground-water quality is difficult to quantify. Therefore high concentrations of dissolved ions in the shallow part of the ground-water system (<50 m bls) may, in part, be a result of both transpiration and application of ground water used for irrigation.

## Pesticides and Volatile Organic Compounds

Pesticides and volatile organic compounds (VOC) usually do not occur naturally, and therefore, the presence of these compounds in ground water is the direct result of human activities. Pesticide is a generic term for organic compounds that are used as fungicides, herbicides, insecticides, and rodenticides, and for the degradation products of these compounds. VOCs are in paints, solvents, gasoline-related compounds, refrigerants, fumigants, and disinfected water. VOCs were categorized by compound class in [Appendix D](#) to help identify likely sources of contamination to the aquifer.

Ten pesticide compounds were detected in 23 ground-water samples from monitoring wells ([Appendix E](#)). 2-Chloro-4-isopropylamino-6-amino-*s*-triazine (CIAT, atrazine deethylated metabolite, also known as deethylatrazine or DEA) and simazine were the most frequently detected pesticides, both occurring in 39 percent (9 of 23) of the monitoring wells. Atrazine was detected in 35 percent (8 of 23) of the ground-water samples, including all but 2 of the samples in which CIAT was detected. Atrazine and simazine have similar chemical properties and both have been used in rights-of-way and agricultural applications in the eastern San Joaquin Valley; although only simazine is currently used in agricultural applications (Burow and others, 1998). None of





**Figure 13.** Isotopic composition of ground-water and surface-water samples collected in October and November of 2003 and 2004 in Modesto, eastern San Joaquin Valley, California.

the ground-water samples had pesticide concentrations above regulatory drinking-water standards; concentrations were typically at least 100 times below regulatory standards.

Results from sampling ground-water indicated that pesticides were detected more widely and at higher concentrations in *water-table* and *shallow* wells and decreased with depth in deeper wells (table 6). All of the *water-table* wells had at least 1 detected pesticide and up to 4 detected pesticides per ground-water sample. About 66 percent of pesticides detected in all ground-water samples were detected in the *water-table* wells, indicating that land activities have directly affected the chemistry of the water recharging the aquifer. Of the 9 *water-table* wells, 2 wells (FPD-1, FPC-1) were in land-use settings that were being farmed or *recently urbanized* (within the last 10 to 20 years). The diuron degradate, 3,4-dichloroaniline, was detected in only these two wells (Appendix E). This pesticide compound is normally associated with agricultural landscapes, whereas pesticide compounds detected in wells located beneath urban landscapes could not be attributed solely to either urban or agricultural land-use settings because the detected pesticides have both agricultural and urban uses. Each of the *shallow* wells and three *intermediate* wells (FPC-2, FPD-2, OFPB-2) had at least one detected pesticide, indicating anthropogenic compounds

that entered the aquifer were transported to deeper depths below the water table. One deep well, FPA-4, had a detection of CIAT; however, the detection is the result of inter-borehole flow within the public-supply well during a prolonged period of non-operation and does not accurately reflect the chemistry of *deep* ground water.

VOCs also were most widely detected in *water-table* and *shallow* wells (table 6). None of the VOCs detected in this study were above drinking water regulatory standards. Trichloromethane (chloroform) was the most frequently detected compound and was present in all but one of the *water-table* wells. Previous USGS studies determined that chloroform, often formed as a byproduct of chlorinating drinking water, is commonly associated with urban landscapes where leaky distribution lines or residential lawn watering allow treated water to infiltrate to the ground-water system (Squillace and others, 1999; Shelton and others, 2001). The *water-table* well where chloroform was not present, FPD-1, was located beneath an agricultural field. Therefore, chloroform from urban sources was not expected in this well. Chloroform was also detected in all of the *shallow* wells, but in only 3 of the 11 deeper wells (Appendix D).

Solvents were the second most widely detected compound class in this study. Tetrachloroethene (PCE) was the most widely detected solvent and was detected in *water-table* and *shallow* wells. This compound was detected at concentrations that were within one-tenth of the drinking water regulatory limit of 5  $\mu\text{g/L}$  at two *shallow* wells (OFPA-2, FPA-2). All other VOCs detected in this study were less than one-tenth of a drinking water standard and were generally less than one-hundredth of a drinking water standard.

Gasoline-related compounds include benzene, toluene, ethylbenzene, and xylene (BTEX) compounds and fuel additives such as methyl *tert*-butyl ether (MTBE). These compounds were detected in 6 of the 9 *water-table* wells, whereas they were detected in only 3 of the 14 deeper wells. No gasoline-related compounds were detected in *deep* wells.

## Pesticides and Volatile Organic Compounds in Storm Runoff

Surface-water samples were collected for pesticides and VOCs during a storm-water runoff event to characterize the composition of precipitation-derived recharge to urban dry wells. Nine different pesticide compounds were detected in two storm-water runoff samples from dry wells near sites FPA and FPE. These compounds were consistent with compounds detected in past studies of pesticides in storm-water runoff (Kratzer, 1998). Although pesticide compounds were prevalent in runoff, only 2 of the 9 pesticide compounds, DCPA and pendimethalin, were detected in ground-water samples; the other 7 compounds may have been degraded or the runoff may have been diluted by native ground water free of these compounds after infiltration into the ground-water system.



**Table 6.** Summary of pesticides and volatile organic compounds (VOC) collected from monitoring wells sampled from October through November of 2003 and 2004 in Modesto, eastern San Joaquin Valley, California.

[% , percent]

Well type	Number of wells	Pesticides				Volatile Organic Compounds (VOC)			
		Total number of detections	Number of wells with one or more detections	Number of detected compounds	Percentage of wells with one or more detections	Total number of detections	Number of wells with one or more detections	Number of detected compounds	Percentage of wells with one or more detections
<i>Water-table</i>	9	25	9	8	100%	31	8	11	89%
<i>Shallow</i>	3	4	2	4	67%	12	3	9	100%
<i>Intermediate</i>	7	5	3	3	43%	4	3	3	43%
<i>Deep</i>	4	1	1	1	25%	3	2	3	50%

Four VOCs, mostly gasoline-related compounds, were detected in the two storm-water runoff samples. *m*- and *p*-xylene were detected in both samples and benzene, 4-isopropyltoluene, and methyl ethyl ketone were detected in the sample from the dry well near FPE. Methyl ethyl ketone is used as a solvent for lacquers, but is also a byproduct of cigarette smoke and gasoline exhaust (Delzer and others, 1996). These compounds are common in urban environments, and could have been entrained in precipitation from the atmosphere or entrained in runoff from petroleum compounds on the ground. As a result, some gasoline constituents in ground water near the water table may have originated in recharge from precipitation-derived runoff. Leaky underground fuel storage tanks likely also contribute gasoline-related compounds to ground water.

### Seasonal Variability of Volatile Organic Compound Occurrence

Concentrations and detection frequencies of VOCs in *water-table* wells varied for samples collected in the winter

(October–November samples) compared with samples in the summer (June and August samples) (table 7). The variability is likely related to sources of recharge and the presence or absence of VOCs in the atmosphere and their susceptibility to degradation. More than 90 percent of the annual precipitation falls during the winter months (November thru April). BTEX compounds were detected most widely during the winter when these compounds may be entrained in precipitation falling on urban landscapes or captured by runoff from compounds on the ground. In residential areas, runoff containing these compounds is routed to dry wells, which allow water to immediately enter the ground-water system. Because these compounds are readily degradable in aerobic environments (Zogorski and others, 2006), their concentrations and the number of detections were lower in summer ground-water samples than in winter ground-water samples. In contrast, the number of detections of compounds such as chloroform and PCE, which are more persistent and not normally detected in runoff, was lower for the winter ground-water samples, as a result of dilution by storm runoff than for summer ground-water samples.

**Table 7.** Comparison of selected volatile organic compounds (VOC) in ground water collected from water-table wells during winter and summer seasons from winter 2003 through summer 2005 in Modesto, eastern San Joaquin Valley, California.

[BTEX, benzene, toluene, ethylbenzene, and xylene (gasoline-related compounds); µg/L, microgram per liter]

Seasonal sample set	BTEX Compounds		Trichloromethane (Chloroform),		Tetrachloro-ethene (PCE)	
	Detection frequency (percent)	Number of detected BTEX compounds	Detection frequency (percent)	Median concentration (µg/L)	Detection frequency (percent)	Median concentration (µg/L)
Winter	46.2	5	84.6	0.12	38.5	0.15
Summer	27.8	3	88.9	0.25	61.1	0.04

## Nitrate and Sulfate

Dissolved nitrate was detected in all 23 ground-water samples and ranged from 1.0 to 17.4 mg/L as nitrogen (as N); the median concentration was 4.0 mg/L (table 8). Nitrate was analyzed as nitrite plus nitrate, but only two samples had detectable levels of nitrite and both concentrations were below the reporting level (0.008 mg/L). Consequently, nitrite plus nitrate is referred to as “nitrate” expressed as elemental nitrogen throughout the report. Six monitoring wells had nitrate concentrations that were above the USEPA maximum contaminant level (MCL) of 10 mg/L (U.S. Environmental Protection Agency, 2003). Although adults are usually not affected by nitrate toxicity, infants and children may develop methemoglobinemia from consuming high concentrations of nitrate (Comly, 1945). Monitoring wells are not used for drinking water and, therefore, are not required to meet drinking water standards. None of the four samples from the public-supply well had concentrations above the MCL. The median nitrate concentration in four samples collected from the public-supply well was 5.5 mg/L. Nitrate ranged from 4.4 to 7.2 mg/L.

Nitrate concentrations exceeded 3.0 mg/L in 35 percent (8 of 23) of the ground-water samples. Concentrations of nitrate less than 3 mg/L in oxic ground water could reflect natural background concentrations (Mueller and Helsel, 1996).

Dissolved nitrate concentrations may be decreased by reducing nitrate to nitrogen gas and, to lesser extent, ammonia. Ammonia was detected below the laboratory reporting limit in two wells (FPA-1, OFPA-2), and excess nitrogen gas was not significant enough to indicate denitrification in most wells. Analysis of redox-sensitive species indicated the aquifer is primarily oxic, although anoxic conditions may occur in microenvironments. As a result, nitrate is expected to persist in ground water in the study area.

In *water-table* wells, nitrate concentrations ranged from 1.5 to 17.4 mg/L (table 8), and the land use above these wells suggests multiple sources of nitrate. Seven out of nine *water-table* wells are located beneath urban land and most had low concentrations of nitrate; the median concentration for these wells was 3.1 mg/L. However, two of these wells, SB and SC, are located in or near unsewered subdivisions. Nitrate concentrations for these two wells were 6.5 and 11.1 mg/L, respectively. The two highest concentrations of nitrate, 17.4 and 12.6 mg/L, were in samples from *water-table* wells located beneath land that was being (FPD-1) or was previously (within the last 10–20 years) being farmed (FPC-1) (table 8).

In samples collected from *shallow*, *intermediate*, and *deep* monitoring wells, nitrate concentrations ranged from 1.0 to 12.9 mg/L and generally decreased with increasing depth. Nitrate concentrations in all three *shallow* monitoring wells were above the MCL of 10 mg/L, ranging from 11.8 to 12.9 mg/L. Nitrate concentrations in *intermediate* wells ranged

from 1.6 to 8.7 mg/L. The variability of nitrate in these wells indicate that some parts of the aquifer are more vertically connected to overlying *shallow* ground water than others. The *deep* wells had the lowest nitrate concentrations, ranging from 1.0 to 2.4 mg/L, which likely reflects natural background concentrations.

Nitrate concentrations were positively correlated to specific conductance (Spearman’s rho = 0.63,  $p = 0.003$ ), which is consistent with past studies of agricultural landscapes throughout the eastern San Joaquin Valley (Nightingale, 1972; Burow and others, 1998; Burow and others, 1999). Nitrate occurs naturally at typically low concentrations (<3 milligrams per liter as N) in ground water; however, in agricultural areas, application of nitrogen fertilizers to increase crop yield has elevated concentrations of nitrate in shallow ground water in the eastern San Joaquin Valley (Nightingale, 1972; Owens and others, 1992; Burow and others, 1998). Dissolution of fertilizers in surface water or ground water used for irrigation, and transpiration during plant growth will increase the concentration of dissolved ions in solution. The correlation between nitrate and specific conductance in this study likely reflects this process.

All of the major ions, except sodium and potassium, were significantly correlated with nitrate concentrations. Nitrate is most strongly correlated with sulfate concentrations (Spearman’s rho = 0.78,  $p \leq 0.001$ ), which is consistent with adding gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ) soil amendments and fertilizer during farm operations (fig. 14A). Because the build-up of salts and the compaction of soils decrease permeability, gypsum is often added to soils to improve infiltration of irrigation water. The highest concentrations of sulfate were from *water-table* wells beneath land that was being (FPD-1) or was previously (within the last 10–20 years) being farmed (FPC-1) and from *shallow* wells, similar to nitrate concentrations. This suggests that the main anthropogenic sources of nitrate and sulfate concentrations in the aquifer were fertilizers and soil amendments.

## Stable Isotopes of Nitrate and Sulfate

The source of nitrate and, to lesser extent, the source of sulfate was further evaluated using stable isotopes of nitrogen and oxygen in dissolved nitrate and sulfur in dissolved sulfate. The isotopic composition of dissolved nitrate can also be an indicator of denitrification in ground water. Isotopic composition typically is expressed as a ratio of the less abundant isotope (usually the heavier isotope) to the widely abundant isotope (usually the lighter isotope), in parts per thousand (per mil); this ratio is expressed using standard delta notation indicated by the delta ( $\delta$ ) symbol followed by the formula for the less abundant isotope.

**Table 8.** Selected inorganic constituents and isotopes in ground water from monitoring wells sampled from October through November of 2003 and 2004 in Modesto, eastern San Joaquin Valley, California.

[The five-digit parameter code is used in the U.S. Geological Survey National Water Information System (NWIS) to uniquely identify a specific constituent or property. LRL, laboratory reporting level; mg/L, milligram per liter; µg/L, microgram per liter; pCi/L, picocurie per liter; per mil, per thousand; E, estimated; —, not detected; nc, not collected. N, nitrogen, P, phosphorous; As, arsenic; CaCO<sub>3</sub>, calcium carbonate]

Well identi- cation no.	Depth category/ well type	Sample date	Nitrite plus nitrate, dissolved (mg/L as N)	Sulfate, dissolved (mg/L)	Arsenic, dissolved (µg/L)	Arsenate (HAsO <sub>4</sub> <sup>-2</sup> ), dissolved (µg/L as As)	Ortho- phosphate, dissolved (mg/L as P)	Alkalinity, dissolved, as CaCO <sub>3</sub> (mg/L)	Uranium (natural), dissolved (µg/L)	Uranium-234 (pCi/L)	Uranium-238 (pCi/L)
Parameter code			00631	00945	01000	62453	00671	29802	22703	22610	22603
LRL			0.06	0.18	0.2	1.2	0.006	0.04	0.04	0.1	0.1
FPA-1	Water-table	10/29/2003	1.49	16.9	15.9	14.2	—	363	24.5	10.9	12.3
FPB-1	Water-table	11/19/2003	3.15	15.4	6.4	7.5	0.755	318	11.1	3.9	4.7
FPC-1	Water-table	10/20/2003	12.6	36.2	3.5	3.0	0.300	2444	23.1	4.8	5.8
FPD-1	Water-table	10/21/2003	17.4	75.5	3.9	3.3	0.590	248	23.4	8.2	8.9
FPE-1	Water-table	10/27/2004	1.77	9.81	9.3	8.8	2.31	208	4.76	1.4	1.7
OFPA-1	Water-table	11/03/2004	3.10	40.0	11.9	12.4	1.47	427	24.9	7.5	8.7
SA	Water-table	10/25/2004	2.40	49.3	2.3		0.040	477	29.9	9.1	10.0
SB	Water-table	10/25/2004	6.46	38.7	3.9		0.033	427	32.2	9.4	11.0
SC	Water-table	10/26/2004	11.1	47.8	6.8		0.044	418	28.5	8.7	10.6
FPA-2	Shallow	11/04/2003	11.8	35.9	10.4	10.4	0.930	285	21.5	7.3	10.9
FPE-2	Shallow	10/27/2004	12.9	63.7	9.1	8.3	0.383	298	21.5	6.0	8.8
OFPA-2	Shallow	11/03/2004	12.5	56.4	8.8	9.8	1.60	384	45.3	13.1	18.1
FPA-3	Intermediate	11/05/2003	3.02	14.4	6.6	6.7	0.737	110	2.56	nc	nc
FPB-2	Intermediate	11/18/2003	3.96	23.4	7.6	7.8	1.33	144	6.57	nc	nc
FPC-2	Intermediate	11/12/2003	8.72	24.9	5.9	5.9	0.75	187	9.99	nc	nc
FPD-2	Intermediate	11/13/2003	3.98	16.4	9.7	9.7	0.507	126	3.37	nc	nc
FPE-3	Intermediate	10/27/2004	5.58	22.5	4.9	4.5	0.281	133	4.33	nc	nc
OFPA-3	Intermediate	11/03/2004	4.42	9.61	5.2	5.5	0.271	129	3.74	nc	nc
OFPB-2	Intermediate	11/02/2004	1.62	6.89	6.7	6.4	2.75	146	4.51	nc	nc
FPA-4	Deep	11/06/2003	2.39	11.1	6.5	6.4	1.31	139	1.52	0.1	0.3
FPB-3	Deep	11/18/2003	1.02	2.73	5.8	6.2	0.592	80.4	0.32	nc	nc
FPC-3	Deep	11/12/2003	1.45	E0.17	5.5	5.5	0.120	79	0.24	nc	nc
FPD-3	Deep	11/17/2003	1.78	5.69	4.4	4.6	0.197	88	0.59	0.1	0.3
MOD025	PSW	11/13/2003	7.23	28.3	6.2	6.0	0.022	288	23.9	nc	nc

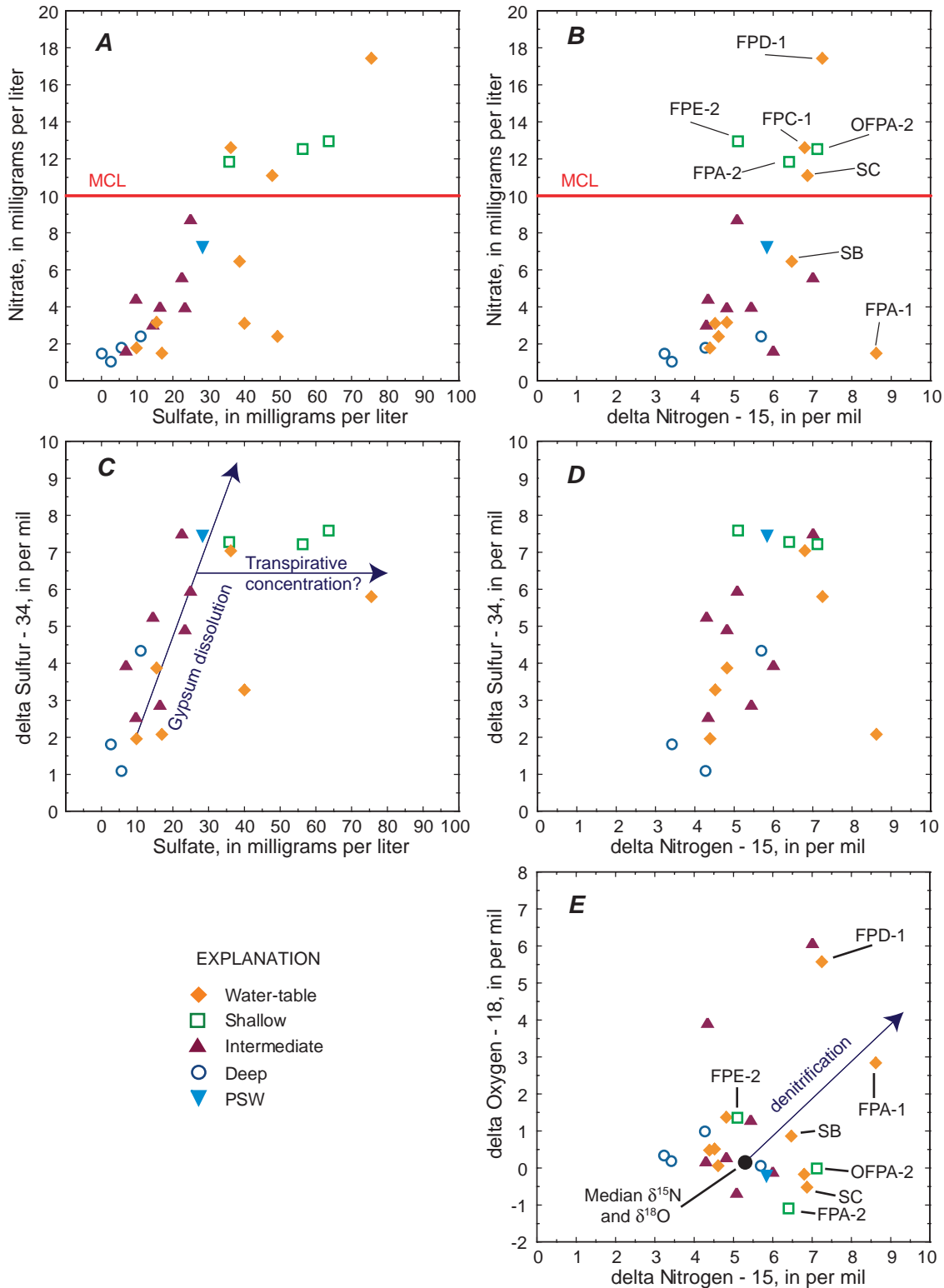
**Table 8.** Selected inorganic constituents and isotopes in ground water from monitoring wells sampled from October through November of 2003 and 2004 in Modesto, eastern San Joaquin Valley, California. —Continued

[The five-digit parameter code is used in the U.S. Geological Survey National Water Information System (NWIS) to uniquely identify a specific constituent or property. LRL, laboratory reporting level; mg/L, milligram per liter; µg/L, microgram per liter; pCi/L, picocurie per liter; per mil, per thousand; E, estimated; —, not detected; nc, not collected. N, nitrogen; P, phosphorus; As, arsenic; CaCO<sub>3</sub>, calcium carbonate]

Well identification no.	Depth category/ well type	Sample date	Uranium-234 to uranium-238 (ratio)	Deuterium/ <sup>2</sup> H protium ratio, unfiltered, per mil	Nitrogen-15/ <sup>15</sup> N Nitrogen-14 ratio in nitrate fraction, water, filtered, per mil	Oxygen-18/ <sup>18</sup> O Oxygen-16 ratio in nitrate fraction, water, filtered, per mil	Oxygen-18/ <sup>18</sup> O Oxygen-16 ratio, water, unfiltered, per mil	Sulfur-34/ <sup>34</sup> S Sulfur-32 ratio in sulfate, water, filtered, per mil
Parameter code			82082	82690	63041	82085	49932	
LRL								
FPA-1	Water-table	10/29/2003	1.13	-64.8	8.6	2.8	-9.0	2.1
FPB-1	Water-table	11/19/2003	1.19	-62.9	4.8	1.4	-8.7	3.9
FPC-1	Water-table	10/20/2003	1.19	-65.9	6.8	-0.2	-9.1	7.0
FPD-1	Water-table	10/21/2003	1.09	-83.8	7.3	5.6	-11.2	5.8
FPE-1	Water-table	10/27/2004	1.22	-57.3	4.4	0.5	-8.1	2.0
OFPA-1	Water-table	11/03/2004	1.16	-61.9	4.5	0.5	-8.6	3.3
SA	Water-table	10/25/2004	1.10	-66.6	4.6	0.1	-9.0	nc
SB	Water-table	10/25/2004	1.17	-59.9	6.5	0.9	-8.4	nc
SC	Water-table	10/26/2004	1.22	-65.1	6.9	-0.5	-8.8	nc
FPA-2	Shallow	11/4/2003	1.49	-70.9	6.4	-1.1	-9.8	7.3
FPE-2	Shallow	10/27/2004	1.46	-72.9	5.1	1.4	-10.0	7.6
OFPA-2	Shallow	11/03/2004	1.38	-68.0	7.1	0.0	-9.3	7.2
FPA-3	Intermediate	11/05/2003	nc	-63.3	4.3	0.2	-8.6	5.3
FPB-2	Intermediate	11/18/2003	nc	-68.4	4.8	0.3	-9.2	4.9
FPC-2	Intermediate	11/12/2003	nc	-73.5	5.1	-0.7	-9.9	6.0
FPD-2	Intermediate	11/13/2003	nc	-61.3	5.4	1.3	-8.3	2.9
FPE-3	Intermediate	10/27/2004	nc	nc	7.0	6.1	nc	7.5
OFPA-3	Intermediate	11/03/2004	nc	nc	4.3	3.9	nc	2.5
OFPB-2	Intermediate	11/02/2004	nc	nc	6.0	-0.1	nc	3.9
FPA-4	Deep	11/06/2003	1.98	-68.2	5.7	0.1	-9.4	4.3
FPB-3	Deep	11/18/2003	nc	-66.4	3.4	0.2	-9.1	1.8
FPC-3	Deep	11/12/2003	nc	-65.1	3.2	0.3	-8.9	nc
FPD-3	Deep	11/17/2003	2.11	-64.8	4.3	1.0	-9.0	1.1
MOD025	PSW	11/13/2003	nc	-66.7	5.8	-0.2	-9.2	7.45

<sup>1</sup>Value from sample collected on 8/15/2006.

<sup>2</sup>Laboratory value.



**Figure 14.** Relations among sulfate, nitrate, and isotopes of nitrogen and oxygen in dissolved nitrate in ground water collected from monitoring wells in October and November of 2003 and 2004. (A) Relation between sulfate and nitrate. (B) Relation between delta nitrogen-15 ( $\delta^{15}\text{N}$ ) and nitrate. (C) Relation between sulfate and delta sulfur-34 ( $\delta^{34}\text{S}$ ). (D) Relation between  $\delta^{15}\text{N}$  and  $\delta^{34}\text{S}$ . (E) Relation between  $\delta^{15}\text{N}$  and delta oxygen-18 ( $\delta^{18}\text{O}$ ). MCL, U.S. Environmental Protection Agency maximum contaminant level; PSW, public-supply well.

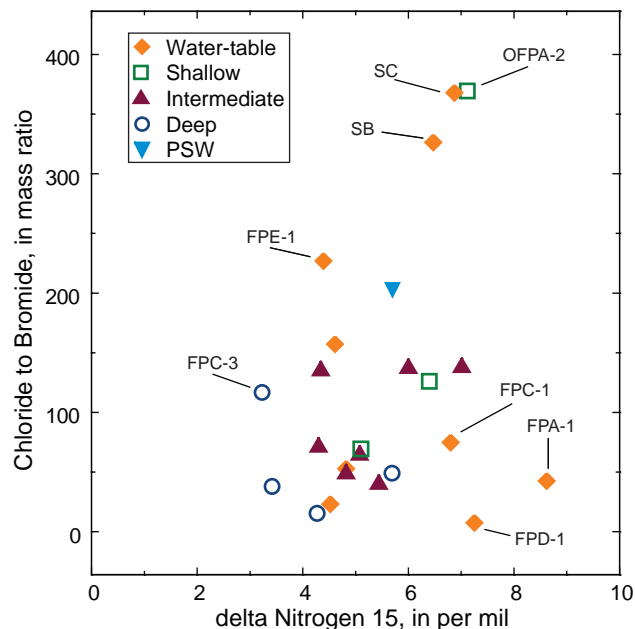


$\delta^{15}\text{N}$  values for dissolved nitrate in ground water ranged from 3.2 to 8.6 per mil and  $\delta^{18}\text{O}$  values for dissolved nitrate ranged from  $-1.1$  to  $6.1$  per mil (table 8). Nitrate from FPA-1 had the heaviest  $\delta^{15}\text{N}$  value,  $8.6$  per mil and had a  $\delta^{18}\text{O}$  value of  $2.8$  per mil (fig. 14E). The isotopic composition of nitrate for this sample was consistent with denitrification of nitrate having an initial composition similar to the median isotopic composition of ground water ( $\delta^{15}\text{N} = 5.1$  per mil,  $\delta^{18}\text{O} = 0.3$  per mil) in the study area (Kendall, 1998). Measurements of redox-sensitive species from this water, such as manganese and iron, suggest this water was partially reduced or was a mixture of water having different redox conditions. Denitrification causes enrichment in nitrogen-15 as well as oxygen-18 in the residual nitrate because less energy is required to break molecular bonds between lighter isotopes (nitrogen-14, oxygen-16) during microbial reduction. As denitrification proceeds, the plotted isotopic composition of the residual nitrate forms a line having a slope of about 0.5 (Kendall, 1998) (fig. 14E). Although denitrification removed some nitrate in ground water from this well (FPA-1), as a whole, nitrate concentrations in ground water in the study area were not significantly affected by denitrification.

The isotopic composition of nitrate in ground water is consistent with multiple sources of nitrogen that include inorganic fertilizers, soil nitrogen, and septic waste (Kendall, 1998). Fogg and others (1998) reported  $\delta^{15}\text{N}$  values derived from inorganic fertilizers that were less than 7 per mil nationwide and typically less than 5 per mil in California. Fogg and others (1998) reported also that  $\delta^{15}\text{N}$  values for septic sources of nitrate are typically greater than 7 per mil nationwide; however,  $\delta^{15}\text{N}$  values below 7 per mil for septic sources are not uncommon.

$\delta^{15}\text{N}$  values generally increased with nitrate concentrations (fig. 14B). High concentrations of nitrate in ground water in the eastern San Joaquin Valley are usually the result of agricultural applications of nitrogen fertilizers, although dairy farms and septic leachate contribute nitrate to ground water in localized parts of the Valley. The absence of dairy farms in the study area suggests nitrate concentrations in local ground water are not influenced by dairy farms. Some older parts of the city remain unsewered, and therefore, septic leachate could be a source of nitrate in the local ground water.

Anion ratios of chloride to bromide (Cl/Br) were used to evaluate the influence of septic sources on nitrate in ground water. Panno and others (2006) report Cl/Br for septic sources within a range of 65 to 5,404 and a median value of 769. As a whole, within the study area, the ratios of chloride to bromide for ground water were low (generally less than 250). However, three wells—SC, SB, and OFPA-2—yielded Cl/Br ratios above 300 and  $\delta^{15}\text{N}$  values greater than 6 per mil (fig. 15). Jagucki and Darner (2001) considered a Cl to Br ratio of 400 to be the theoretical upper limit for natural water, but ratios between 110 and 400 could indicate anthropogenic sources. Because wells that yielded Cl to Br ratios between 110 and 250 included wells that had low nitrate concentrations (FPE-1, SA, FPC-3) and deep ground water that was recharged before



**Figure 15.** Relation of delta nitrogen-15 in dissolved nitrate and chloride to bromide ratios (Cl/Br) in ground-water samples collected from monitoring wells in October and November of 2003 and 2004 in Modesto, eastern San Joaquin Valley, California. PSW, public-supply well.

the area was developed, a more conservative range is 250 to 400 for wells that may be influenced by septic sources in the study area. However, the anion ratios derived for our study area were significantly lower than the median value reported by Panno and others (2006). This indicates that septic leachate may be in some ground water, but probably is not the most significant source of nitrate in ground water in the study area.

High nitrate concentrations (greater than 10 mg/L) in ground water beneath land that was being farmed (FPD-1) or was previously (within the last 10–20 years) being farmed (FPC-1) yielded two of the highest  $\delta^{15}\text{N}$  values (7.25 and 6.8, respectively); the two wells in these areas had oxic water and yielded low Cl/Br ratios (fig. 15). This suggests that fertilizer applied during farm operations was enriched in nitrogen-15; however,  $\delta^{15}\text{N}$  values for other wells containing nitrate concentrations greater than 10 mg/L varied between about 5 and 7 per mil. The lowest nitrate concentrations (less than 3 mg/L) and lightest  $\delta^{15}\text{N}$  values (less than 5 per mil) were from deep wells and are consistent with natural nitrogen sources in soil reported by Fogg and others (1998). This indicates that the source of nitrate for concentrations between 3 and 10 mg/L is likely a mixture of natural and fertilizer sources of nitrogen.

$\delta^{34}\text{S}$  values for naturally-occurring sulfur compounds throughout the environment range from less than  $-50$  per mil to greater than  $50$  per mil (Krouse and Mayer, 2000). The wide range in  $\delta^{34}\text{S}$  is due to the wide range in valence states ( $-2$  to  $+6$ ) and its many functional groups (Krouse and Mayer, 2000). The isotopic composition of sulfur in marine evaporite deposits reflects the isotopic composition of seawater at the time of deposition. The isotopic composition of sulfate

in seawater has varied between 10 per mil and 35 per mil through geologic time (Krouse and Mayer, 2000). The isotopic composition of sulfate in modern seawater is 21 per mil (Clark and Fritz, 1997).

Values of  $\delta^{34}\text{S}$  for dissolved sulfate in ground water in the study area ranged from about 1 per mil for *deep* ground water to almost 8 per mil for many wells that had sulfate concentrations greater than 20 mg/L (fig. 14C, table 8). The lower  $\delta^{34}\text{S}$  values (less than about 2.0 per mil) for low sulfate samples were interpreted as indicating natural sources of sulfate, such as the atmosphere. Low sulfate concentrations and low  $\delta^{34}\text{S}$  values could result from sulfate reduction also, although no hydrogen sulfide was detected in the ground water. The highest  $\delta^{34}\text{S}$  values are most likely from application of gypsum soil amendments, which is enriched in  $^{34}\text{S}$ . Ground water in some wells had higher sulfate concentrations than could be explained by the application of gypsum. Sulfate concentrations from these wells could have been affected by transpiration and recycling of ground water.

The isotopic composition of nitrate is positively correlated to the isotopic composition of sulfate in oxic ground water (Spearman's  $\rho = 0.72$ ,  $p$ -value = 0.003; note: FPA-1 was removed because of theorized denitrification; fig. 14D). This correlation indicates that sources of sulfate and nitrate in ground water were likely derived from agricultural practices. Some of the major forms of fertilizer in the study area are calcium-nitrate, urea, and ammonium-sulfate (Vance Kennedy, retired USGS and local farmer, oral commun. 2005). In addition, gypsum is added annually to promote infiltration (Vance Kennedy, retired USGS and local farmer, oral commun. 2005). The dissolution of these compounds during irrigation is consistent with the strong correlations among dissolved nitrate, sulfate, and the isotopic composition of nitrogen and sulfur in ground water.

## Arsenic

Arsenic, a naturally-occurring trace element, is common in drinking water, but can be hazardous to human health at high concentrations. The MCL for arsenic was lowered from 50 to 10  $\mu\text{g/L}$  as of January 23, 2006. Arsenic was detected in all ground-water samples and ranged from 2.3 to 15.9  $\mu\text{g/L}$ : the median concentration was 6.5  $\mu\text{g/L}$  (table 8). The public-supply well was sampled twice; arsenic concentrations from these samples were 6.2 and 5.8  $\mu\text{g/L}$ .

Granitic rocks of the Sierra Nevada contain minerals that have arsenic as a minor constituent (Welch and Lico, 1998), and arsenopyrite is a common mineral associated with sulfide deposits within the western metamorphic belt of the Sierra Nevada (Diggles and others, 1996). Arsenic in these minerals can be released into solution by weathering and then removed from the water because of strong attractions to mineral grain surfaces and organic material. The sediment and organic material in the eastern San Joaquin Valley was transported and deposited there by streams draining the Sierra Nevada during

a series of glacial advances and retreats in the Pleistocene and, in lesser amounts, during deposition of fluvial sediments in the Holocene. Arsenic concentrations from soils of the eastern San Joaquin Valley are generally less than 4 mg/kg (Tidball and others, 1986).

Within the study area, concentrations of  $\text{HNO}_3$  extractable iron and arsenic from aquifer sediments were weakly correlated (Appendix A; Spearman's  $\rho = 0.75$ ,  $p$ -value = 0.1,  $n = 6$ ), which suggests arsenic is adsorbed to ferric oxyhydroxides and that concentrations in ground water are predominately controlled by adsorption processes. The adsorption of arsenic is a function of the interrelationship of mineral surfaces, dissolved arsenic species, pH, and competing ions (Stollenwerk, 2003).

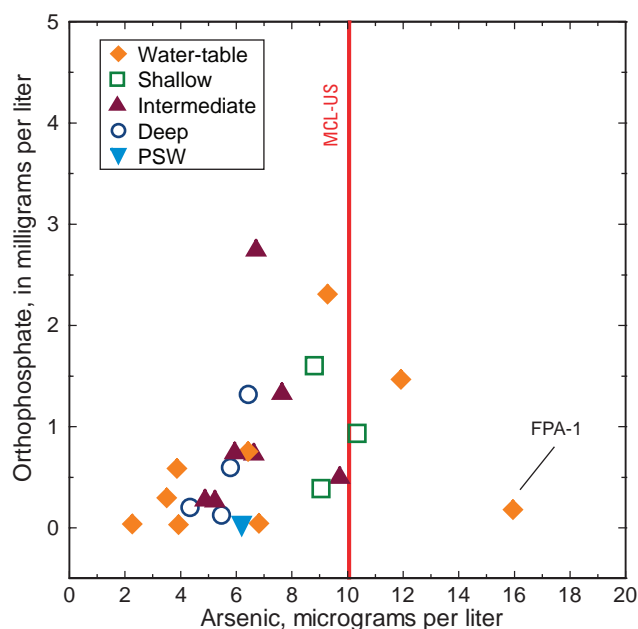
Arsenic in ground water is normally a protonated inorganic oxyanion of trivalent arsenite ( $\text{H}_3\text{AsO}_3^0$ ) or pentavalent arsenate ( $\text{HAsO}_4^{2-}$ ). Arsenate predominates in oxidizing environments, whereas arsenite predominates in reducing environments. In alkaline ground water, both arsenate and arsenite are more weakly adsorbed as pH increases because deprotonation of the mineral surface causes sorption sites to be less abundant (Stollenwerk, 2003). Previous investigations found that, in general, arsenic is more weakly adsorbed to aquifer sediments when pH values are greater than 7.5 (Manning and Goldberg, 1997; Welch and others, 2000).

Under reducing conditions, ferric oxyhydroxides can dissolve causing arsenic to be liberated from adsorption sites, leading to increased dissolved arsenic concentrations in solution. The species of arsenic liberated by this process may be either arsenate or arsenite, depending on which species was adsorbed. Because arsenate species generally predominate in the range of redox potential at which iron oxyhydroxides are stable, the primary form of adsorbed arsenic in the aquifer is expected to be arsenate (Hem, 1989; Stollenwerk, 2003). Therefore, the presence of dissolved iron and arsenate in ground water may indicate reductive dissolution. The presence of arsenite and absence of dissolved iron and sulfide may indicate reductive desorption.

Speciated arsenic samples were collected sequentially with non-speciated arsenic samples to determine the dominant form of arsenic in ground water (table 8). Arsenite was not detected above the reporting limit of 1  $\mu\text{g/L}$ . This finding suggests the redox state of ground water was above the redox potential for arsenate reduction and was consistent with an oxic environment. However, FPA-1 had the highest non-speciated arsenic concentration (15.9  $\mu\text{g/L}$ ) and the highest dissolved iron and manganese concentrations (Appendix E) of all ground-water samples. Although oxygen was present in the ground-water sample, the presence of dissolved iron and manganese was inconsistent with an oxic redox state and suggests this water was partially reduced. Because arsenic was dissolved as arsenate, reductive dissolution of iron oxyhydroxides and subsequent release of adsorbed arsenic was likely responsible for the elevated arsenic concentrations in this ground water.

Arsenic was weakly correlated to dissolved manganese (Spearman's  $\rho = 0.40$ ,  $p$ -value = 0.06) and iron concentrations (Spearman's  $\rho = 0.38$ ,  $p$ -value = 0.07) in ground water. Both metals form oxyhydroxides and are potential sorption sites for many trace elements. However, both metals are generally insoluble in oxidizing ground water and the weak correlation reflects the redox condition of the aquifer more than the source of arsenic. Therefore, dissolved arsenic in local ground water may be controlled by other processes that affect arsenic adsorption to aquifer sediments.

A previous investigation of arsenic concentrations in the San Joaquin Valley found arsenic concentrations were positively correlated with pH, indicating that higher pH inhibit dissolved arsenic from adsorbing to aquifer sediments (Belitz and others, 2003). In that study, 42 percent of wells with arsenic concentrations greater than 10  $\mu\text{g/L}$  had pH values greater than 8. In this study, arsenic and pH were not correlated (Spearman's  $\rho = -0.13$ ,  $p$ -value = 0.5), suggesting pH was not a dominant control on dissolved arsenic concentrations in the study area. However, only three wells had pH values that were greater than or equal to 8 and the highest pH value was 8.1. The number of ground-water samples having a pH higher than 8 may have been too small to indicate a correlation with arsenic concentrations.



**Figure 16.** Relation between arsenic concentrations and orthophosphate in ground-water samples collected from monitoring wells in October and November of 2003 and 2004 in Modesto, eastern San Joaquin Valley, California. MCL, U.S. Environmental Protection Agency maximum contaminant level; PSW, public-supply well.

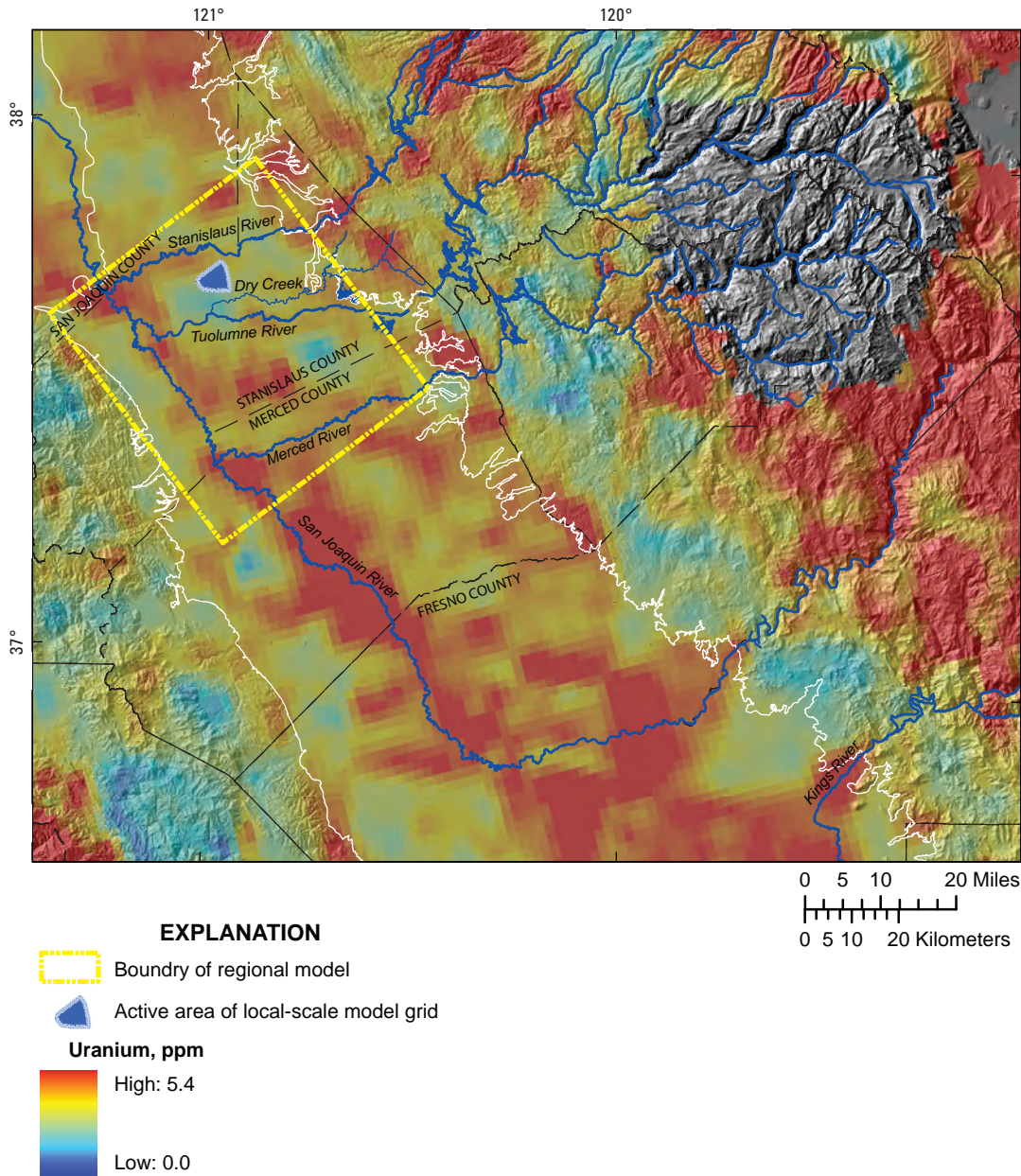
Anions may effectively compete for sorption sites with arsenic if the number of sorption sites in aquifer sediments is limited. Orthophosphate was positively correlated with arsenic concentrations, suggesting that phosphate anions may prevent the adsorption of arsenic (Spearman's  $\rho = 0.5$ ,  $p$ -value = 0.02; [fig. 16](#)). Phosphate and arsenate form similar surface species, and arsenate adsorption generally decreases with increasing phosphate concentrations for several adsorbents (Manning and Goldberg, 1996; Stollenwerk, 2003). Orthophosphate concentrations ranged from 0.03 to 2.75  $\text{mg/L}$ ; the median concentration was 0.59  $\text{mg/L}$  ([table 8](#)). Neither arsenic nor orthophosphate were related to land use or specific depth zones within the aquifer.

## Uranium

Uranium concentrations in ground-water samples ranged from 0.2 to 45.3  $\mu\text{g/L}$ ; the median concentration was 10.0  $\mu\text{g/L}$  ([table 8](#)). Samples were collected from the public-supply well twice. Concentrations of dissolved uranium from these samples were 23.9  $\mu\text{g/L}$  and 11.2  $\mu\text{g/L}$ . Two ground-water samples from monitoring wells had uranium concentrations that were above the MCL of 30  $\mu\text{g/L}$ , although these wells were not required to meet drinking water standards. Uranium is a kidney toxin (National Academy of Sciences, 1980; U.S. Environmental Protection Agency, 2003) and a radionuclide (U.S. Environmental Protection Agency, 2003).

Granitic rocks of the Sierra Nevada contain minerals that have uranium as a minor constituent, and weathering of these minerals releases uranium to water (Otton and others, 1989; Thomas and others, 1993). Dissolved uranium that adsorbed to local sediment was transported to the eastern San Joaquin Valley by glacial and fluvial processes during the Pleistocene and Holocene. Soil samples collected south of the study area were analyzed for uranium as part of the National Uranium Resource Evaluation (NURE) study (Smith, 2001) and had an average abundance of 3.1  $\text{mg/kg}$  soil. Average uranium abundance in soils in the study area were not analyzed during the NURE program; however, aerial gamma-ray surveys of uranium in the San Joaquin Valley ([fig. 17](#)) have shown similar concentrations (Phillips and others, 1993). Concentrations of extractable uranium in aquifer sediments in the study area increased with the depth of the sediments ([Appendix A](#); Spearman's  $\rho = 0.75$ ,  $p$ -value < 0.03,  $n = 10$ ). Uranium adsorption experiments showed adsorption of uranium is not limited in *intermediate* and *deep* sediments. However, uranium did not adsorb to *shallow* and *water-table* sediments in the experiments, suggesting that geochemical conditions in the shallow parts of the aquifer (<50 m bls) may favor the release of uranium from sediments.





**Figure 17.** Aerial gamma-ray survey of uranium concentrations in soils in the San Joaquin Valley (Phillips and others, 1993). ppm, parts per million.

Uranium (VI) is the most stable valence under oxidizing conditions, and in the absence of complexing ions in solution, the uranyl cation ( $\text{UO}_2^{+2}$ ) is the predominate species of uranium in alkaline ground water (Langmuir, 1978). If ground water was under these conditions, mobilization and transport of uranium (VI) would be limited by its strong adsorption to mineral surfaces (Waite and others, 1994; Kohler and others, 1996; Pabalan and others, 1998; Davis and others, 2004; Catalano and Brown, 2005). However, carbonate and phosphate form strong neutral and anionic complexes with uranyl, which can inhibit the attraction of uranyl to mineral grain surfaces and lead to higher dissolved uranium concentrations in ground water (Langmuir, 1978;

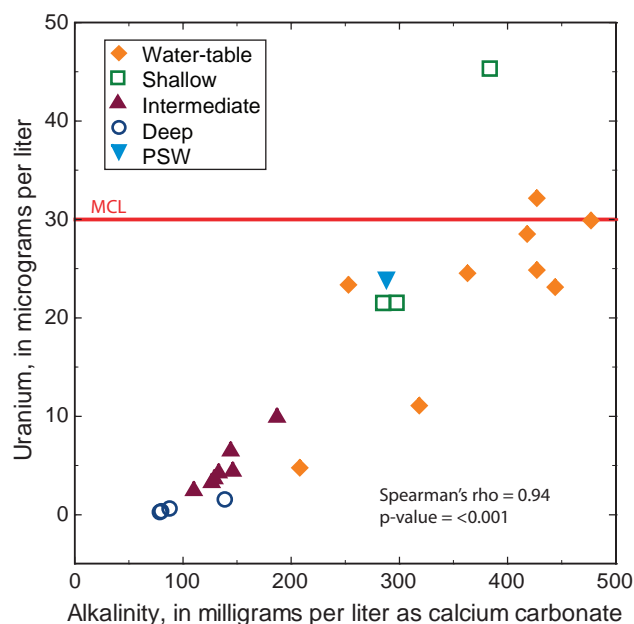
Davis and others, 2004). In addition, Bernhard and others (2001) reported the existence of two calcium-uranyl-carbonate species,  $\text{Ca}_2\text{UO}_2(\text{CO}_3)_3^0$  and  $\text{CaUO}_2(\text{CO}_3)_3^{-2}$ , and subsequent studies reported that these species may predominate in many ground-water systems (Brooks and others, 2003).

Uranium concentrations in ground water were highest in *water-table* and *shallow* wells and decreased with increasing depth below the water table (Spearman's rho = -0.84,  $p$ -value  $\leq 0.001$ ; [table 8](#)). Uranium concentrations in ground water beneath urban and agricultural land were similar, indicating that present-day land use is not a major factor controlling dissolved uranium in ground water ([tables 1, 8](#)).

The redox state of ground water within the study area is predominantly oxidic; dissolved oxygen concentrations were above 1.0 mg/L in all samples. This suggests that uranium was in hexavalent form.

Uranium concentrations were strongly correlated to alkalinity (as  $\text{CaCO}_3$ ) (Spearman's  $\rho = 0.94$ ,  $p\text{-value} \leq 0.001$ ) (fig. 18), but were not correlated with concentrations of phosphate in ground water (Spearman's  $\rho = -0.49$ ,  $p\text{-value} = 0.60$ ). The principal source of alkalinity is bicarbonate. Because there has been some question as to which uranium complexes, phosphate or carbonate, predominate in oxidic ground water (Langmuir, 1978; Grenthe and others, 1992; Sandino and Bruno, 1992), uranium was speciated using PHREEQC version 2.12.5 (Parkhurst and Appelo, 1999). Uranium speciation was calculated using inorganic data, field measurements of pH, dissolved oxygen, and alkalinity from the monitoring wells. Speciation results indicate that  $\text{Ca}_2\text{UO}_2(\text{CO}_3)_3^0$  is the dominant form of dissolved uranium in ground-water from the study area, accounting for more than 90 percent of uranium species. This indicates that carbonate complexes predominate in ground water in the study area and that phosphate complexes were minimal. Additional calculations of saturation indices for uranium minerals indicated that dissolved uranium is not likely to precipitate into solid-phases.

Uranium was strongly correlated with calcium also (Spearman's  $\rho = 0.96$ ,  $p\text{-value} < 0.001$ ; fig. 19). The



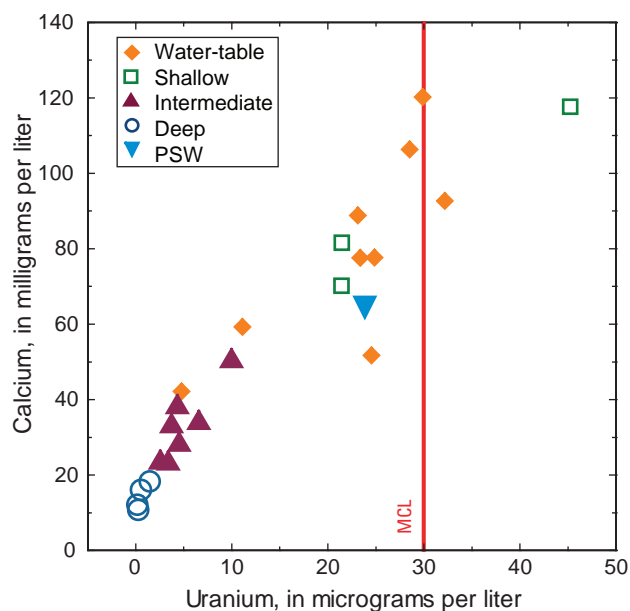
**Figure 18.** Relation between uranium concentrations and alkalinity measurements from ground-water samples collected from monitoring wells in October and November of 2003 and 2004 in Modesto, eastern San Joaquin Valley, California. MCL, U.S. Environmental Protection Agency maximum contaminant level; PSW, public-supply well.

correlations support speciation calculations that indicate uranium in ground water in the study area forms a complex that includes calcium.

Uranium, alkalinity, and calcium concentrations decrease with depth. This suggests that calcium-uranyl-carbonate complexes have caused or have been causing adsorbed uranium in *water-table* and *shallow* sediments to dissolve into ground water. In *deep* ground water, the concentrations of uranium were always less than 2  $\mu\text{g/L}$  and usually less than 1  $\mu\text{g/L}$ . Although bicarbonate and calcium are present in deep ground water, concentrations of these constituents are not high enough to dissolve uranium from the mineral surface. Consequently, geochemical conditions in deep ground water favor uranyl adsorption.

## Uranium Isotopes

Natural uranium is composed of three radioactive isotopes: uranium-234, uranium-235, and uranium-238. The concentration of each isotope is reported as an activity concentration, which is the number of disintegrations per minute per liter of water. The total activity concentration of uranium (uranium-234 plus uranium-235 plus uranium-238) has a California MCL for public water systems of 20 picocuries per liter (pCi/L).



**Figure 19.** Relation between uranium and calcium concentrations in ground-water samples collected in October and November of 2003 and 2004 in Modesto, eastern San Joaquin Valley, California.

MCL, U.S. Environmental Protection Agency maximum contaminant level; PSW, public-supply well.



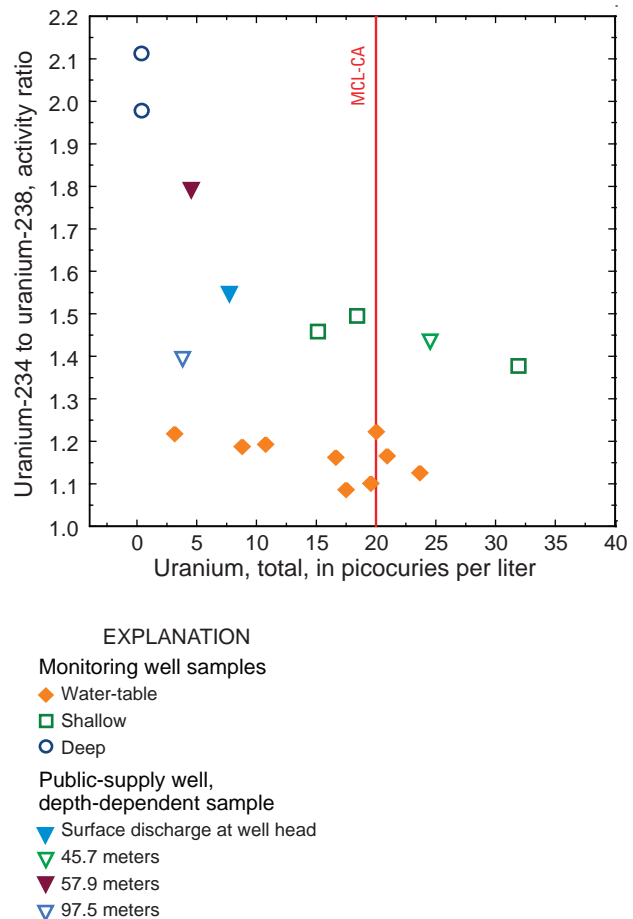
The decay of uranium-238 produces two short-lived daughters, thorium-234 and protactinium-234, which decay to the long-lived uranium-234 isotope. Given enough time, the activity ratio of uranium-234 to uranium-238 (UAR) will reach secular equilibrium (UAR = 1) provided the mineral remains undisturbed. However, as uranium-238 decays, an alpha particle is ejected and the daughter product, thorium-234, recoils in the opposite direction, damaging the crystal structure of the mineral. This can lead to the preferential loss of thorium-234. Thorium can be displaced as far as 550 angstroms from the mineral, which may be enough to be ejected completely from the mineral or to be concentrated near the mineral rind (Osmond and Cowart, 2000). As thorium decays, uranium-234 accumulates and leads to an increase of uranium-234 activity relative to uranium-238 activity (UAR >1). Auto-oxidation during thorium-234 decay and subsequent exposure of the rind to water can also lead to the complexation and removal of uranium-234 (Clark and Fritz, 1997). As a result, the uranium activity ratio can be used to infer mixing, leaching, alpha-recoil, dilution, and (or) decay along a ground-water flow path. However, because some or all of these processes may occur simultaneously, determining which of these processes is most responsible for the activity ratio for ground water is difficult. In this study, geochemical conditions in ground water which favor the mobility of uranium were most likely influenced by leaching and mixing processes, whereas geochemical conditions in ground water which favor uranium adsorption were more likely influenced by alpha-recoil.

Uranium isotopes were collected from 14 monitoring wells to help understand the mobilization and movement of high concentrations of uranium in ground water within the study area. Twelve samples were from *water-table* and *shallow* monitoring wells and two were from *deep* wells. The total activity concentration of uranium from these samples ranged from 0.4 to 32.0 pCi/L and the median was 15.9 pCi/L (table 8).

Although the *water-table* and *shallow* ground-water samples had similar uranium concentrations, the UAR for *shallow* samples were slightly higher (median = 1.46) than those for the *water-table* samples (median = 1.17 [table 8; fig. 20]). Because dissolved uranium likely maintains equilibrium with the population of adsorbed uranium in the surrounding sediment, the UAR of dissolved ground water should reflect the UAR of adsorbed uranium. This would suggest that the adsorbed uranium in the *shallow* sediments had undergone alpha-recoil to a greater extent prior to being mobilized than the sediments near the water table. The highest activity ratios were associated with *deep* ground water, which also had the lowest total activity concentration of uranium (fig. 20). Because geochemical conditions favor the adsorption or immobility of uranium in *deep* ground water, uranium-234 can accumulate in sediment as a result of alpha-recoil to a much greater extent than *water-table* and *shallow* sediments where uranium is mobile.

## Composition of Ground Water and Surface Water

The chemical composition of ground water in the Modesto study area is primarily the result of weathering of granitic sediment and of applying natural and anthropogenic chemicals associated with land-use practices. A trilinear or “Piper” diagram is a useful tool for evaluating the relative proportions of major cations and anions in ground water (fig. 21). Bicarbonate (from alkalinity measurements) was the dominant anion in ground water (fig. 21), comprising more than 60 percent in all ground water. Most ground water contained less than 30 percent sulfate plus chloride plus nitrate, but wells affected by agricultural fertilizers and soil amendments contained larger percentages of nitrate and sulfate (fig. 21, process 2). The cation composition was generally a mix of calcium, magnesium, and sodium; however, the percentage of magnesium was higher in ground water from

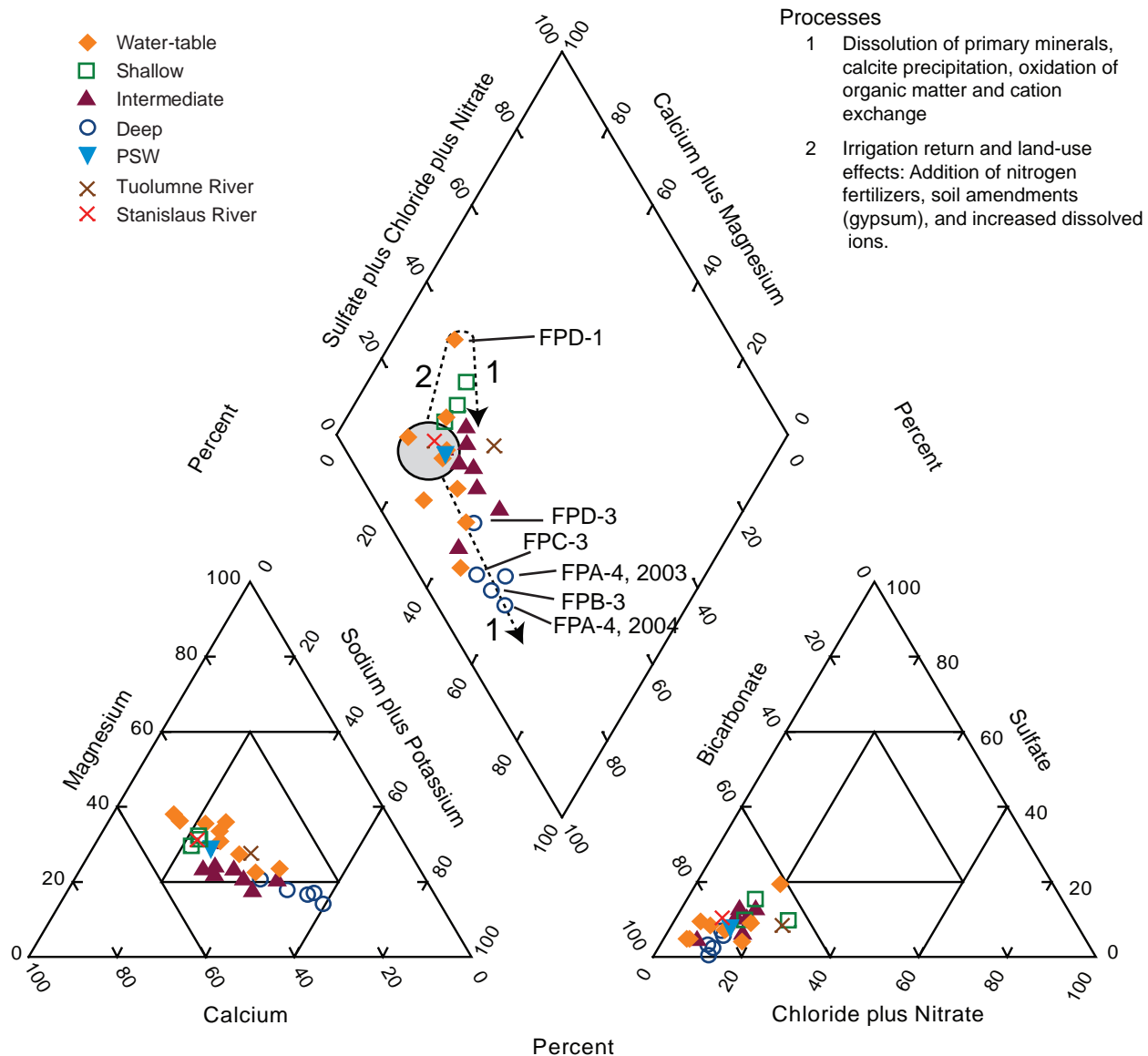


**Figure 20.** Relation between total uranium activity and the uranium activity ratio (UAR) in ground-water, depth-dependent samples from the public-supply well and ground-water samples from monitoring wells collected in August, October, and November of 2004 in Modesto, eastern San Joaquin Valley, California. MCL-CA, California maximum contaminant level.

the *water-table* and *shallow* monitoring wells than from the *intermediate* and *deep* wells (fig. 21).

The cation composition of the water in *intermediate* and *deep* wells suggest ground water evolves from a calcium-magnesium-sodium type composition to a composition dominated by sodium (fig. 21, process 1). The percentage of sodium plus potassium increases and calcium plus magnesium decreases along a north-south transect (fig. 3) in deep monitoring wells: FPD-3, FPC-3, FPB-3, and FPA-4 (collected in 2004). The major-ion chemistry and carbon-14 data for wells along this transect are consistent with cation exchange and indicate that recharge may have originated from the Stanislaus River before ground-water development.

The dissolution of primary minerals (mainly plagioclase), calcite precipitation, and cation exchange are the principal reactions affecting the major-ion chemistry as ground water moves from recharge areas to deeper parts of the aquifer. Dissolution of plagioclase can cause the pH of ground water to increase and the partial pressure of carbon dioxide to decrease. Both calcite precipitation and cation exchange will remove the cations of calcium and magnesium from solution, and calcite precipitation will also remove bicarbonate and lower the pH of ground water. Calcite was determined through calculations to be saturated mostly in *water-table* and *shallow* ground water, which suggests calcite precipitation is the dominant reaction controlling the composition of young ground water



**Figure 21.** Major ion composition of ground-water samples collected in October and November 2003 and 2004 in Modesto, eastern San Joaquin Valley, California. The Tuolumne and Stanislaus river samples are averaged compositions from previous studies. Major ion composition of recharge that occurred under natural conditions (pre-development) is represented by the shaded circle.

(<100 years) ([Appendix C](#)). Plagioclase dissolution is very slow once contact with the CO<sub>2</sub>-rich soil atmosphere is removed. Ground water is normally separated from the atmosphere as ground water moves downward below the water table. For this reason, plagioclase dissolution and cation exchange are most likely the major reactions controlling the composition of old ground water, although minor amounts of calcite precipitation is still likely to occur.

Although the cation composition of ground water from some *water-table* wells appears to follow a geochemical trend similar to that for deeper wells, this ground water is generally a mixture of surface water (Tuolumne River), precipitation recharge, and (or) *deep* ground water applied as irrigation in urban and agricultural areas. Stable isotopes of water indicate that surface water is not a major component of recharge in urban *water-table* wells. Consequently, ground water in *water-table* wells within the urban area having larger percentages of sodium likely originated not from surface water, but from *deep* ground water applied to the surface.

Two *water-table* wells and three *shallow* wells had higher percentages of calcium, sulfate, and nitrate than other wells within in the study area ([fig. 21](#), process 2). The *water-table* well, FPD-1, is located in an agricultural land-use setting where fertilizers and soil amendments are applied annually. Some of the major forms of fertilizer used in the study area are calcium-nitrate, urea, and ammonium-sulfate (Vance Kennedy, retired USGS and local farmer, oral commun. 2005). In addition, gypsum (CaSO<sub>4</sub>·2H<sub>2</sub>O) is added annually to promote infiltration (Vance Kennedy, retired USGS and local farmer, oral commun. 2005). The dissolution of these chemicals in oxic irrigation water is consistent with the higher concentrations of dissolved calcium, nitrate, and sulfate relative to other dissolved constituents in the two *water-table* wells (including FPD-1) and the three *shallow* wells. Although the three *shallow* wells are located beneath urban land, most urban *water-table* wells had less than 5 mg/L of nitrate, which suggests that at least part of the *shallow* ground water was recharged under agricultural land.

Since development of the Valley for agricultural production, the source of recharge in the study area has no longer been dominated by precipitation and recharge along streams and rivers. The composition of ground water that was recharged naturally is likely similar to the composition represented by the shaded circle on [figure 21](#). Many of the *water-table* wells in the study area appeared to have chemical compositions that were altered from natural conditions. The compositions varied as a result of applying surface water and pumped ground water to the surface and adding fertilizers and soil amendments to irrigation water. The changes in recharge and chemical compositions are an important concern because applying irrigation water to urban and agricultural landscapes

and adding fertilizers and soil amendments tend to increase the concentrations of dissolved ions in recharge water reaching the ground water.

Dissolved ion content of *water-table* wells and *shallow wells* is significantly higher than that in *deep* ground water ([table 5](#)). The dissolved ion content of *deep* ground water was likely similar to the dissolved ion content of natural recharge. Dissolved ions in *water-table* and *shallow* ground water likely increased in response to the application of irrigation water for urban and agricultural purposes during summer months and subsequent geochemical reactions in the biologically active unsaturated zone. The predominant shifts in major-ion chemistry resulting from this process have been increases in magnesium, calcium, and bicarbonate.

## Depth-Dependent Sampling

To characterize the water-quality of different parts of the aquifer that contribute water to the public-supply well, ground-water samples were collected at multiple depths within the pumping public-supply well in August 2004. For comparison of results, ground-water samples also were collected at the adjacent monitoring wells (at site FPA) at that time.

Depth-dependent samples collected from the pumping public-supply well indicate that the highest concentrations of uranium, nitrate, arsenic, and organic constituents entered the well at *shallow* depths ([table 9](#)). Even though about 80 percent of the water discharged from the well was from the *intermediate* and *deep* zones having low concentrations of uranium, nitrate and arsenic, the *shallow* ground water had a significant effect on the overall quality of water.

The chemistry of shallow ground water (DDS-45.7, depth-dependent sample from 45.7 m bls) within the public-supply well was consistent with the type, number, and concentrations of inorganic constituents and organic compounds found in the adjacent monitoring well ([table 9](#)) and the other wells screened in the shallow zone ([tables 5, 6, 8](#)). The shallow depth-dependent sample (DDS-45.7) had the highest specific conductance, alkalinity measurement, and nitrate, sulfate, arsenic, and uranium concentrations of the public-supply well depth-dependent samples ([table 9](#)). The uranium concentration (35.8 µg/L) in this sample was above the MCL, and nitrate was detected at a concentration (9.7 mg/L) near the MCL of 10 mg/L. This sample also had the highest number of detections and concentrations of VOCs (4) and pesticides (3) of the depth-dependent samples ([table 9](#)). None of the VOCs or pesticides were detected at concentrations above an MCL and most concentrations were less than one-hundredth of the MCL.

**Table 9.** Volatile organic compounds, pesticides, and selected inorganic constituents and isotopes in ground water from depth-dependent public-supply well samples and samples collected at adjacent monitoring wells during August and September 2004 in Modesto, eastern San Joaquin Valley, California.

[The five-digit parameter code is used in the U.S. Geological Survey National Water Information System (NWIS) to uniquely identify a specific constituent or property. VOC, volatile organic compound; CaCO<sub>3</sub>, calcium carbonate; N, nitrogen; E, estimated; LRL, laboratory reporting level; DDS-X, depth-dependent sample and depth below land surface. m, meter; µS/cm @ 25°C, microsiemens per centimeter at 25 degrees Celsius; µg/L, microgram per liter; mg/L, milligram per liter; —, not detected]

Well identification no.	Depth category	Sample date	Field parameters					VOCs—Disinfection byproducts and solvents				
			Sampling depth (meter)	Specific conductance, (µS/cm @ 25°C)	Alkalinity (mg/L as CaCO <sub>3</sub> )	Trichloro-methane (chloroform) (µg/L)	Bromodichloro-methane (µg/L)	Tetrachloro-ethene (µg/L)	Tetrachloro-methane (µg/L)			
<b>Parameter code</b>			<b>00003</b>	<b>00095</b>	<b>29802</b>	<b>32106</b>	<b>32101</b>	<b>34475</b>	<b>32102</b>			
<b>LRL</b>						<b>0.024</b>	<b>0.028</b>	<b>0.06</b>	<b>0.06</b>			
DDS-Composite	Composite	8/17/2004	0	414	174	0.14	—	E0.06	—	—	—	
DDS-45.7	Shallow	8/17/2004	45.7	852	378	0.54	E0.03	0.23	E0.02	E0.02	E0.02	
DDS-51.8	Intermediate	8/24/2004	51.8	292	113	E0.04	—	—	—	—	—	
DDS-57.9	Intermediate	8/25/2004	57.9	311	118	E0.04	—	—	—	—	—	
DDS-88.4	Deep	8/23/2004	88.4	270	108	E0.04	—	—	—	—	—	
DDS-97.5	Deep	8/19/2004	97.5	336	133	E0.09	—	—	—	—	—	

Well identification no.	Depth category	Sample Date	Pesticides					Inorganic constituents				
			2-Chloro-4-isopropylamino-6-amino-s-triazine (CIAT), (µg/L)	Atrazine, (µg/L)	Simazine, (µg/L)	Sulfate, dissolved (mg/L)	Arsenic, dissolved (µg/L)	Uranium (natural), dissolved (µg/L)	Nitrite plus nitrate, dissolved (mg/L as N)			
<b>Parameter code</b>			<b>04040</b>	<b>39632</b>	<b>04035</b>	<b>00945</b>	<b>01000</b>	<b>22703</b>	<b>00631</b>			
<b>LRL</b>			<b>0.006</b>	<b>0.007</b>	<b>0.005</b>	<b>0.18</b>	<b>0.2</b>	<b>0.04</b>	<b>0.06</b>			
DDS-Composite	Composite	8/17/2004	E0.007	E0.006	0.006	15.5	5.8	11.2	4.50	4.50	4.50	
DDS-45.7	Shallow	8/17/2004	E0.03	0.024	0.020	41.1	7.0	35.8	9.73	9.73	9.73	
DDS-51.8	Intermediate	8/24/2004	—	—	—	9.47	5.6	5.41	3.10	3.10	3.10	
DDS-57.9	Intermediate	8/25/2004	—	—	—	10.2	5.2	6.02	3.02	3.02	3.02	
DDS-88.4	Deep	8/23/2004	E0.003	—	E0.004	5.33	5.5	3.20	1.91	1.91	1.91	
DDS-97.5	Deep	8/19/2004	E0.005	E0.006	0.005	8.79	5.2	4.91	2.30	2.30	2.30	

**Table 9.** Volatile organic compounds, pesticides, and selected inorganic constituents and isotopes in ground water from depth-dependent public-supply well samples and samples collected at adjacent monitoring wells during August and September 2004 in Modesto, eastern San Joaquin Valley, California.—Continued

[The five-digit parameter code is used in the U.S. Geological Survey National Water Information System (NWIS) to uniquely identify a specific constituent or property. VOC, volatile organic compound; CaCO<sub>3</sub>, calcium carbonate; N, nitrogen; E, estimated; LRL, laboratory reporting level; DDS-X, depth-dependent sample and depth below land surface. m, meter; µS/cm @ 25°C, microsiemens per centimeter at 25 degrees Celsius; µg/L, microgram per liter; mg/L, milligrams per liter; —, not detected]

Well identification no.	Depth category	Sample date	Field parameters			VOCs—Disinfection byproducts and solvents				cis-1,2-Dichloroethene (µg/L)
			Specific conductance, (µS/cm @ 25°C)	Alkalinity (mg/L as CaCO <sub>3</sub> )	Trichloromethane (chloroform) (µg/L)	Bromodichloromethane (µg/L)	Tetrachloroethene, (µg/L)	Trichloroethene (µg/L)		
<b>Parameter code</b>			<b>00095</b>	<b>29802</b>	<b>32106</b>	<b>32101</b>	<b>34475</b>	<b>39180</b>	<b>77093</b>	
<b>LRL</b>					<b>0.024</b>	<b>0.028</b>	<b>0.06</b>	<b>0.38</b>	<b>0.24</b>	
FPA-1	Water-table	9/1/2004	830	434	E0.08	—	1.90	0.11	—	E0.02
FPA-2	Shallow	9/1/2004	766	333	0.13	—	0.81	—	—	—
FPA-3	Intermediate	9/1/2004	275	98	—	—	—	—	—	—
FPA-4	Deep	9/1/2004	195	82	—	—	—	—	—	—

Well identification no.	Depth category	Sample Date	Field parameters			Pesticides						Nitrite plus (mg/L as N)		
			Specific conductance, (µS/cm @ 25°C)	Alkalinity (mg/L as CaCO <sub>3</sub> )	2-Chloro-4-isopropyl-amino-6-amino-s-triazine (CIAT), (µg/L)	Atrazine, (µg/L)	Simazine, (µg/L)	Dichloroaniline, (µg/L)	3,4-Desufinyl-fipronil, (µg/L)	Prometon, (µg/L)	Sulfate dissolved (mg/L)		Arsenic, dissolved (µg/L)	Uranium (natural), dissolved (µg/L)
<b>Parameter code</b>			<b>00095</b>	<b>29802</b>	<b>04040</b>	<b>39632</b>	<b>04035</b>	<b>61625</b>	<b>62170</b>	<b>04037</b>	<b>00945</b>	<b>01000</b>	<b>22703</b>	<b>00631</b>
<b>LRL</b>					<b>0.006</b>	<b>0.007</b>	<b>0.005</b>	<b>0.0045</b>	<b>0.012</b>	<b>0.005</b>	<b>0.18</b>	<b>0.2</b>	<b>0.04</b>	<b>0.06</b>
FPA-1	Water-table	9/1/2004	830	434	E0.008	0.009	0.009	E0.003	E0.007	0.001	19.6	8.8	39.5	2.21
FPA-2	Shallow	9/1/2004	766	333P	E0.007	—	—	—	—	—	37.8	9.0	25.8	14.46
FPA-3	Intermediate	9/1/2004	275	98	E0.005	—	—	—	—	—	13.4	5.5	2.39	3.01
FPA-4	Deep	9/1/2004	195	82	—	—	—	—	—	—	2.23	5.5	0.43	0.90



Chloroform was the only VOC detected in the two *intermediate* depth-dependent public-supply well samples (DDS-51.8, DDS-57.9; [table 9](#)). Pesticides were not detected in either sample. The two samples from this zone were composite samples of water from the *deep* zone and water from the *intermediate* zone. As a result, the concentration and detection of compounds in these samples were a flow-weighted average of the concentrations of constituents contributed from *deep* depths plus *intermediate* depths. Chloroform was detected at a concentration of 0.37 µg/L and was the lowest concentration among the depth-dependent samples ([table 9](#)). Inorganic constituents in *intermediate* depth-dependent samples were generally at or below concentrations detected in the *intermediate* monitoring wells.

Two *deep* depth-dependent samples (DDS-88.4, DDS-97.5) had higher concentrations and more detections of organic compounds than *intermediate* samples ([table 9](#)). This suggests that the organic compounds in the *intermediate* zone could be the result of the introduction of water from the *deep* zone. Chloroform, simazine and CIAT were detected in both *deep* samples. These compounds were found in the *shallow* sample also, but at higher concentrations.

The *deep* aquifer zone can be further divided into an upper and lower part on the basis of borehole flow data, each contributing approximately 13 percent of the total flow to the public-supply well. The sample from 97.5 m (320 ft) bls represents the average chemistry of water that enters the well below 97.5 meters (320 ft) bls, and the sample from 88.4 m (290 ft) bls is the average chemistry of water that enters the well below 88.4 m (280 ft) bls, and therefore includes the water chemistry at 97.5 m (320 ft) bls. On the basis of specific conductance (SC) values at 88.4 m and 97.5 m ([table 9](#)), water entering the well between 88.4 m and 97.5 m (280 to 320 ft) bls, must be more dilute (lower SC) than the water entering the well below 97.5 m.

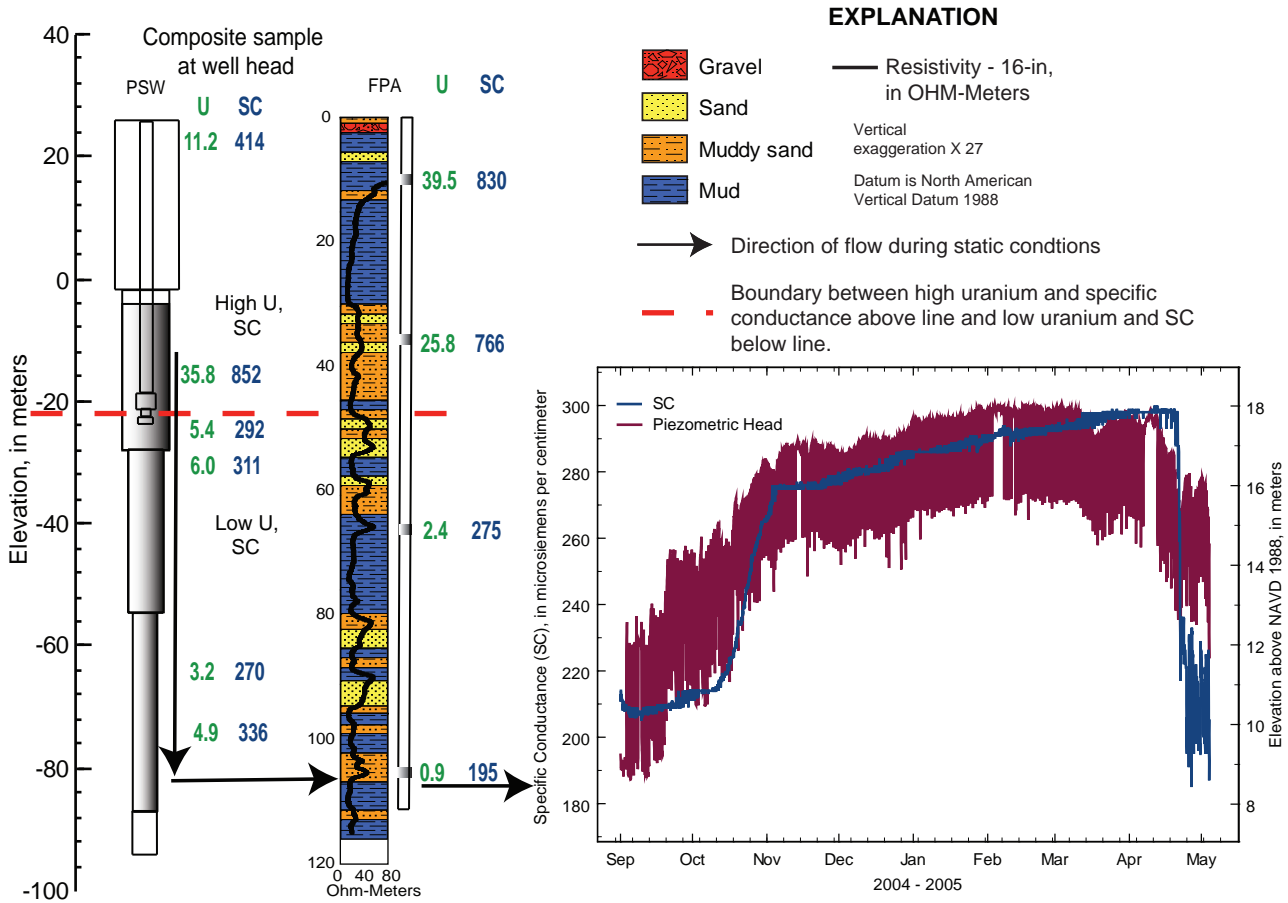
Uranium and nitrate were detected at higher concentrations in the deepest sample (DDS-97.5) than in the sample collected at 88.4 m bls. These concentrations were greater than concentrations in *deep* monitoring wells, excluding the sample from FPA-4 in November 2003 (tables 8,9). The sample collected at 97.5 m bls had the same three pesticide compounds as those collected from the *shallow* depth. The concentrations were lower in this sample than in the *shallow* sample but were higher than the sample collected at 88.4 m bls. On the basis of the observation that the concentrations and number of detections of organic and inorganic constituents in the deepest sample also were higher than those detected in the adjacent monitoring wells and

other monitoring wells screened in the *deep* aquifer zone, the water chemistry below 97.5 m was likely affected by well construction and hydraulic conditions of the aquifer.

## Well Construction and Operation Effects on Water-Quality

Because the public supply well is perforated over a long interval ([fig. 4](#), [table 1](#)), during static conditions the well can act as a conduit for flow from the shallow aquifer, where hydraulic head is high, to the deep aquifer, where the hydraulic head is low. As a result, the chemistry of the water in the deep aquifer zone surrounding the well is strongly influenced by the water chemistry of the *shallow* zone and by well operation schedules. [Figure 22](#) shows the concentration of uranium and specific conductance measurements for depth-dependent samples taken within the PSW and results from the nearby monitoring wells at site FPA. [Figure 22](#) also shows the effects of well-bore leakage through the PSW on the nearby *deep* monitoring well (FPA-4). FPA-4 is approximately 40 m (130 ft) upgradient of the public-supply well and is perforated between 104.5 and 106.1 m (343–348 ft) bls. The specific conductance and hydraulic head in FPA-4 was at a minimum during summer (maximum pumping), whereas specific conductance and hydraulic head in FPA-4 increased dramatically during winter (minimum pumping) and downward flow from the high specific conductance *shallow* aquifer zone was greatest.

The effects of well operation and construction on contaminant transport to the *deep* part of the aquifer were first identified in samples collected from FPA-4 in October, 2003. At that time, the public-supply well had been offline for over a month while a new sediment filtration system was installed on the well. Although the public-supply well became operational just before sampling, chloroform, tetrachloroethene, and CIAT were detected in samples from FPA-4 ([Appendices D, E](#)). The following year, the deep monitoring well (FPA-4) was sampled a second time as part of the depth-dependent sampling. At that time, the public-supply well had been pumped regularly for most of the summer. VOCs and pesticide compounds were not detected in this sample ([table 9](#)) and concentrations of inorganic species were lower than those in the flow-path sample (taken in October 2003) listed in [table 8](#). This suggests that a significant portion of the water that migrated into the *deep* aquifer zone from the *shallow* zone through the public-supply well had been evacuated as a result of prolonged pumping. Ground water from the *shallow* (DDS-45.7) and



**Figure 22.** Uranium (U) concentrations in and specific conductance (SC) measurements for ground water, depth-dependent samples collected from the public-supply well, and ground-water samples collected from monitoring wells at site FPA in August 2004 in Modesto, eastern San Joaquin Valley, California.

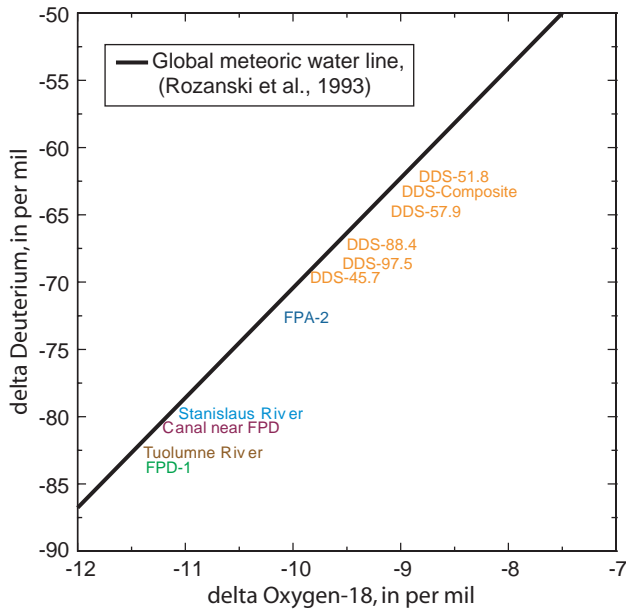
Piezometric head and specific conductance (SC) measured in well FPA-4 from September 2004 through May 2005. in., inch; PSW, public-supply well.

the *deep* depth-dependent samples (DDS-88.4, DDS-97.5) was isotopically lighter (deuterium, oxygen-18) than that in samples from the *intermediate* depth-dependent samples (fig. 23). Surface water had the lightest isotopic composition of water in the study area. The *shallow* sample (DDS-45.7) had the lightest composition of the depth-dependent samples and was likely influenced by surface water used for irrigation, although much less than other *shallow* wells such as well FPA-2. Ground water from the *deep* depth-dependent samples was a mixture of *shallow* and native *deep* ground water. The ground-water sample collected from the public-supply well at 97.5 m bls was lighter than the sample from 88.4 m bls, which indicates *shallow* ground water was preferentially stored in more permeable hydrofacies below 97.5 m bls during static conditions (table 9, fig. 23).

Uranium activity ratios indicated that the source of uranium in *deep* depth-dependent samples originated from *shallow* ground water. Uranium concentrations and activity ratios for the *shallow* depth-dependent sample (DDS-45.7)

was similar to those for the *shallow* monitoring wells (fig. 20). Uranium concentrations from the *deep* depth-dependent sample was higher than those from the *deep* monitoring wells and had uranium activity ratios similar to those for *shallow* ground water. The combination of higher uranium activity ratios and lower concentrations of uranium in the *intermediate* depth-dependent sample was similar to that for ground water from *deep* monitoring wells. This suggests the *intermediate* aquifer was not significantly affected by ground water from the *shallow* zone.

The percentage of terrigenic helium in samples from the public-supply well increased from 43 percent in October 2003 to more than 85 percent in August 2004 (fig. 10). This increase likely was the result of increased contributions of more native, *deep* ground water entering the well in August 2004. This change is consistent with storage of *shallow* water stored in the *deep* aquifer at the time ground-water samples were collected in October 2003.



**Figure 23.** Isotopic composition of ground water from public-supply well depth-dependent samples (depth of sample after dash) and ground-water and surface-water samples in Modesto, eastern San Joaquin Valley, California.

## Factors Affecting the Transport of Contaminants to the Public-Supply Well

### Contaminants Reaching the Public-Supply Well

Contaminants reaching the public-supply well that pose the greatest drinking water risk are uranium, nitrate, and to a lesser extent, arsenic. None of the composite samples collected from the public-supply well had concentrations of uranium, nitrate or arsenic above the MCL, but each of these constituents was detected at concentrations above half the MCL (tables 8,9). *Shallow* depth-dependent samples contained concentrations of uranium (35.8 µg/L) above the MCL of 30 µg/L and concentrations of nitrate (9.7 mg/L) near the MCL of 10 mg/L. This part of the aquifer contributes approximately 20 percent of the total flow to the well. Arsenic has an MCL of 10 µg/L and also was elevated (7.0 µg/L) in the *shallow* depth-dependent sample. However, arsenic concentrations are not sufficiently high in this sample or any other depth-dependent sample to threaten the

public-supply well given current geochemical conditions. Since the geochemical conditions that might favor widespread arsenic desorption, such as increases in phosphate and pH or changes in redox states, are not likely to occur, arsenic in ground water from the public-supply well is expected to remain elevated but unlikely to exceed the MCL.

Consequently, uranium and nitrate pose the most imminent threat to the public-supply well as a source of drinking water.

Organic constituents entering the public-supply well are below current MCLs, but their presence indicates the well is vulnerable to point-source contamination. Three VOCs were detected, most notably chloroform and tetrachloroethene (PCE), but the concentration of each were below one-tenth of any MCL. Three pesticides (CIAT or DEA, atrazine, and simazine) were detected at concentrations below one-hundredth the concentration of each corresponding MCL (CIAT or DEA does not have an MCL). Because the concentrations necessary for these constituents to exceed an MCL were not found in any of the depth-dependent samples or monitoring wells, these contaminants were not expected to pose an imminent contamination risk to the public-supply well.

### Factors Affecting the Transport of Nitrate and Uranium

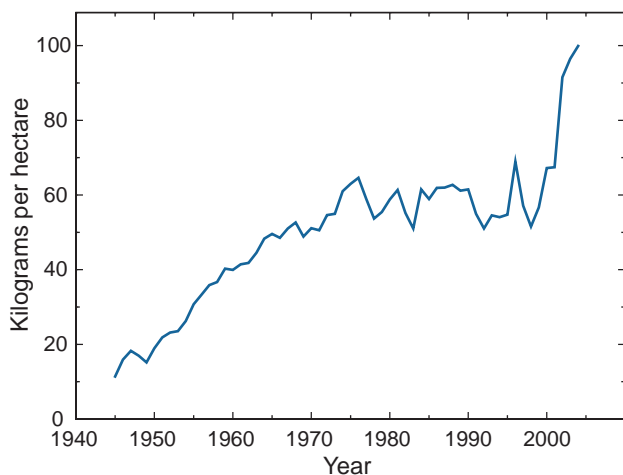
Elevated levels of uranium and nitrate in the public-supply well are primarily related to five factors: ground-water age, well construction, source strength, redox conditions, and alkalinity. These factors are described individually below and then presented together as they relate to uranium and nitrate transport in the following section.

**Ground-water age**—Ground-water pumping throughout the study area for irrigation and drinking-water supply has increased the rates of downward movement of shallow ground water. The distribution of mean ages interpreted from tracers collected at monitoring wells indicate that young (generally less than 50 years) ground water migrated to depths of up to about 60 m bls in parts of the aquifer (fig. 12). The age of most ground water below this depth was generally on the order of 100s to 1000s of years old. Young ground water contains elevated levels of uranium (>20 µg/L) and nitrate (>5 mg/L), whereas most older ground water contained background concentrations of nitrate (<3 mg/L) and low concentrations of uranium (<2 µg/L). Continued downward movement of shallow ground water will likely cause the amount of aquifer containing young ground water to increase.

**Well Construction**—The public-supply well is screened from 27.7 m (91 ft) to 111.6 m (366 ft) bls and has an open bottom. During static conditions, strong vertical hydraulic gradients cause *shallow* ground water to migrate from the upper part of the well screen to the near bottom of the well screen and into the *deep* part of the aquifer, where it was stored until the next pumping cycle. Because the well was operated on a limited schedule during the winter (wet season), uranium and nitrate have been historically high in winter samples in comparison to summer samples.

**Source Strength**—The concentration of nitrate in ground water is primarily affected by the amount of fertilizers applied on agricultural land. The amount of fertilizers applied over agricultural land has tripled over the last 50 years (Ruddy and others, 2006; [fig. 24](#)). In contrast to nitrate, uranium exists naturally in aquifer sediments and is unrelated to land use. Geochemical conditions which favor desorption of uranium can cause uranium concentrations in ground water to exceed the MCL.

**Redox Conditions**—Ground water within the study area was predominately oxic, although there were some localized reducing microenvironments. Uranium and nitrate are mobile in oxic ground water. Although some dissolved nitrate may be depleted in localized, reduced microenvironments, denitrification is not a significant factor affecting high concentrations of nitrate in ground water. Sulfidic reducing conditions, which may occur in localized, microenvironments, could facilitate the formation of uranium minerals, but like nitrate, is not a significant factor affecting high concentrations of uranium in ground water.



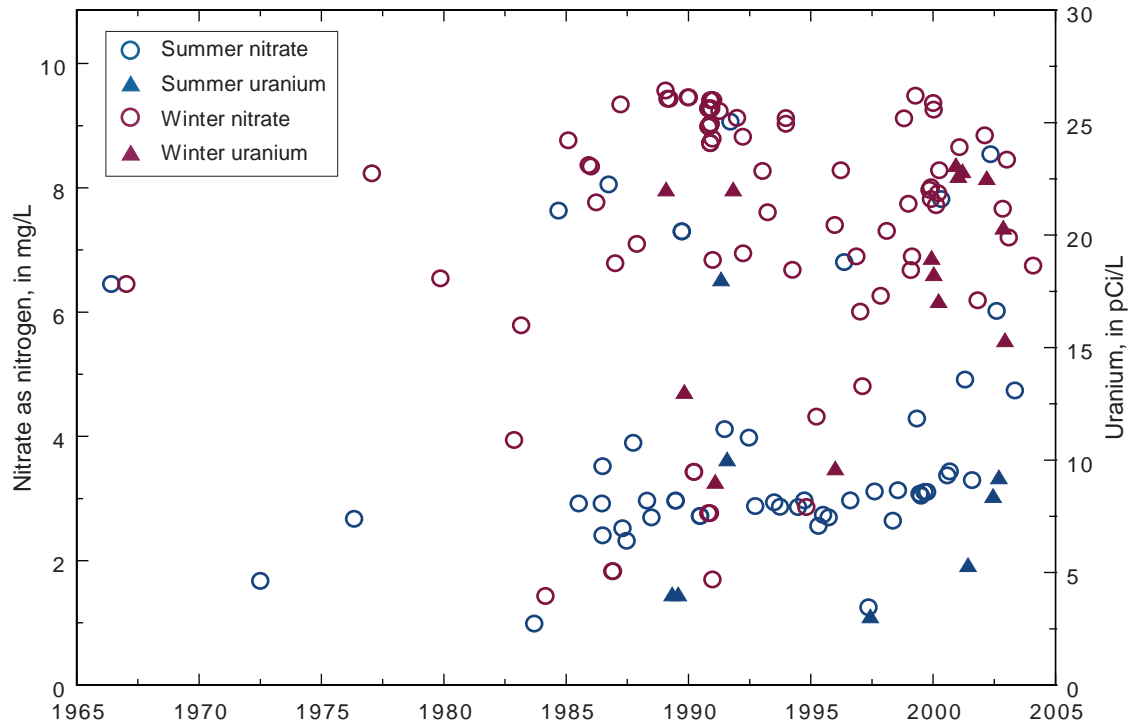
**Figure 24.** Application of nitrogen fertilizers in Stanislaus County since 1945 (Ruddy and others, 2006).

**Alkalinity**—Alkalinity is a measure of the capacity of water to resist changes in pH. The principal source of alkalinity in the study area is bicarbonate, which is the primary product of mineral dissolution. Bicarbonate liberates adsorbed uranium from sediment, leading to higher concentrations of dissolved uranium in ground water. Applying irrigation water to crops in agricultural areas and lawn grasses in urban areas increases bicarbonate concentrations, and hence alkalinity, in water reaching the ground-water system. Alkalinity above 250 mg/L (as  $\text{CaCO}_3$ ) in ground water in the study area had elevated uranium; alkalinity above 400 mg/L in some ground water in the study area had uranium above the MCL of 30  $\mu\text{g/L}$ . Nitrate is unaffected by alkalinity in ground water.

## Historical and Long-term Vulnerability to Nitrate and Uranium Contamination

Historically, seasonal water-quality samples collected from the public-supply well have been significantly affected by the water chemistry of *shallow* ground water entering the well ([fig. 25](#)). Nitrate concentrations in samples collected from the public-supply well since 1966 were significantly higher during the winter season (October through May) than during summer ( $p$ -value  $\leq 0.001$ , Kruskal-Wallis test). The median nitrate concentration in PSW samples collected during the winter season was 8.1 mg/L compared with 3.0 mg/L in samples collected during summer. Similar effects are indicated in public-supply well records of uranium concentrations in samples collected since 1989; the median uranium concentration for the winter season samples (19.6 pCi/L) was higher than the median for the summer samples (6.8 pCi/L) ( $p$ -value = 0.001, Kruskal-Wallis test).

Results from this study indicate that nitrate and uranium pose the greatest threat to the long-term sustainability of the ground-water resource in the study area and perhaps in other areas within the eastern San Joaquin Valley ([fig. 26](#)). If water management practices and land use do not change, dispersion and continued downward movement of ground water will cause the fraction of anthropogenically affected ground water that has high concentrations of nitrate and uranium to increase in the public-supply well, and possibly other wells in the eastern San Joaquin Valley.



**Figure 25.** Nitrate and uranium concentrations in ground water from the public-supply well in Modesto, eastern San Joaquin Valley, California, between 1966 and 2005. Nitrate and uranium data were separated on the basis of seasonal pumping cycles. mg/L, milligram per liter; pCi/L, picocurie per liter.

Nitrate concentrations in ground water mostly depend on the amount of nitrate applied on agricultural lands and the amount of recharge contributed to the aquifer within urban areas. If application rates of nitrogen fertilizers increase as indicated by nitrogen sales data (Ruddy and others, 2006; [fig. 24](#)), concentrations in the aquifer could increase. On the other hand, if the amount of urban recharge, which had comparatively low nitrate, increases as a result of urbanization of agricultural lands, concentrations could level off and decline over time.

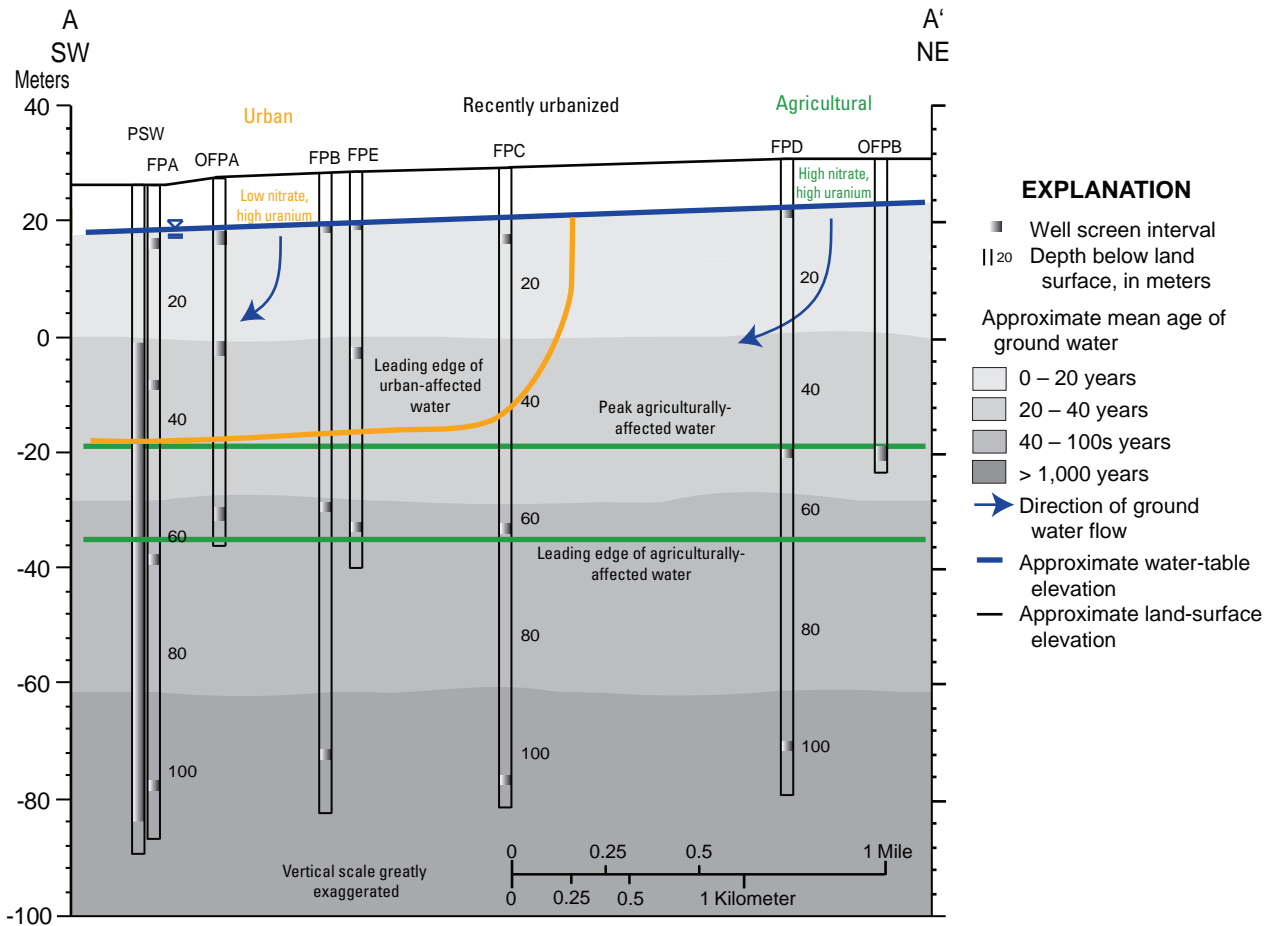
Nitrate in ground water is expected to behave conservatively and persist in the study area. The persistence of nitrate in ground water is limited mainly by redox conditions. In oxic ground water, nitrate does not degrade, has limited adsorptive properties, and does not tend to form minerals. In contrast, reducing redox conditions in ground water usually facilitate the removal of nitrate by denitrification. However, reducing conditions in the study area occurred in localized, microenvironments only and did not appear to significantly affect nitrate concentrations in ground water.

The mobility of uranium (VI) in ground water depends on the presence and concentration of strong aqueous complexes and the tendency of uranium to form solid-phase minerals or adsorb to aquifer sediments. Results from uranium extractions, adsorption experiments, and analysis of uranium isotopes

indicated that uranium was leached from shallow sediments and transported to deeper parts of the aquifer ([fig. 26](#)). Mobilized uranium was prevalent in ground-water samples collected from near the water table to depths of at least 50 m bls, likely owing to the downward movement of high-alkalinity (dominately bicarbonate anion), oxygen-rich ground water. At depths below 50 m bls, geochemical conditions favor adsorption processes that limit dissolved uranium concentrations.

Uranium concentrations in the aquifer are not expected to decrease over the long-term. Uranium adsorbed on *intermediate* and *deep* aquifer sediments represents a lasting source of uranium available for transport. Continued downward migration of oxygenated, high-alkalinity ground water from shallower depths is likely to mobilize the available fraction of uranium from these deeper sediments. The rate at which uranium concentrations may increase in the *intermediate* and *deep* parts of the aquifer will depend on the vertical rate of ground-water movement, which varies spatially owing to aquifer heterogeneity and differences in hydraulic stresses.





**Figure 26.** Movement of anthropogenically influenced ground water and approximate ground-water age distribution in Modesto, eastern San Joaquin Valley, California.

## Summary and Conclusions

The hydrogeology, water chemistry, and factors affecting the transport of contaminants in the zone of contribution of a public-supply well was investigated in Modesto, eastern San Joaquin Valley, California, as part of the U.S. Geological Survey's National Water Quality Assessment (NAWQA) Program's Transport of Anthropogenic and Natural Contaminants (TANC) to public-supply wells topical study. Beginning in 2003 and ending in 2005, twenty-three monitoring wells were installed within the zone of contribution of a public-supply well, and the chemistry of aquifer materials and ground-water samples were collected and analyzed to characterize the local ground-water system.

The local study area was in the northeastern part of the San Joaquin Valley in Modesto, California. The aquifer is mostly made-up of unconsolidated deposits of interlayered lenses of sand, gravel, silt, and clay that were deposited by streams draining the Sierra Nevada during glacial cycles. Aquifer sediments are predominantly granitic in origin and contain arsenic and uranium.

High rates of recharge in the agricultural area surrounding the city of Modesto and large ground-water withdrawals within the city have caused ground water near the water table to move downward and laterally towards the city. As a result, the chemistry of ground water near the water table has affected the chemistry of ground water deeper in the aquifer than would be expected under natural conditions.

The chemistry of ground-water samples collected near the water table has been affected by overlying land-use practices. Pesticides were present in *water-table* wells beneath agricultural and urban land-use settings; however, VOCs generally were detected beneath urban land only. Nitrate and sulfate concentrations beneath urban land were generally lower than would be expected beneath agricultural land. In contrast to anthropogenically influenced constituents, uranium is ubiquitous in sediments, and dissolved uranium concentrations in ground-water samples in *water-table* wells were high beneath both land-use settings. Alkalinity was strongly correlated with uranium concentrations. The principal source of alkalinity is bicarbonate, which forms a complex

with uranium and increases its solubility in water. Alkalinity concentrations in water reaching the water table can be increased by irrigation practices in both agricultural and urban (residential) areas.

The ground-water chemistry in *shallow* wells (between 25 and 35 m bls [meters below land surface]) resulted from a mixture of ground water that was influenced by both agricultural and urban land-use practices. Because the amount of recharge from agricultural irrigation is greater than urban recharge and because the majority of the study area was farmed prior to about 1960, the chemistry of ground water at these depths—where water can be up to 40 years old—is likely influenced more by agricultural practices than by urban practices. Nitrate concentrations were generally high in the *shallow* ground water throughout the study area. Concentrations of PCE, however, indicated that this ground water also was locally influenced by urban practices. In addition, concentrations of uranium in *shallow* wells were elevated, and the concentration of uranium in the shallow depth-dependent sample from the public-supply well was above drinking water standards. Because the age of the *shallow* ground water was generally post industrial, the water quality in this part of the aquifer has largely determined, and will continue to determine, the vulnerability of the public-supply well to contamination.

The quality of the ground water from *intermediate* wells (between 45 and 70 m bls) is generally good, although VOCs and pesticides were detected in 3 out of 7 wells. Nitrate concentrations were higher than background concentrations (3 mg/L) in 5 out of the seven monitoring wells. Because much of the land was farmed before urbanization, *intermediate* ground water was more affected by agricultural practices than by urban practices. The lower specific conductance, higher pH values, and older ground-water ages indicate that *intermediate* ground water is a mixture of water affected by agricultural and, to lesser extent, urban practices and older more pristine water that was recharged under more natural conditions. As a result, ground-water from *intermediate* monitoring wells was generally older than 40 years and likely older than post-industrial atmospheric age tracers.

*Deep* ground water (between 100 and 120 meters bls) has been unaffected by land-use practices, and reflected ground water that evolved under natural conditions. As a result, VOCs and pesticides were not detected in the deep part of the aquifer except where well construction and operation allowed contaminants to migrate from *shallow* ground water. Nitrate concentrations were generally less than 3 mg/L, which are indicative of natural background concentrations. Concentrations of uranium were generally less than 1  $\mu\text{g/L}$ . Ground-water samples from the deep monitoring wells were “tritium dead.” Uncorrected carbon-14 ages indicated the age of ground water from this part of the aquifer was greater than 1,000 years.

Well-bore flow data within the pumping public-supply well showed water that discharged from the well head consisted of 20 percent *shallow* water, 55 percent *intermediate*

water, and 25 percent *deep* water. However, during static conditions, *shallow* ground water moved downward through the public-supply well borehole and into the *deep* part of the aquifer. Because the chemistry of water from the *shallow* zone was of poorer-quality than that from the *deep* zone, prolonged static conditions during the winter allowed large volumes of contaminated water to accumulate in the *deep* part of the aquifer near the public-supply well. Historical water-quality data show that the quality of water that is pumped from the public-supply well is substantially affected by seasonal changes in pumping. The concentrations of tracers of ground-water age in composite samples from the public-supply well were affected by well-bore leakage and the mixture of young and very old ground water and concentrations of contaminants within the borehole. As a result, the age of ground water pumped from the public-supply well depended on the time of year, pumping history, and hydrologic conditions.

Although increased pumping during winter months could cause winter water-quality samples to be below drinking water standards, continued downward migration of contaminated ground water to deeper parts of the aquifer threatens the long-term sustainability of the aquifer as a source of clean drinking water. Application rates of nitrogen fertilizers leveled off during the mid-1970s to late-1990s, but recently may be increasing again, which could cause nitrate concentrations in the aquifer to rise. Increases in urban recharge or loss of agricultural recharge as urban areas expand into farmed land may significantly decrease the nitrate concentrations at the public-supply well. Alkalinity measurements were relatively high beneath both land-use settings, and movement of high alkalinity water to deeper depths is likely to increase uranium concentrations throughout the aquifer and eventually at the well unless flow patterns change. The quantitative effects of both these hypotheses were tested and are reported in the companion report describing the local-scale ground-water flow model.

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## Appendix A: Collection and Analysis of Aquifer Solids.

Core samples were collected from various depths and boreholes to obtain representative vertical, lateral, and textural profiles of the aquifer material. Eight cores were collected by the mud-rotary drilling method using a wireline coring device with a split-barrel sampler lined with a 5.1-cm-diameter acrylic sleeve. Two cores were collected by the hollow stem auger method using the same coring device but with a slightly larger diameter sleeve. After retrieval from the borehole, core sleeves were capped and taped at each end to prevent exposure to the atmosphere. Core sleeves were then transferred to a nitrogen-filled plastic bag, and subsamples of the core were cut, capped, and taped. Core samples were analyzed for heavy minerals, mineralogical content, particle size, bulk density, and carbon content. Acid extractions were performed to determine concentrations and the distribution of trace elements, iron content and iron-reducible sulfides in aquifer material. In addition, adsorption experiments and another series of extractions were done to understand the source and movement of arsenic and uranium in the aquifer.

### Mineralogical Analyses and Carbon Content

The mineralogy of samples was determined by using powder X-ray diffraction, for bulk mineralogy and clay separates. Heavy mineral separations and magnetic-susceptibility separations were done on sediment samples to identify minerals that may contain sulfides, oxides, and other more reactive minerals that may be relevant to aquifer weathering. The sediment core subsamples were small (10 g) and, therefore, may not adequately represent the lithology, but they provided some information that was useful in assessing geochemistry and provenance. Samples for heavy minerals were sieved to <60 mesh, separated using heavy liquids (density >2.7 g/cm<sup>3</sup>), and then by magnetic susceptibility. Half of the sample was ground for emission spectroscopy, which provided semi-quantitative analysis for 35 elements, and the other half was examined with light microscopy and powder XRD to help identify the grains. The nonmagnetic fraction, which includes most sulfides, oxides, siderite, and silicates, and the slightly magnetic fraction were analyzed to target the more reactive minerals of interest (Arbogast, 1990).

The relative abundances of the bulk minerals and clay composition determined by X-ray diffraction were consistent with granitic source rocks of the Sierra Nevada and optical mineralogical descriptions of previous investigations (table A1). Quartz was the most abundant mineral and was typically followed in order of decreasing abundance by plagioclase and potassium feldspar, and minor amounts of hornblende. The most abundant clay mineral was smectite, which was usually followed in sequence by illite and kaolinite, and lesser amounts of chlorite, hornblende, and goethite. Smectite

is the primary weathering product in arid and semi-arid environments, where less rain increases soil residence times and the concentrations of dissolved ions (Appelo and Postma, 1996).

Heavy minerals were separated from four core samples, and the slightly-magnetic and non-magnetic fractions were analyzed (table A2). The heavy mineral assemblage was consistent with common accessory minerals found in granitic environments. Amphiboles/pyroxenes were the most abundant mineral followed by lesser amounts of sphene, epidote, zircon, and biotite.

Carbon in aquifer sediments was extracted and converted to CO<sub>2</sub>(g) using an elemental analyzer and measured with a continuous-flow isotope-ratio mass spectrometer (Brenna, 1997; Revesz and Qi, 2003). Carbon isotopic results are reported in parts per thousand (per mil) relative to the VPDB (Vienna Peedee belemnite) standard by assigning a value of +1.95 per mil to National Bureau of Standard 19 CaCO<sub>3</sub> (Coplen, 1994). Total carbon content of aquifer sediments ranged from 0.1 g/kg, less than the detection level, to a maximum of 0.6 g/kg. Carbon content was greater in shallow sediments than in deep sediments, but differences between concentrations were usually within analytical precision. The primary form of carbon in sediments was organic carbon. Inorganic carbon was not detected above the detection level of 0.2 g/kg (table A3). Small differences between total carbon and organic carbon content may suggest some inorganic carbon is present in aquifer sediments, although the difference between total and organic carbon was within the analytical error. Carbonate minerals, such as calcite, are likely the only source of inorganic carbon in the aquifer. Calcite was not detected by X-ray diffraction analysis, but calcite can form authigenically (through in-place precipitation) on the surfaces of clay minerals and may not be detected by X-ray diffraction methods (Izbicki and others, 2002).

Although organic carbon content of the sediments analyzed in this study was not high, the amount of organic carbon generally decreased in deeper sediments (Spearman's rho = -0.65, *p*-value = 0.05; table A3). This could indicate that reduction of organic carbon may have caused the lower dissolved oxygen levels measured in *deep* monitoring wells (median = 2.7). Microbes utilize organic carbon as a source of energy by changing the valence state of carbon and another element or compound. Where sources of carbon are high, microbial reactions can significantly affect the reduction-oxidation (redox) conditions of ground water. Depending on the redox state, oxygen and nitrate can be removed, and dissolved manganese and iron concentrations may become elevated. However, the presence of dissolved oxygen in *deep* ground water indicated that ground water remained oxic and could indicate that organic carbon content in aquifer materials was not sufficient to cause substantial reduction of nitrate, and oxides of manganese and iron.



**Table A1.** Relative abundance of (I) bulk minerals and (II) minerals in particles less than 1 micrometer from core samples collected during monitoring well installation in 2003 and 2004 in Modesto, eastern San Joaquin Valley, California.

[Lower integers indicate higher relative abundance.  $\mu\text{m}$ , micrometer; <, less than]

I. Relative abundance of bulk minerals												
Borehole ID	Depth to top of core segment (meters)	Depth to bottom of core segment (meters)	Clay (percent)	Silt (percent)	Sand (percent)	Quartz	Plagioclase	K-Spar	Total clay	Hornblende		
SA	8.5	8.8	6	47	47	1	2	3	4			
SB	8.5	8.8	4	26	70	1	2	3	4			
FPA	8.8	10.4	3	21	76	1	2	3	4			
OFPA	18.3	19.8	3	12	85	1	2	3	4			
FPA	42.4	43.9	7	48	46	1	2	3	5	4		
OFPA	57.0	58.5	2	8	90	1	3	2	5			
FPD	63.1	64.6	12	38	50	1	2	4	3			
FPA	75.9	77.4	13	48	39	1	2	3	4			
FPD	107.9	109.4	12	51	38	1	2	3	4	5		
FPA	109.4	111.0	8	34	57	1	2	3	5	trace		

II. Relative abundance of minerals in particles <1 $\mu\text{m}$												
Borehole ID	Depth to top of core segment (meters)	Depth to bottom of core segment (meters)	Clay (percent)	Silt (percent)	Sand (percent)	Smectite	Illite	Chlorite	Kaolinite	Hornblende	Goethite	
SA	28	29	6	47	47	1	2	5	3	4		
SB	28	29	4	26	70	1	2	4	3	5		
FPA	29	34	3	21	76	1	2	trace	3	trace		4
OFPA	60	65	3	12	85	1	2	trace	3			
FPA	139	144	7	48	46	1	2	trace	3			4
OFPA	187	192	2	8	90	2	1	4	3	5		
FPD	207	212	12	38	50	2	1	trace	3	trace		
FPA	249	254	13	48	39	1	2	trace	3	trace		4
FPD	354	359	12	51	38	1	2	trace	3	trace		4
FPA	359	364	8	34	57	1	4	trace	2	trace		3

**Table A2.** Percentage of non-magnetic and slightly magnetic heavy minerals separated from core samples collected during monitoring well installation in 2003 and 2004 in Modesto, eastern San Joaquin Valley, California.

Borehole ID	Depth to top of core segment (meter)	Depth to bottom of core segment (meter)	Non-magnetic	Weight percentage (combined)	Slightly magnetic	Weight percent
SB	8.5	8.8	Amphibole/pyroxene	50	Hematite	90
			Sphene	40	Sphene	trace
			Zircon, biotite	10	epidote biotite	trace trace
OFPA	57.0	58.5	Sphene	70	Hematite	100
			Amphibole/pyroxene	20	Sphene	trace
			Hematite, zircon	10	Amphibole	trace
FPA	75.9	77.4	Amphibole/pyroxene	60	Amphibole/ pyroxene	70
			Sphene	20	Sphene	trace
			Zircon, epidote, biotite	10	Epidote	trace
					Biotite	trace
FPD	107.9	109.4	Amphibole/pyroxene	20	Amphibole/ pyroxene	90
			Epidote	trace	Sphene and epidote	10
			Zircon	trace		
			Sphene	trace		

**Table A3.** Total Carbon and organic carbon content of sediments from core samples collected during monitoring well installation in 2003 and 2004 in Modesto, eastern San Joaquin Valley, California.

[—, not detected;  $\delta^{13}\text{C}$ , delta carbon-13. m, meter; g/kg, gram per kilogram; per mil, per thousand; <, less than]

Borehole ID	Depth to top of core segment (m)	Depth to bottom of core segment (m)	Total carbon (inorganic plus organic) (g/kg)	$\delta^{13}\text{C}$ of Total carbon (per mil)	Organic carbon, (g/kg)	$\delta^{13}\text{C}$ of Organic carbon (per mil)
SA <sup>1</sup>	28	29	0.7	-19	0.6	-27.2
SB <sup>1</sup>	28	29	0.4	-25.1	—	—
FPA <sup>2</sup>	29	34	0.3	—	0.3	—
OFPA <sup>1</sup>	60	65	0.2	-25.9	—	—
FPA <sup>2</sup>	139	144	<0.1	—	<0.2	—
OFPA <sup>1</sup>	187	192	0.3	-26.1	0.3	-27.1
FPD <sup>2</sup>	207	212	0.2	—	<0.2	—
FPA <sup>2</sup>	249	254	<0.1	—	<0.2	—
FPD <sup>2</sup>	354	359	0.3	—	0.2	—
FPA <sup>2</sup>	359	364	<0.1	—	<0.2	—

<sup>1</sup>Analyzed at the Reston Stable Isotope Laboratory in Reston, Virginia.

<sup>2</sup>Analyzed at the National Water Quality Laboratory in Lakewood, Colorado.

## Arsenic and Uranium Extractions

Most arsenic (As) and uranium (U) in aquifer sediments that are available for transport in ground water are adsorbed to surfaces of coatings on sediment grains. The abundances of As and U in grain coatings or possibly other mineral phases from core samples were evaluated using a 10-percent nitric acid (HNO<sub>3</sub>) extraction. The nitric acid extraction method was primarily intended to target ferric oxyhydroxides and their associated trace elements, but the extraction can also isolate other oxides, clays, and carbonate and sulfide phases to varying degrees. The extraction was done on wet sediments,

but the moisture content was determined for a separate subsample and used to correct the analytical concentrations to dry weight. The sample/solution ratio was 5 g  $\pm$  1 g wet weight to 15 mL of acid solution. The sediment-acid aliquots were set on a shaker table for 6 hours, then centrifuged, filtered with 0.45  $\mu\text{m}$ -pore filters, and analyzed for several minor elements by inductively-coupled-plasma optical-emission spectroscopy. Dilution to a 5-percent nitric acid solution was required for analysis of As and U, which yielded lower detection limits.

Poorly-crystalline iron oxyhydroxides isolated from the nitric acid extracts yielded concentrations ranging from 950 to 2,600 mg/kg (mg of Fe per kg of bulk sediment). The extracts also contained 0.23 to 1.2 mg/kg of uranium and 0.12 to 0.30 mg/kg of arsenic, and generally represent iron-reducible and loosely bound concentrations in sediments, although iron, arsenic, and uranium associated with organic matter could also be liberated by this extraction. Arsenic and iron concentrations in the sediment extracts were weakly correlated (spearman's rho = 0.75,  $p$ -value = 0.1,  $n$  = 6), but suggest that arsenic in ground water is controlled by adsorption to ferric oxyhydroxides. Uranium concentrations in the sediment extracts significantly increased with sample depth (spearman's rho = 0.75,  $p$ -value <0.03,  $n$  = 10) and were not correlated to either iron or arsenic extractions. Adsorption of dissolved species to mineral surfaces depended on the availability of adsorption sites and the geochemical conditions of the solution. Although ferric oxyhydroxides varied spatially within the study area, iron concentrations were several orders of magnitude greater than the extractable concentrations of uranium, indicating adsorption sites for uranium likely were not limited. Therefore, uranium may have been leached from adsorption sites in *shallow* sediments because of geochemical conditions different from the deeper conditions which support uranium adsorption.

The extractions can overestimate the fraction of uranium and arsenic that can be mobilized by ground water. Hypothetically, if all of the extractable uranium and arsenic had been dissolved in ground water, their concentrations could have ranged from about 900 to 2,000  $\mu\text{g/L}$  of arsenic and from about 1,600 to 8,100  $\mu\text{g/L}$  of uranium, based on a porosity of

0.28 (table A4). These hypothetical concentrations suggest that neither arsenic nor uranium in ground water are limited by their abundance in sediments. However, the sediment is not likely to come into contact with water of a similar geochemical make-up as the acid extractions used in this experiment and; therefore, is an overestimate of the fraction of uranium and arsenic available for transport in sediments.

The fraction of uranium in sediments available for transport was determined using an alkaline (pH = 9.45), sodium bicarbonate extraction (Kohler and others, 2004). The extraction was performed on nine core sediments and drill cutting samples collected from soils and from various depths throughout the aquifer. The extraction was done by combining 35 mL of sodium-bicarbonate solution and 2 g of sediment in 40-mL polypropylene centrifuge tubes. The sediment-solution was mixed continuously for five days and then centrifuged to separate the extractant. Uranium was measured as U(VI) by inductively coupled plasma-mass spectrometry (ICP-MS).

The sodium bicarbonate extractions indicate uranium may be liberated from *intermediate* and *deep* sediments. In contrast, uranium concentrations from the shallowest sediments were not detected, which suggests that the fraction of uranium available for transport had already been leached from adsorption sites in these sediments or that less uranium (all fractions) had been in the shallow sediments than in the deeper sediments. These findings are consistent with the results of the 10-percent nitric acid extractions.

**Table A4.** Selected trace element concentrations from extractions performed on core and cutting samples collected during monitoring well installation in 2003 and 2004 in Modesto, eastern San Joaquin Valley, California.

[HCO<sub>3</sub>], bicarbonate; mg/L, milligram per liter; mg/kg, milligram per kilogram;  $\mu\text{g/L}$ , microgram per liter; na, not analyzed; —, not detected; %, percent

Borehole ID	Depth to top of core segment	Depth to bottom of core segment	Extractant: 10% nitric acid (1.5 normality) solution					Extractant: 1,050 mg/L HCO <sub>3</sub> ; pH 9.45	
			Iron	Arsenic	Equivalent	Uranium	Equivalent	Uranium	Equivalent
SA	0.9	1.5	na	na	na	na	na	—	—
SA	8.5	8.8	na	0.3	2,000	0.23	1,600	—	—
SB	8.5	8.8	na	0.15	1,000	0.47	3,200	na	na
FPA	8.8	10.4	2,000	0.24	1,600	0.56	3,800	—	—
OFPA	18.3	19.8	na	0.19	1,300	0.76	5,200	0.02	120
FPA	42.4	43.9	2,600	0.21	1,400	0.99	6,700	0.05	370
OFPA	57.0	58.5	na	0.13	900	0.34	2,300	0.05	320
FPD	63.1	64.6	1,300	0.12	800	0.95	6,500	0.25	1,700
FPA	75.9	77.4	1,900	0.15	1,000	0.9	6,100	na	na
FPD	107.9	109.4	1,000	0.14	900	0.96	6,500	0.11	800
FPA	109.4	111.0	950	0.14	900	1.2	8,100	0.08	500

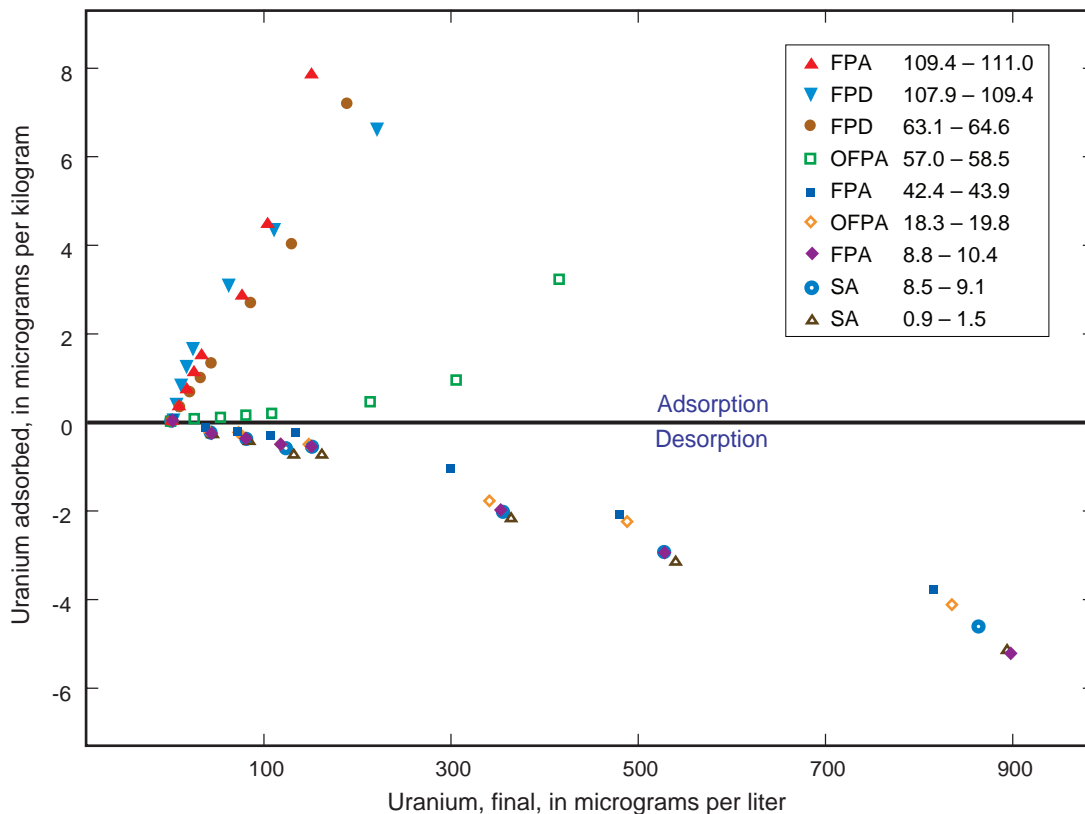
<sup>1</sup>The median porosity from 6 cores was 0.28. This value was used to estimate hypothetical ground water concentrations.

### Uranium Adsorption Experiments

Batch reactor experiments were used to quantify adsorption of U(VI) onto sediments from core and drill-cutting samples collected from surface soils and at various depths throughout the aquifer. Experiments were done by combining 35 mL of deionized water with 2 g of sediment in 40-mL polypropylene centrifuge tubes. Adsorption isotherms for U(VI) were determined by diluting U(VI) stock solutions prepared from uranium oxide (UO<sub>3</sub>), to obtain initial concentrations ranging from 0 to 600 µg/L. Sodium bicarbonate was added to each set of samples to approximate the native concentrations of the bicarbonate ion (HCO<sub>3</sub><sup>-</sup>) in ground water associated with each core sample. Initial pH values were adjusted with 0.1N sulfuric acid to the approximate pH of native ground water.

The suspensions were mixed continuously on an end-rotating mixer at two revolutions per minute (rpm). An equilibration time of five days was used. It was determined in preliminary experiments that U(VI) adsorption was rapid; 90 percent was adsorbed within a few hours, and equilibrium was attained within two days. Solutions were separated from the sediment by centrifuging at 15,000 rpm for 15 minutes and filtering with a 0.2-µm pore filter. The pH was then measured, and the bicarbonate concentration was determined by titration using 0.2 N sulfuric acid to a pH 4.5 endpoint. U(VI) in solution was determined by ICP-MS.

Adsorption-test samples consisting of drill cuttings and sediment material from depths ranging from the soil zone (1 meter) to the *shallow* part of the aquifer system (40 m) showed that the final uranium concentration was greater than the initial concentration (fig. A1). This indicates that the introduced uranium was not adsorbed to sediments and an additional amount of native uranium was released from sediments. The amount of native uranium also increased with increasing amounts of introduced uranium. To ensure the result was not due to experimental error, the adsorption experiments were rerun. Results verified the initial experiment. Only sediments from the *intermediate* and *deep* zones of the aquifer showed any appreciable adsorption of uranium. Linear isotherms for these sediments indicate uranium adsorption was not limited by the concentrations used in the experiment. The amount adsorbed or desorbed followed a general trend from deepest to shallowest, with the most adsorbed from the deepest and the most desorbed from the shallowest sample (fig. A1). The adsorption isotherm for site OFPA, 57.0–58.5, appeared to mark the boundary between adsorption and desorption. Native uranium and alkalinity measurements in ground water were high above this depth, generally greater than 20 µg/L and 250 mg/L, respectively, and decreased below this depth, less than 10 µg/L and 200 mg/L. These results suggest that desorption or dissolution of uranium into ground water is not solely related to its presence or concentration in the sediments, but also to the presence of bicarbonate.



**Figure A1.** Relation between uranium concentrations and uranium adsorbed to aquifer sediment collected at various depths in Modesto, eastern San Joaquin Valley, California.

## Appendix B: Quality-Control Analysis

Quality-control analysis was done for all data collected during the TANC study. Not all data collected for this study is presented or analyzed in this report. Data from this study can be retrieved online from the NAWQA Data Warehouse at <http://infotrek.er.usgs.gov/traverse/?p=NAWQA:HOME:2677137420746277>

Quality-control samples (blanks, replicates, and spikes) were collected to monitor for bias and variability in the environmental data. Bias can be either negative or positive error caused by loss of analyte (for example, by degradation) or adding an analyte (for example, by cross-contamination). Variability is an expression of the difference between comparable measurements; since ground-water quality did not vary much during the short time when samples were collected, variability between replicate samples were likely mainly due to differences in sample handling or analyses.

Blanks were used to monitor for positive bias caused by sample contamination. A ground-water sample was believed to have been contaminated during collection, handling, or processing if (1) a constituent was detected in an equipment or field blank, (2) that constituent was detected in ground-water samples, and (3) the minimum concentration detected in the ground-water samples was less than the maximum concentration detected in field blanks. If a constituent was detected in an equipment or field blank, then the concentration detected in the blank was compared with that in the associated source-solution blank to determine if the contaminant came from the blank water itself.

Field blank detections that could not be attributed to contamination by blank water, laboratory methods or procedures, or storage were compared with detections of constituents in associated ground-water samples and evaluated with respect to criterion 3 above. An associated ground-water sample is defined as any ground-water sample collected immediately before or after a field blank. Detecting a constituent in the field blank that was also detected in an associated ground-water sample may indicate carry-over contamination. Carry-over contamination occurs when a constituent is introduced into a sample from the sampling equipment in spite of cleaning procedures. If carry-over contamination was identified as the cause of the detection in the field blank, subsequent ground-water samples and field blanks also was evaluated for evidence of carry-over contamination. A constituent that was detected in a field blank but was not detected in an associated ground-water sample was not the result of carry-over contamination.

Ground-water results were censored when detection of a constituent was caused by incidental contamination of the sample from equipment or field procedures. The threshold

concentration for censoring data was determined by adding the blank concentration to the long-term method detection level (LT-MDL) for the constituent in question. For example, if toluene was detected in a field blank at a concentration of 0.02 µg/L, and the LT-MDL for toluene is 0.02 µg/L, then the concentration of toluene in the associated ground-water sample would have to be greater than or equal to 0.04 µg/L to be reported as a detection.

If a constituent was detected in multiple blanks (equipment or field) and the constituent could not be attributed to the source solution or to carry-over contamination, then any ground-water sample that had the constituent in question was censored at a threshold concentration. The threshold concentration was determined by averaging the blank concentrations and adding three times the standard deviation of blank samples. All ground-water samples containing constituent concentrations less than or equal to the threshold concentration were censored. Censored values are indicated by a "V" preceding the value in the tables, and are excluded from the summary statistics.

Replicate samples, collected sequentially, were used to assess variability caused by differences in sample handling or analysis. At least one replicate sample pair was collected for each schedule of analytes sampled during this study. Multiple replicate pairs were collected for analysis of VOCs, major ions, nutrients, dissolved organic carbon, ultra-violet absorbance, and trace elements, the most frequently sampled constituents. Relative standard deviation (RSD) was used as a measure of variability between replicate pairs and is defined as the absolute value of the standard deviation divided by the mean concentration for each replicate pair, multiplied by 100 percent. RSD values were calculated using raw, unrounded values of concentrations. If a compound was detected in the environmental sample but was not detected in the duplicate sample or vice versa, the concentration used to calculate the RSD for the compound in the replicate pair was assigned a value of one-fourth the minimum detection level. RSD values less than 20 percent were considered acceptable in this study.

Spikes, including surrogates and matrix spikes, were collected by adding solutions containing known amounts of selected pesticides or VOCs to some replicate ground-water samples. The concentration of each compound in solution was compared with the spike solution concentration and expressed as a percentage of the spiked concentrations. Recoveries of surrogate and matrix-spike compounds were used to evaluate bias for pesticide or VOC analyses. Recoveries between 70 and 130 percent were considered acceptable in this study.



## Major Ions, Nutrients, Trace elements, Dissolved Organic Carbon and Ultra-Violet Absorbance

### Blanks

Four field blanks and three equipment blanks were collected during this study and analyzed for major ions. (One field blank was removed from quality-control analysis because a bottle mix-up led to the partial analysis of an environmental sample in place of the blank.) Calcium, magnesium, sodium, silica, bromide, fluoride and manganese were detected in one or more blanks at concentrations lower than those in ground-water samples. Only bromide, fluoride and manganese concentrations were within two orders of magnitude of their concentrations in ground-water. These results indicate that concentrations found in ground-water samples may partly be due to contamination introduced during sampling or analysis. Fluoride was not frequently detected and was not used in the data-analysis part of this report. Bromide concentrations less than 0.031 mg/L (three standard deviations of the mean blank concentration) and manganese concentrations less than 4.3 µg/L (three standard deviations of the mean blank concentration) were removed from analysis. As a result, one bromide sample and 28 manganese samples were censored, as indicated by a “V” next to the value reported in [Appendix E](#).

Four field blanks, one source-solution blank, and nine equipment blanks were analyzed for nutrients. Nutrients were not detected in the field blanks and the source-solution blank. Orthophosphate was detected in one equipment blank at a concentration one-fifth of the lowest concentration in all ground-water samples. Since eight of the blank samples did not contain detectable orthophosphate, this compound was not considered to significantly contribute to ground-water sample concentrations and was not censored.

Eleven trace elements were detected in field blanks and equipment blanks. Seven of these trace elements—barium, cadmium, cobalt, copper, molybdenum, nickel, and zinc—were not censored because the constituent would not be used for data analysis. Barium, cadmium, and molybdenum concentrations in blank samples were generally one-tenth of the concentration in a ground-water sample. Therefore, censoring values for these constituents would not cause the censoring of ground-water samples. Censoring values for cadmium, cobalt, copper, nickel and zinc were 1.2, 0.1, 0.5, 2.7, 7.8 µg/L, respectively. Aluminum was detected in one equipment blank at a concentration similar to that in the following ground-water sample. This ground-water sample was censored. A field blank done immediately following that ground-water sample did not contain detectable concentrations of aluminum. Arsenic, strontium, and vanadium were detected in blanks but were not censored because the detections were at least ten times below the lowest concentration detected in ground water.

Four field blanks were analyzed for dissolved organic carbon and three were analyzed for ultra-violet absorbing organic constituents (UV absorbance). Dissolved organic carbon was detected in all four field blanks. The median concentration for blanks was greater than the median concentration for ground-water samples. This result could have been due to analytical difficulties or to a lack of total removal of methanol used to clean the equipment between sampling ground-water and collecting field blanks. As a result, dissolved organic carbon concentrations in ground water are unreliable and were not used for data analysis. Ultra-violet absorbing organic constituents were not detected in any of the blanks.

### Replicates

Five replicate pairs of ground-water samples were analyzed for major ions, four replicate pairs were analyzed for nutrients, two replicate pairs were analyzed for trace elements, four replicate pairs were analyzed for dissolved organic carbon, and three replicate pairs were analyzed for ultra-violet absorbance at 254 nanometers and 280 nanometers. Fifty out of fifty-three analytes (94 percent) had a mean relative standard deviation less than 15 percent and forty-one (77 percent) had RSDs less than 5 percent ([table B1](#)). The mean relative standard deviation for zinc was 62 percent. Zinc was not used for data analysis in this report.

## Pesticides and Volatile Organic Compounds (VOC)

### Blanks

One field blank and three equipment blanks were collected and analyzed for pesticides. Pesticides were not detected in these blanks.

Toluene was the most frequently detected compound among 14 equipment, 9 field, and 7 source-solution blanks; the combined detection frequency was 63 percent. Toluene was detected more frequently in the equipment (78 percent) and the field (71 percent) blanks than in the source-solution blanks (43 percent). Because of the widespread low-level detection of this compound in quality-control samples, toluene detections in the environmental data was censored at 0.19 µg/L, which is the average toluene concentration in blank samples plus 3 times the standard deviation of the toluene concentrations. The highest toluene concentration was 1.97 µg/L, which is over 7 times higher than any other sample. Toluene from this sample was considered an outlier and was removed from the calculation of the censored value. Since the censoring protocol would reduce the number of detections in ground water to one, toluene was left out of the VOC data analysis.

**Table B1.** Summary of mean relative standard deviations for replicate sample pairs of inorganic and nutrient analytes in ground-water samples collected in October and November of 2003 and 2004 in Modesto, eastern San Joaquin Valley, California.

[The number of pairs used is in parentheses. Duplicate non-detect values were not compared. RSD, relative standard deviation; UV, ultraviolet; %, percent; >, greater than]

<5%	<10%	<15%	>20%
Calcium (5)	Fluoride <sup>1</sup> (2)	UV absorbance (280nm) <sup>2</sup>	Zinc (2)
Magnesium (5)	Iron (1)	Dissolved organic carbon	Methane recoverable (1)
Potassium (5)	Manganese <sup>3</sup> (4)	Uranium-235 (4)	Radium-226
Sodium (5)	UV absorbance (254nm)		
Bromide (4)	Gross beta radioactivity, Cs-137 curve (1)		
Chloride (5)	Dissolved oxygen lab (1)		
Silica (5)			
Sulfate <sup>1</sup> (5)			
Residue on evaporation (4)			
Ammonia plus organic nitrogen (1)			
Nitrite plus nitrate (4)			
Orthophosphate (4)			
Total nitrogen <sup>1</sup> (3)			
Aluminum <sup>1</sup> (2)			
Antimony (1)			
Arsenic (2)			
Barium (2)			
Boron (2)			
Chromium (2)			
Cobalt <sup>1</sup> (2)			
Lithium (2)			
Molybdenum (2)			
Nickel (2)			
Selenium (1)			
Strontium (2)			
Vanadium (2)			
Uranium (2)			
Alpha radioactivity 2-sigma combined uncertainty, Th-230 curve (1)			
Beta radioactivity 2-sigma combined uncertainty, Cs-137 curve (1)			
Deuterium/Protium ratio (1)			
Oxygen-18/Oxygen-16 ratio (1)			
Nitrogen-15/Nitrogen-14 ratio in nitrate fraction (1)			
Oxygen-18/Oxygen-16 ratio in nitrate fraction (1)			
Radon-222 2-sigma combined uncertainty (1)			
Radon-222 (1)			
Sulfur-34/Sulfur-32 ratio in sulfate (1)			
Uranium-234 (4)			
Uranium-238 (4)			
Dissolved nitrogen gas (1)			
Argon (1)			
Tritium <sup>4</sup>			

<sup>1</sup>One sample pair exceeded mean RSD but was less than 20%.

<sup>2</sup>One sample pair exceeded mean RSD but was less than 25%.

<sup>3</sup>One sample pair exceeded 30%.

<sup>4</sup>Lamont-Doherty Earth Observatory.

Gasoline compounds (MTBE, benzene, ethylbenzene, xylene, and excluding toluene) were detected in 4 equipment and 4 field blanks. These detections and gasoline compounds detected in two ground-water samples (FPC-1, FPD-1) were caused by contamination from one of two sources: (1) the use of contaminated VOC vials or (2) equipment and field blank processing procedures. Concentrations of gasoline compounds from FPC-1 and FPD-1 (samples from October–November, 2003) and two equipment blanks and one field blank were likely caused by VOC vial contamination, indicated by a “V” next to the value ([Appendix D](#)). VOC vials used for these samples were contaminated only by gasoline compounds because of exposure of the vials to exhaust fumes and gasoline. The other two equipment and three field blanks were contaminated because of equipment blank and field blank processing errors. The processing of equipment and field blanks requires nitrogen-purged, VOC-free blank water to flow through sampling equipment before collection of quality control (QC) samples. Because the amount of VOC-free water was limited, care had to be given to ensure that the timing of the QC sample coincided with the arrival VOC-free water. Sampling before the arrival of VOC-free water caused the gasoline compounds to contaminate the equipment and field blanks. To correct the contamination, more time was given for blank water to flow through the equipment before the blanks were collected. This problem was discovered late in the project, and no gasoline compounds, excluding toluene, were detected in the last equipment and field blanks collected in this study.

## Replicates

One of the 36 environmental pesticide samples was collected in replicate and used to calculate RSD values for detected pesticides. The same four compounds were detected in both the environmental and the replicate samples. The mean RSD value for the four detected compounds was 2.9 percent, and the RSD did not exceed 5 percent for any of the compounds detected.

Four of the 59 VOC samples (environmental plus QC) were collected in replicate and used to calculate RSD values for detected VOCs. The mean RSD value for tetrachloroethene, trichloromethane, bromodichloromethane, and MTBE was 7.3, 5.9, 11.1, and 105, respectively. The RSD for MTBE was over 105 because MTBE was detected in the environmental sample but not in the duplicate sample. Consequently, the concentration used to calculate the RSD for MTBE in the replicate pair was one-fourth the minimum detection level. Four analytes were detected in this replicate pair, and RSD values for the other three compounds were greater than 10 percent but less than 15 percent. The higher overall RSD values from this replicate pair likely indicate problems with analytical instruments or sample processing.

## Spikes (Surrogates and Matrix Spikes)

Surrogate compounds were added to all of the samples that were analyzed for pesticides and VOCs, including gasoline oxygenates. Surrogate compounds are constituents that behave like pesticide or VOC analytes but are not normally found in the environment and are added to each sample just before analysis. Surrogates are used to evaluate the performance of the analytical methods in detecting similar compounds in each sample, and to determine whether the chemistry of each sample would interfere with the pesticide or VOC analysis (referred to as “matrix interference”). The results of surrogate compounds are reported as a percentage of the total amount of surrogate added to each sample and are referred to as a “recovery.” A 70- to 130-percent recovery is considered acceptable — although this range varies for individual compounds — and values outside this range indicate possible problems with the processing and analysis of samples.

Two surrogates,  $\alpha$ -HCH-*d*6 and diazinon-*d*10, were added to each of the 42 pesticide samples (environmental plus QC samples) in this study. The mean recovery was 88 percent (standard deviation = 8.8) for alpha-HCH-*d*6 and 87 percent (standard deviation = 15.6) for diazinon-*d*10. Only five of the 42 samples of the diazinon-*d*10 surrogate had recoveries less than 70 percent. Four of those five samples were collected at site FPA as part of the depth-dependent sampling. Pesticide samples collected from these wells during the previous year (October 2003) had acceptable surrogate recoveries, which suggests that matrix interference was unlikely and that the lower recovery was probably the result of laboratory processing or equipment problems.

Three surrogates were added to each of the 94 VOC samples (environmental plus QC samples), and one surrogate was added to each of the 40 gasoline oxygenate samples (environmental plus QC samples) that were collected for this study. Mean VOC surrogate recoveries for 1,2-dichloroethane-*d*4, 1-bromo-4-fluorobenzene, and toluene-*d*8 were 111 percent (standard deviation = 7.9), 91 percent (standard deviation = 9.4), and 98 percent (standard deviation = 4.6), respectively. Only one sample had a recovery of 1-bromo-4-fluorobenzene that was lower than 70 percent, and 3 samples had recoveries of 1,2-dichloroethane-*d*4 greater than 130 percent. The mean gasoline oxygenate recovery for isobutyl alcohol-*d*6 was 95 percent (standard deviation = 11.5) and all samples had recoveries between 70 and 130 percent.

A spike solution containing 31 pesticides was added to one replicate ground-water sample and analyzed for pesticides. The average matrix-spike recovery was 73 percent and the standard deviation was 21 percent. 2-Chloro-4-isopropylamino-6-amino-s-triazine (CIAT, a metabolite of atrazine, also known as deethylatrazine or DEA), which is a degradation product of atrazine and is frequently detected in ground-water, had the lowest spike recovery at 11 percent. Such a low recovery suggests the possibility of false negatives and that CIAT could be more prevalent than was detected and (or) exist at higher concentrations than were reported.

A spiked solution containing 86 VOCs was added to three duplicate ground-water samples that were collected sequentially with environmental samples and analyzed for VOCs. No compound had recoveries below 70 percent. Five compounds had one spike recovery greater than 130 percent in three spike samples. An average recovery was calculated for each of these compounds. The average minimum recovery of the three spiked samples was 99.8 percent (standard deviation = 7.8), and the average maximum recovery was 114 percent (standard deviation = 8.8). The average median recovery was 105.5 percent (standard deviation = 7.6).

## Miscellaneous Compounds

Replicate samples were collected for stable isotopes, radioactive isotopes, gross-alpha radioactivity, gross-beta radioactivity, dissolved gases, and tritium ([table B1](#)). Most analytes had relative standard deviations (RSD) less than five percent ([table B1](#)). Methane and radium-226 had an RSD greater than 20 percent and were not used in the data analysis. A RSD for radium-228 was not calculated because the certainty that the concentration of radium-228 in the replicate pair were greater than zero was less than 95 percent. Four replicate samples of uranium isotopes were used to evaluate the reproducibility of uranium isotope values. The average RSDs for replicate pairs for uranium-238 and uranium-234 were less than 3 percent, whereas the average RSD for uranium-235 was 14 percent.

Arsenic speciation samples were collected immediately after the trace element samples were collected. The sums of arsenate and arsenite were compared to the non-speciated arsenic results from the trace element sample, and RSDs were calculated between the two methods. Differences between the two methods was expected to be low because any additional arsenic species, such as organic ligands, was likely negligible. Thirty-one arsenic speciation samples were used to calculate the RSDs between schedules. The average RSD among all samples was less than 5 percent, and the highest RSD was less than 15 percent.

**Appendix C:** Major ion composition, pH, and calcite saturation in ground water from monitoring wells



**Table C1.** Major ion composition, pH, and calcite saturation in ground water from monitoring wells sampled in October and November of 2003 and 2004 in Modesto, eastern San Joaquin Valley, California.

[The five-digit parameter code is used in the U.S. Geological Survey National Water Information System (NWIS) to uniquely identify a specific constituent or property. °C, degree Celsius; CO<sub>2</sub>(g), carbon dioxide gas; LRL, laboratory reporting level; mg/L, milligram per liter; µg/L, microgram per liter; g, gram; ppm, parts per million; —, not detected; E, estimated; V, some or all of concentration could be due to contamination; PSW, public supply well. Calculated partial pressure of carbon dioxide gas is reported as a log concentration. Saturation index for calcite is the ratio of the calculated reaction quotient to the equilibrium constant; Alkalinity, sulfate and nitrate are reported in [table 8](#)]

Well identification no.	Depth category/ well type	Sample date	Residue on evaporation, dried at 180°C, dissolved (mg/L)	Calcium, dissolved (mg/L)	Magnesium, dissolved (mg/L)	Potassium, dissolved (mg/L)	Sodium, dissolved (mg/L)	Bromide, dissolved (mg/L)	Chloride, dissolved (mg/L)
Parameter code			70300	00915	00925	00935	00930	71870	00940
LRL			10	0.02, 0.01 <sup>1</sup>	0.008	0.16	0.2, 0.1	0.02, 0.016 <sup>1</sup>	0.2
FPA-1	Water-table	10/29/2003	466	51.7	23.0	3.25	82.3	0.28	11.8
FPB-1	Water-table	11/19/2003	412	59.3	26.5	2.33	44.6	0.14	7.33
FPC-1	Water-table	10/20/2003	626	88.9	37.6	3.90	86.8	0.24	18.1
FPD-1	Water-table	10/21/2003	486	77.6	36.7	2.11	24.4	1.56	11.7
FPE-1	Water-table	10/27/2004	328	42.1	24.2	1.57	33.3	0.13	29.9
OFPA-1	Water-table	11/03/2004	578	77.7	27.8	3.33	93.3	1.06	24.6
SA	Water-table	10/25/2004	668	120	54.9	2.91	45.1	0.12	18.6
SB	Water-table	10/25/2004	642	92.7	46.0	2.87	68.7	—	32.6
SC	Water-table	10/26/2004	698	106	53.5	2.93	62.4	E0.12	43.4
FPA-2	Shallow	11/04/2003	484	70.0	30.3	4.04	37.1	0.10	13
FPE-2	Shallow	10/27/2004	536	81.4	34.0	3.09	45.2	0.21	14.3
OFPA-2	Shallow	11/03/2004	676	118	43.5	4.01	58.5	0.21	76.7
FPA-3	Intermediate	11/05/2003	280	23.7	7.13	4.70	22.5	0.09	6.37
FPB-2	Intermediate	11/18/2003	279	34.2	11.3	4.88	29.7	0.17	8.25
FPC-2	Intermediate	11/12/2003	338	50.6	15.8	6.82	34.0	0.15	9.61
FPD-2	Intermediate	11/13/2003	239	23.5	8.48	3.42	34.8	0.23	9.57
FPE-3	Intermediate	10/27/2004	276	38.4	10.8	5.67	21.6	0.06	8.59
OFPA-3	Intermediate	11/03/2004	245	33.4	9.15	3.81	22.9	0.07	9.36
OFPB-2	Intermediate	11/02/2004	223	28.4	7.21	3.43	31.4	0.04	5.1
FPA-4	Deep	11/06/2003	245	18.2	6.89	6.58	39.6	0.18	8.93
FPB-3	Deep	11/18/2003	175	10.6	3.71	4.86	20.6	0.13	4.75
FPC-3	Deep	11/12/2003	137	12.0	3.95	4.83	18.1	0.04	4.45
FPD-3	Deep	11/17/2003	173	15.9	5.33	5.39	17.6	0.39	5.81
MOD025	PSW	11/13/2003	437	64.5	25.7	3.86	42.3	0.08	16.7

**Table C1.** Major ion composition, pH, and calcite saturation in ground water from monitoring wells sampled in October and November of 2003 and 2004 in Modesto, eastern San Joaquin Valley, California.—Continued

[The five-digit parameter code is used in the U.S. Geological Survey National Water Information System (NWIS) to uniquely identify a specific constituent or property. °C, degree Celsius; CO<sub>2</sub>(g), carbon dioxide gas; LRL, laboratory reporting level; mg/L, milligram per liter; µg/L, microgram per liter; g, gram; ppm, parts per million; —, not detected; E, estimated; V, some or all of concentration could be due to contamination; PSW, public supply well. Calculated partial pressure of carbon dioxide gas is reported as a log concentration. Saturation index for calcite is the ratio of the calculated reaction quotient to the equilibrium constant; Alkalinity, sulfate and nitrate are reported in [table 8](#)]

Well identification no.	Depth category/ well type	Sample date	Residue on evaporation, dried at 180°C, dissolved (mg/L)	Silica, dissolved (mg/L)	Iron, dissolved (µg/L)	Manganese, dissolved (µg/L)	pH, field, standard units	Calculated partial pressure of CO <sub>2</sub> (g) (ppm, log concentration)	Saturation index of calcite
Parameter code			70300	00955	01046	01056	00400		
LRL			10	0.04	6, 6.4	0.6, 0.8			
FPA-1	Water-table	10/29/2003	466	63.1	47	43.3	7.1	-1.48	-0.05
FPB-1	Water-table	11/19/2003	412	67.1	E6	4.9	7.4	-1.84	0.26
FPC-1	Water-table	10/20/2003	626	21.2	—	V0.6	7.2	-1.51	0.33
FPD-1	Water-table	10/21/2003	486	45.1	—	V1.8	7.3	-1.84	0.16
FPE-1	Water-table	10/27/2004	328	59.0	11	10.5	7.0	-1.64	-0.48
OFPA-1	Water-table	11/03/2004	578	71.3	—	V1.0	6.8	-1.12	-0.16
SA	Water-table	10/25/2004	668	74.7	E4	V2.5	7.0	-1.28	0.27
SB	Water-table	10/25/2004	642	73.4	—	V2.5	7.0	-1.33	0.12
SC	Water-table	10/26/2004	698	71.1	10	V1.7	7.1	-1.46	0.23
FPA-2	Shallow	11/04/2003	484	64.9	9	6.6	7.4	-1.91	0.23
FPE-2	Shallow	10/27/2004	536	66.8	—	VE0.1	7.4	-1.89	0.31
OFPA-2	Shallow	11/03/2004	676	68.0	—	V0.9	7.1	-1.49	0.25
FPA-3	Intermediate	11/05/2003	280	62.7	13	8.3	7.4	-2.29	-0.53
FPB-2	Intermediate	11/18/2003	279	63.3	20	11.5	7.7	-2.49	0.00
FPC-2	Intermediate	11/12/2003	338	66.0	E4	4.9	7.6	-2.28	0.16
FPD-2	Intermediate	11/13/2003	239	57.6	—	6.7	7.8	-2.64	-0.10
FPE-3	Intermediate	10/27/2004	276	61.0	—	VE0.1	7.6	-2.42	-0.08
OFPA-3	Intermediate	11/03/2004	245	63.6	—	—	7.4	-2.23	-0.33
OFPB-2	Intermediate	11/02/2004	223	50.7	E4	13.8	7.4	-2.18	-0.35
FPA-4	Deep	11/06/2003	245	63.4	19	23.7	7.4	-2.19	-0.54
FPB-3	Deep	11/18/2003	175	63.6	E3	8.8	8.0	-3.02	-0.38
FPC-3	Deep	11/12/2003	137	63.7	—	VE0.1	8.1	-3.13	-0.22
FPD-3	Deep	11/17/2003	173	62.4	—	V0.3	8.1	-3.09	-0.08
MOD025	PSW	11/13/2003	437	64.5	—	VE0.1	7.5	-2.01	0.30

<sup>1</sup> Laboratory reporting levels (LRL) are revised annually based on method performance. The first LRL was applied to samples collected in 2003, the second LRL was applied to samples in 2004.

**Appendix D:** Volatile organic compounds (VOC) detected in ground water from monitoring wells

**Table D1.** Volatile organic compounds (VOC) detected in ground water from monitoring wells sampled from October through November of 2003 and 2004 in Modesto, eastern San Joaquin Valley, California.

[The five-digit parameter code is used in the U.S. Geological Survey National Water Information System (NWIS) to uniquely identify a specific constituent or property; LRL, laboratory reporting level; µg/L, micrograms per liter; —, not detected; E, estimated; V, some or all of concentration could be due to contamination; NC, not collected; PSW, public supply well]

Compound class:				Trihalomethanes			Solvents				
Well identification no.	Depth category/well type	Sample date	Number of detections	Trichloro-methane (chloroform) (µg/L)	Bromo dichloro-methane (µg/L)	Tetra-chloro-ethene (PCE) (µg/L)	Trichloro-ethene (TCE) (µg/L)	cis-1,2-Dichloro-ethene (µg/L)	1,1-Dichloro-ethene (µg/L)	1,1,1-Trichloro-ethane (µg/L)	1,1-Dichloro-ethane (µg/L)
Parameter code				32106	32101	34475	39180	77093	34501	34506	34496
LRL				0.024	0.028	0.03, 0.06 <sup>1</sup>	0.038	0.024	0.024	0.032	0.035
FPA-1	Water-table	10/29/2003	3	0.12	—	—	—	—	—	—	—
FPB-1	Water-table	11/19/2003	3	0.11	—	0.12	—	—	—	—	—
FPC-1	Water-table	10/20/2003	4	3.53	0.12	E0.01	—	—	—	E0.02	—
FPD-1	Water-table	10/21/2003	0	—	—	—	—	—	—	—	—
FPE-1	Water-table	10/27/2004	1	0.13	—	—	—	—	—	—	—
OFPA-1	Water-table	11/03/2004	5	0.21	—	E0.05	—	—	—	—	—
SA	Water-table	10/25/2004	4	0.15	—	—	—	—	—	—	—
SB	Water-table	10/25/2004	3	1.85	E0.04	—	—	—	—	—	—
SC	Water-table	10/26/2004	8	2.75	E0.04	—	—	—	—	—	—
FPA-2	Shallow	11/04/2003	2	E0.06	—	0.56	—	—	—	—	—
FPE-2	Shallow	10/27/2004	3	1.00	E0.05	—	—	—	—	—	—
OFPA-2	Shallow	11/03/2004	7	0.47	—	1.21	E0.03	E0.02	E0.03	—	0.17
FPA-3	Intermediate	11/05/2003	0	—	—	—	—	—	—	—	—
FPB-2	Intermediate	11/18/2003	1	E0.02	—	—	—	—	—	—	—
FPC-2	Intermediate	11/12/2003	1	—	—	—	—	—	—	—	—
FPD-2	Intermediate	11/13/2003	0	—	—	—	—	—	—	—	—
FPE-3	Intermediate	10/27/2004	0	—	—	—	—	—	—	—	—
OFPA-3	Intermediate	11/03/2004	0	—	—	—	—	—	—	—	—
OFPB-2	Intermediate	11/02/2004	2	E0.01	—	—	—	—	—	—	—
FPA-4	Deep	11/06/2003	2	E0.08	—	E0.04	—	—	—	—	—
FPB-3	Deep	11/18/2003	0	—	—	—	—	—	—	—	—
FPC-3	Deep	11/12/2003	0	—	—	—	—	—	—	—	—
FPD-3	Deep	11/17/2003	1	—	—	—	—	—	—	—	—
PSW <sup>2,3</sup>	PSW	11/13/2003	3	1.65	0.24	0.2	—	—	—	—	—
<b>Number of wells with detections</b>				14	4	6	1	1	1	1	1
<b>Detection frequency (percent)</b>				61	17	26	4	4	4	4	4
<b>Minimum detection</b>				0.01	0.04	0.01	0.03	0.02	0.03	0.02	0.17
<b>Median detection</b>				0.1423	0.05	0.08	0.03	0.02	0.03	0.02	0.17
<b>Maximum detection</b>				3.534	0.12	1.21	0.03	0.02	0.03	0.02	0.17

**Table D1.** Volatile organic compounds (VOC) detected in ground water from monitoring wells sampled from October through November of 2003 and 2004 in Modesto, eastern San Joaquin Valley, California.—Continued

[The five-digit parameter code is used in the U.S. Geological Survey National Water Information System (NWIS) to uniquely identify a specific constituent or property; LRL, laboratory reporting level; µg/L, micrograms per liter; —, not detected; E, estimated; V, some or all of concentration could be due to contamination; PSW, public supply well]

Compound class:				Gasoline-related compounds						Refrigerants	
Well identi- fication no.	Depth category/ well type	Sample date	Number of detc- tions	Methyl <i>tert</i> - butyl ether (µg/L)	<i>m</i> -Xylene plus <i>p</i> -xylene (µg/L)	Ethyl- benzene (µg/L)	1,2,4- Trimethyl- benzene (µg/L)	<i>o</i> -Xylene (µg/L)	1,2- Dichloro- benzene (µg/L)	Trichloro- fluoro- methane (µg/L)	1,1,2- Trichloro- 1,2,2- trifluoro- ethane (µg/L)
Parameter code				78032	85795	34371	77222	77135	34536	34488	77652
LRL				0.1, 0.17 <sup>1</sup>	0.06	0.03	0.056	0.038	0.048	0.08, 0.16 <sup>1</sup>	0.038
FPA-1	<i>Water-table</i>	10/29/2003	3	E0.2	—	—	—	—	—	0.27	—
FPB-1	<i>Water-table</i>	11/19/2003	3	E0.1	—	—	—	—	—	—	—
FPC-1	<i>Water-table</i>	10/20/2003	4	V0.2	VE0.09	V0.02	—	V0.03	—	—	—
FPD-1	<i>Water-table</i>	10/21/2003	0	—	V0.02	—	—	—	—	—	—
FPE-1	<i>Water-table</i>	10/27/2004	1	—	—	—	—	—	—	—	—
OFPA-1	<i>Water-table</i>	11/03/2004	5	1.0	E0.06	E0.01	—	—	—	—	—
SA	<i>Water-table</i>	10/25/2004	4	—	E0.08	E0.02	—	E0.03	—	—	—
SB	<i>Water-table</i>	10/25/2004	3	0.2	—	—	—	—	—	—	—
SC	<i>Water-table</i>	10/26/2004	8	0.1	E0.09	E0.02	E0.03	E0.03	—	—	E0.03
FPA-2	<i>Shallow</i>	11/04/2003	2	—	—	—	—	—	—	—	—
FPE-2	<i>Shallow</i>	10/27/2004	3	—	—	—	—	—	E0.02	—	—
OFPA-2	<i>Shallow</i>	11/03/2004	7	—	—	—	—	—	—	E0.04	—
FPA-3	<i>Intermediate</i>	11/05/2003	0	—	—	—	—	—	—	—	—
FPB-2	<i>Intermediate</i>	11/18/2003	1	—	—	—	—	—	—	—	—
FPC-2	<i>Intermediate</i>	11/12/2003	1	—	—	—	E0.07	—	—	—	—
FPD-2	<i>Intermediate</i>	11/13/2003	0	—	—	—	—	—	—	—	—
FPE-3	<i>Intermediate</i>	10/27/2004	0	—	—	—	—	—	—	—	—
OFPA-3	<i>Intermediate</i>	11/03/2004	0	—	—	—	—	—	—	—	—
OFPB-2	<i>Intermediate</i>	11/02/2004	2	—	E0.04	—	—	—	—	—	—
FPA-4	<i>Deep</i>	11/06/2003	2	—	—	—	—	—	—	—	—
FPB-3	<i>Deep</i>	11/18/2003	0	—	—	—	—	—	—	—	—
FPC-3	<i>Deep</i>	11/12/2003	0	—	—	—	—	—	—	—	—
FPD-3	<i>Deep</i>	11/17/2003	1	—	—	—	—	—	—	E0.08	—
PSW <sup>2,3</sup>	<i>PSW</i>	11/13/2003	3	—	—	—	—	—	—	—	—
<b>Number of wells with detections</b>				5	4	3	2	2	1	3	1
<b>Detection frequency (percent)</b>				23	19	13	8.7	8.7	4.3	13	4.3
<b>Minimum detection</b>				0.12	0.04	0.01	0.03	0.03	0.02	0.04	0.03
<b>Median detection</b>				0.16	0.07	0.02	0.05	0.03	0.02	0.08	0.03
<b>Maximum detection</b>				0.97	0.09	0.02	0.07	0.03	0.02	0.27	0.03

<sup>1</sup> Laboratory reporting levels (LRL) are revised annually based on method performance. The first LRL was applied to samples collected in 2003; the second LRL applies to samples in 2004.

<sup>2</sup> PSW was not included in compound statistical summary.

<sup>3</sup> Dibromochloromethane and tribromomethane were detected in the PSW but were not included in the compound list because these compounds were not detected in ground-water samples.



**Appendix E:** Pesticide compounds detected in ground water from monitoring wells and the public-supply well

**Table E1.** Pesticide compounds detected in ground water from monitoring wells and the public-supply well sampled in October and November of 2003 and 2004 in Modesto, eastern San Joaquin Valley, California.

[The five-digit parameter code is used in the U.S. Geological Survey National Water Information System (NWIS) to uniquely identify a specific constituent or property. DCPA, Dacthal; LRL, laboratory reporting level; E, estimated; µg/L, microgram per liter; —, not detected; PSW, public supply well]

Well identi- fication no.	Depth category/ well type	Sample date	Number of detections	2-Chloro-4- isopropyl- amino-6- amino-s- triazine (µg/L)		Simazine (µg/L)	Atrazine (µg/L)	Prometon (µg/L)	3,4- Dichloro- aniline (µg/L)	Pendimethalin (µg/L)	Metolachlor (µg/L)	Diazinon (µg/L)	Dieldrin (µg/L)	DCPA µg/L
				04040 0.006	04035 0.005									
FPA-1	Water-table	10/29/2003	4	E0.007	0.012	0.009	0.01	—	—	—	—	—	—	—
FPB-1	Water-table	11/19/2003	4	E0.004	0.020	0.013	—	—	E0.014	—	—	—	—	—
FPC-1	Water-table	10/20/2003	4	E0.011	0.108	0.044	—	—	0.013	—	—	—	—	—
FPD-1	Water-table	10/21/2003	4	E0.096	0.048	0.013	—	—	0.015	—	—	—	—	—
FPE-1	Water-table	10/27/2004	3	—	0.013	—	E0.010	—	—	—	—	0.005	—	—
OFPA-1	Water-table	11/03/2004	2	E0.008	0.006	—	—	—	—	—	—	—	—	—
SA	Water-table	10/25/2004	1	—	—	—	—	—	—	—	—	—	—	E0.002
SB	Water-table	10/25/2004	2	—	0.018	0.017	—	—	—	—	—	—	—	—
SC	Water-table	10/26/2004	1	—	0.023	—	—	—	—	—	—	—	—	—
FPA-2	Shallow	11/04/2003	0	—	—	—	—	—	—	—	—	—	—	—
FPE-2	Shallow	10/27/2004	3	E0.010	0.007	0.009	—	—	—	—	—	—	E0.005	—
OFPA-2	Shallow	11/03/2004	1	—	—	—	—	—	—	—	—	—	—	—
FPA-3	Intermediate	11/05/2003	0	—	—	—	—	—	—	—	—	—	—	—
FPB-2	Intermediate	11/18/2003	0	—	—	—	—	—	—	—	—	—	—	—
FPC-2	Intermediate	11/12/2003	2	E0.005	—	0.008	—	—	—	—	—	—	—	—
FPD-2	Intermediate	11/13/2003	1	—	—	—	—	—	—	—	E0.004	—	—	—
FPE-3	Intermediate	10/27/2004	0	—	—	—	—	—	—	—	—	—	—	—
OFPA-3	Intermediate	11/03/2004	0	—	—	—	—	—	—	—	—	—	—	—
OFPB-2	Intermediate	11/02/2004	2	E0.013	—	0.059	—	—	—	—	—	—	—	—
FPA-4	Deep	11/06/2003	1	E0.004	—	—	—	—	—	—	—	—	—	—
FPB-3	Deep	11/18/2003	0	—	—	—	—	—	—	—	—	—	—	—
FPC-3	Deep	11/12/2003	0	—	—	—	—	—	—	—	—	—	—	—
FPD-3	Deep	11/17/2003	0	—	—	—	—	—	—	—	—	—	—	—
PSW <sup>2</sup>	PSW	11/13/2003	3	E0.006	0.009	0.013	—	—	—	—	—	—	—	—
<b>Number of wells with detections<sup>2</sup></b>				9	9	8	2	2	2	1	1	1	1	1
<b>Detection frequency (percent)</b>				39.1	39	35	9	9	9	4	4	4	4	4
<b>Minimum detection</b>				0.004	0.006	0.008	0.010	0.010	0.013	0.014	0.004	0.006	0.006	0.002
<b>Median detection</b>				0.0079	0.018	0.013	0.010	0.010	0.014	0.014	0.004	0.006	0.006	0.002
<b>Maximum detection</b>				0.096	0.108	0.059	0.010	0.010	0.015	0.014	0.004	0.006	0.006	0.002

<sup>1</sup> PSW was not included in compound statistical summary.

<sup>2</sup> Laboratory reporting levels (LRL) are revised annually based on method performance. The first LRL was applies to samples collected in 2003, the second LRL applies to samples in 2004



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