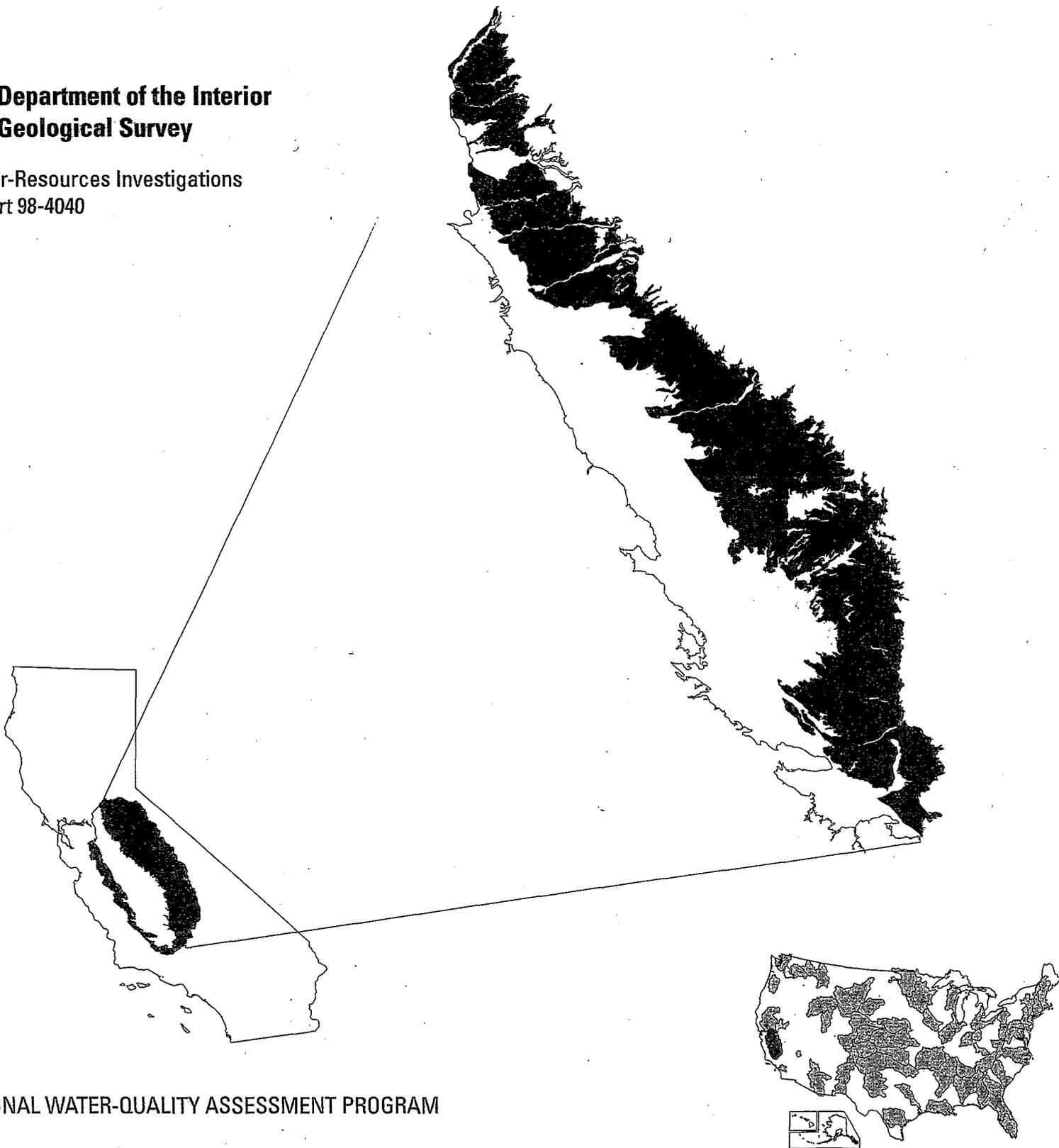


Nitrate and Pesticides in Ground Water in the Eastern San Joaquin Valley, California: Occurrence and Trends

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

Water-Resources Investigations
Report 98-4040



NATIONAL WATER-QUALITY ASSESSMENT PROGRAM

D - 0 3 9 8 8 8

D-039888

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By KAREN R. BUROW, SYLVIA V. STORK, and NEIL M. DUBROVSKY

U.S. GEOLOGICAL SURVEY

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6440-36

Sacramento, California
1998



D - 0 3 9 8 8 9

D-039889

U.S. DEPARTMENT OF THE INTERIOR
BRUCE BABBITT, Secretary

U.S. GEOLOGICAL SURVEY
Thomas J. Casadevall, Acting Director



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FOREWORD

The mission of the U.S. Geological Survey (USGS) is to assess the quantity and quality of the earth resources of the Nation and to provide information that will assist resource managers and policymakers at Federal, State, and local levels in making sound decisions. Assessment of water-quality conditions and trends is an important part of this overall mission.

One of the greatest challenges faced by water-resources scientists is acquiring reliable information that will guide the use and protection of the Nation's water resources. That challenge is being addressed by Federal, State, interstate, and local water-resource agencies and by many academic institutions. These organizations are collecting water-quality data for a host of purposes that include: compliance with permits and water-supply standards; development of remediation plans for specific contamination problems; operational decisions on industrial, wastewater, or water-supply facilities; and research on factors that affect water quality. An additional need for water-quality information is to provide a basis on which regional- and national-level policy decisions can be based. Wise decisions must be based on sound information. As a society we need to know whether certain types of water-quality problems are isolated or ubiquitous, whether there are significant differences in conditions among regions, whether the conditions are changing over time, and why these conditions change from place to place and over time. The information can be used to help determine the efficacy of existing water-quality policies and to help analysts determine the need for and likely consequences of new policies.

To address these needs, the U.S. Congress appropriated funds in 1986 for the USGS to begin a pilot program in seven project areas to develop and refine the National Water-Quality Assessment (NAWQA) Program. In 1991, the USGS began full implementation of the program. The NAWQA Program builds upon an existing base of water-quality studies of the USGS, as well as those of other Federal, State, and local agencies. The objectives of the NAWQA Program are to:

- Describe current water-quality conditions for a large part of the Nation's freshwater streams, rivers, and aquifers.

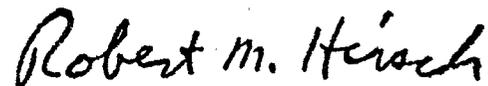
- Describe how water quality is changing over time.
- Improve understanding of the primary natural and human factors that affect water-quality conditions.

This information will help support the development and evaluation of management, regulatory, and monitoring decisions by other Federal, State, and local agencies to protect, use, and enhance water resources.

The goals of the NAWQA Program are being achieved through ongoing and proposed investigations of 60 of the Nation's most important river basins and aquifer systems, which are referred to as study units. These study units are distributed throughout the Nation and cover a diversity of hydrogeologic settings. More than two-thirds of the Nation's freshwater use occurs within the 60 study units and more than two-thirds of the people served by public water-supply systems live within their boundaries.

National synthesis of data analysis, based on aggregation of comparable information obtained from the study units, is a major component of the program. This effort focuses on selected water-quality topics using nationally consistent information. Comparative studies will explain differences and similarities in observed water-quality conditions among study areas and will identify changes and trends and their causes. The first topics addressed by the national synthesis are pesticides, nutrients, volatile organic compounds, and aquatic biology. Discussions on these and other water-quality topics will be published in periodic summaries of the quality of the Nation's ground and surface water as the information becomes available.

This report is an element of the comprehensive body of information developed as part of the NAWQA Program. The program depends heavily on the advice, cooperation, and information from many Federal, State, interstate, Tribal, and local agencies and the public. The assistance and suggestions of all are greatly appreciated.



Robert M. Hirsch
Chief Hydrologist

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CONVERSION FACTORS, ABBREVIATIONS, ACRONYMS, AND WELL-NUMBERING SYSTEM

Multiply	By	To obtain
acre	4,047	square meter
inch (in.)	2.54	centimeter
foot (ft)	0.3048	meter
mile (mi)	1.609	kilometer
square mile (mi ²)	2.590	square kilometer
pound, avoirdupois (lb)	0.4536	kilogram
pound per acre (lb/acre)	1.12	kilograms per hectare

Abbreviations:

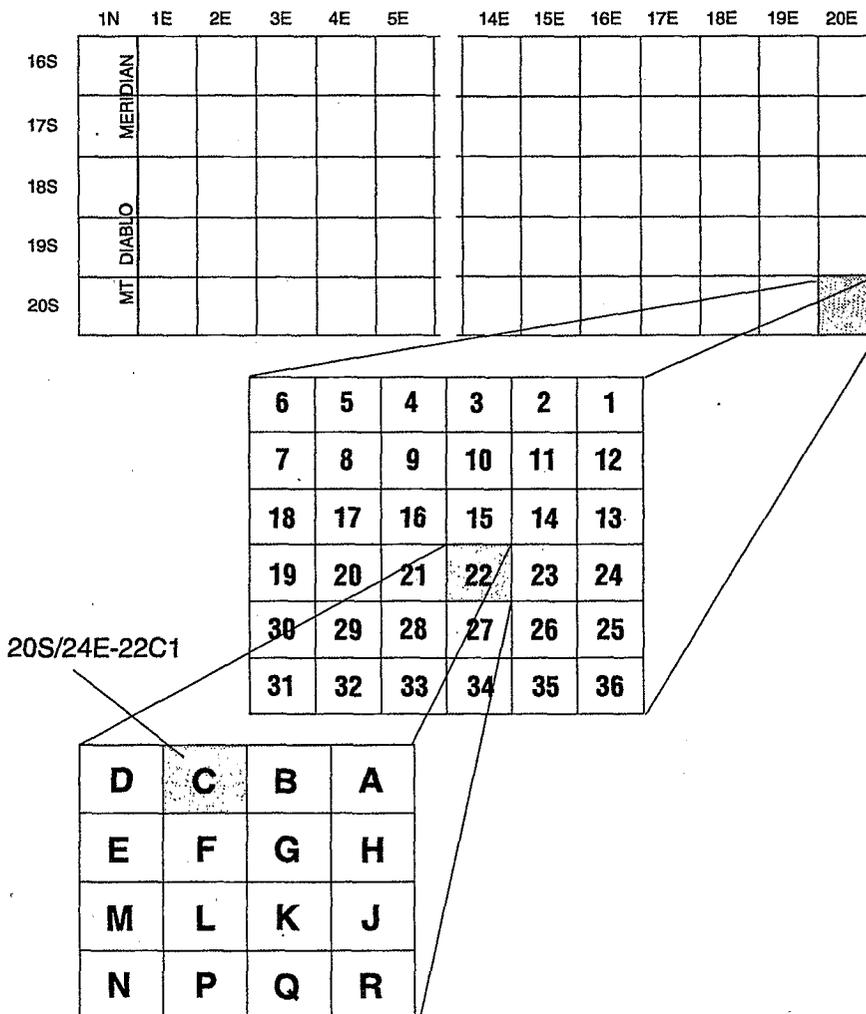
µg/L	microgram per liter
µm	micrometer
µS/cm	microsiemen per centimeter
L	liter
mg/L	milligram per liter
mL	milliliter
pCi/L	picocuries per liter
a.i	active ingredient
DBCP	1,2-dibromo-3-chloropropane
DCPA	chlorobenzoic acid
EDB	1,2-dibromoethane
EPTC	thiocarbamate
GC/ECD	gas chromatography/electron-capture detection
GC/MS	gas chromatography/mass spectrometry
HCH	organochlorine
HPLC	high performance liquid chromatography
MCL	maximum contaminant level
MCPA	chlorophenoxy acid
MDL	method detection limit
MRL	method reporting limit
QC	quality control
VOC	volatile organic compound

Acronyms:

NAWQA National Water Quality Assessment
 NWQL National Water Quality Laboratory
 RASA Regional Aquifer-System Analysis
 USGS U.S. Geological Survey

Well-Numbering System

Wells are identified and numbered according to their location in the rectangular system for the subdivision of public lands. Identification consists of the township number, north or south; the range number, east or west; and the section number. Each section is divided into sixteen 40-acre tracts lettered consecutively (except I and O), beginning with "A" in the northeast corner of the section and progressing in a sinusoidal manner to "R" in the southeast corner. Within the 40-acre tract, wells are sequentially numbered in the order they are inventoried. The final letter refers to the base line and meridian. In California, there are three base lines and meridians; Humboldt (H), Mount Diablo (M), and San Bernardino (S). All wells in the study area are referenced to the Mount Diablo base line and meridian (M) Well numbers consist of 15 characters and follow the format 020S024E22C01. In this report, well numbers are abbreviated and written 20S/24E-22C1. Wells in the same township and range are referred to only by their section designation, 22C1. The following diagram shows how the number for well 20S/24E-22C1 is derived.



Nitrate and Pesticides in Ground Water in the Eastern San Joaquin Valley, California: Occurrence and Trends

By Karen R. Burow, Sylvia V. Stork, and Neil M. Dubrovsky

ABSTRACT

The occurrence of nitrate and pesticides in ground water in California's eastern San Joaquin Valley may be greatly influenced by the long history of intensive farming and irrigation and the generally permeable sediments. This study, which is part of the U.S. Geological Survey National Water-Quality Assessment Program, was done to assess the quality of the ground water and to do a preliminary evaluation of the temporal trends in nitrate and pesticides in the alluvial fans of the eastern San Joaquin Valley. Ground-water samples were collected from 30 domestic wells in 1995 (each well was sampled once during 1995). The results of the analyses of these samples were related to various physical and chemical factors in an attempt to understand the processes that control the occurrence and the concentrations of nitrate and pesticides. A preliminary evaluation of the temporal trends in the occurrence and the concentration of nitrate and pesticides was done by comparing the results of the analyses of the 1995 ground-water samples with the results of the analyses of the samples collected in 1986-87 as part of the U.S. Geological Survey Regional Aquifer-System Analysis Program.

Nitrate concentrations (dissolved nitrate plus nitrite, as nitrogen) in ground water sampled in 1995 ranged from less than 0.05 to 34 milligrams per liter, with a median concentration of 4.6 milligrams per liter. Nitrate concentrations exceeded the maximum contaminant level of 10 milligrams per liter (as nitrogen) in 5 of the 30

ground-water samples (17 percent), whereas 12 of the 30 samples (40 percent) had nitrate concentrations less than 3.0 milligrams per liter. The high nitrate concentrations were associated with recently recharged, well-oxygenated ground water that has been affected by agriculture (indicated by the positive correlations between nitrate, dissolved-oxygen, tritium, and specific conductance).

Twelve pesticides were detected in 21 of the 30 ground-water samples (70 percent) in 1995, although only 5 pesticides were detected in more than 10 percent of the ground-water samples. All 12 pesticides were detected at concentrations below the maximum contaminant levels, except the banned soil fumigants 1,2-dibromo-3-chloropropane (3 detections) and 1,2-dibromoethane (1 detection). Atrazine and desethyl atrazine (a transformation product of atrazine) were the most frequently detected pesticides; they were detected in 11 ground-water samples. The frequent detections of atrazine and desethyl atrazine may be related either to past applications of atrazine or to recent application on rights-of-way. Simazine was detected in 10 ground-water samples and diuron was detected in 4 ground-water samples. The detections of simazine and diuron are generally consistent with their reported applications on the crops near the wells where they were detected. 1,2,3-trichloropropane, a manufacturing by-product of 1,2-dichloropropane and 1,3-dichloropropene formulations, was detected in 4 ground-water samples. The occurrence of 1,2,3-trichloropropane, 1,2-dibromo-3-chloropropane, and 1,2-dibromoethane is probably related to past

use. Similar to nitrate concentrations, pesticide occurrence was positively correlated to dissolved-oxygen concentrations, indicating that areas with high dissolved-oxygen concentrations may be vulnerable to contamination by nitrate and pesticides. High dissolved-oxygen concentrations may be associated with water that has been rapidly recharged.

A comparison of the concentrations and the occurrence of nitrate and pesticides between 1986–87 and 1995 indicates that nitrate concentrations may pose a greater threat to the quality of the ground-water resource in this region than pesticides, in the context of current drinking-water standards. Nitrate concentrations were significantly higher in the 1995 ground-water samples than in the 1986–87 samples collected from the same wells. Although the number of pesticide detections in 1995 is higher than the number of pesticide detections in 1986–87, the difference in detections is attributed to the lower detection limits that have resulted from improvements in analytical methods. When the data are censored at the highest detection or reporting limit, the number of pesticide detections between the 1986–87 and the 1995 samples did not increase. Furthermore, the concentrations of the detected pesticides may have decreased. The difference in temporal trends between the occurrence and the concentrations of nitrate and pesticides may be related to the large spatial variability in the amounts and the locations of the pesticide applications or to the difference in chemical properties of the pesticides; however, the results of this comparison may also be affected by the relatively small data set.

INTRODUCTION

Ground water is the principal source of drinking water and a significant source of water for agricultural supply in the San Joaquin–Tulare Basins of the San Joaquin Valley of California (fig. 1). Most of the population and 96 percent (in 1988) of the ground-water use within the San Joaquin Basin (north) and the hydrologically closed Tulare Basin (south) is in the eastern alluvial fan physiographic region (Fred Stumpf, California Department of Water Resources,

written commun., 1990). This area has been intensively farmed and irrigated since the early 1900's. The large quantity of fertilizers and pesticides used in this area, the intense irrigation, and the generally permeable sediments have resulted in a history of problems related to ground-water contamination from nitrate and pesticides (Page and LeBlanc, 1969; Cohen, 1986; Troiano and Segawa, 1987; Anton and others, 1988; Domagalski and Dubrovsky, 1991; Miller and others, 1994; Pease and others, 1995).

This study was done to assess the quality of ground water in the eastern San Joaquin Valley and to do a preliminary evaluation of temporal trends in the occurrence and the concentrations of nitrate and pesticides. The focus of many previous studies has been on the distribution of nitrate and pesticides and on factors related to measured concentrations; none of the studies, however, have been on trends in nitrate and pesticide occurrence and concentrations in the eastern alluvial fan region of the San Joaquin Valley. This study is part of the U.S. Geological Survey (USGS) National Water-Quality Assessment (NAWQA) ground-water studies in the San Joaquin–Tulare Basins (Burow and others, in press; Gronberg and others, in press). Because few assessments have been done to date on trends in ground-water quality in the United States, this study provides an important preview of the evaluation of trends by the NAWQA Program. The NAWQA Program was designed to assess the status of and trends in the quality of the Nation's ground- and surface-water resources and to link the status and trends with an understanding of the natural and the human factors that affect the quality of water (Gilliom and others, 1995). As part of this study, ground-water samples were collected from 30 domestic wells in the eastern San Joaquin Valley in 1995. To evaluate the temporal trends in nitrate and pesticides, chemical data for the 1995 samples were compared with the chemical data for samples collected in 1986–87 as part of the USGS Regional Aquifer-System Analysis (RASA) Program.

Background

Elevated concentrations of nitrate in ground water pose a serious threat to the quality of ground-water resources throughout the United States (Hallberg, 1989; Mueller and others, 1995). The maximum contaminant level (MCL) for nitrate concentrations in drinking water supplied by public water suppliers is 10 mg/L, as nitrogen (U.S. Environmental Protection

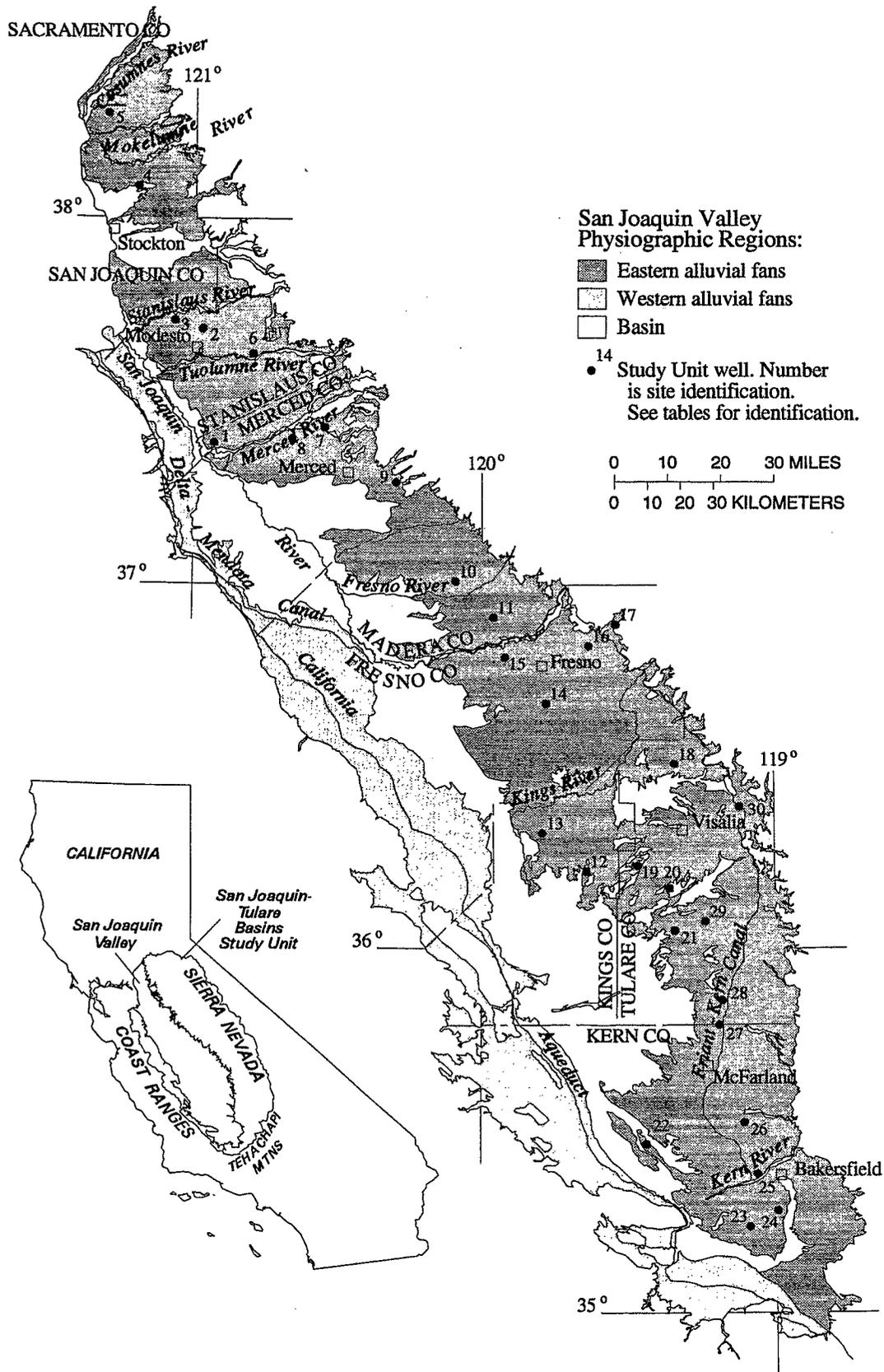


Figure 1. Location of study area and San Joaquin Valley physiographic regions.

Agency, 1996). Nitrate concentrations above the MCL have been linked to infant methemoglobinemia (a blood disorder) (Comly, 1945). Elevated nitrate concentrations may also be a factor in the incidence of non-Hodgkin's lymphoma (Weisenburger, 1991; Ward and others, 1996).

Nitrate contamination of ground water in California is an issue of concern, in part, because nitrate concentrations have increased over time (Nightingale, 1970; Schmidt, 1972; Madison and Brunett, 1985; Lowry, 1987; Anton and others, 1988). Nitrate occurs naturally in ground water; however, in agricultural areas, elevated concentrations of nitrate occur as the result of farming operations where nitrogen fertilizers are applied (Nightingale, 1972; Owens and others, 1992). Furthermore, the use of nitrogen fertilizer generally has increased since the 1950's (Alexander and Smith, 1990). However, other sources of nitrogen, such as animal waste and sewage effluent, have also been linked to the elevated concentrations (Behnke and Haskell, 1968; Schmidt, 1972; Lowry, 1987; Davis, 1995; MacLeod and others, 1995; Vowinkel and Tapper, 1995). Nitrate has also been linked to the hydrogeology of the area; to well-construction factors, such as well depth and water use (Nightingale and Bianchi, 1980; Troiano and Sitts, 1990; Knox and Moody, 1991; MacLeod and others, 1995); and to general water-quality characteristics, such as specific conductance and dissolved-oxygen concentrations (Schmidt, 1983).

Pesticides, a generic term for compounds used as fungicides, herbicides, insecticides, nematocides, and rodenticides, are widely used throughout the United States in agricultural and nonagricultural settings. Since the 1970's, at least 143 pesticides and 21 of their transformation products have been detected in ground water in more than 43 states (Barbash and Resek, 1996). The concentrations of these pesticides typically are less than the maximum concentrations allowed by State and Federal drinking-water standards (Barbash and Resek, 1996); however, the health effects from exposure to low concentrations of pesticides and the cumulative long-term effect on regional water quality are not fully understood. Furthermore, the widespread, diffuse nature of the occurrence of pesticides makes the effects difficult to assess. In the San Joaquin Valley, where a large quantity and a wide variety of pesticides are used, compounds frequently detected in ground water include soil fumigants such as 1,2-dibromo-3-chloropropane (DBCP) (Cohen, 1986); 1,2-dibromoethane (EDB); 1,2-dichloropropane; 1,3-dichloropro-

pene; and other pesticides, such as simazine, atrazine, diuron, bromacil, and diazinon (Domagalski and Dubrovsky, 1991; Miller and others, 1994; Pease and others, 1995).

Pesticides in ground water result from both agricultural and nonagricultural use. Study of the factors related to the occurrence of pesticides in ground water can aid in identifying areas that are more vulnerable to pesticide contamination. It is difficult, however, to establish a causal relation between these factors and the occurrence of pesticides in ground water because of the complex interaction of physical, chemical, and biological processes. Barbash and Resek (1996) indicate that more pesticide detections occur in areas with high soil permeability, rapid infiltration rates, and shallow wells. Zalkin and others (1984) correlated the occurrence of EDB and simazine in the unsaturated zone to organic content in shallow soils (less than 8 ft below land surface) and to moisture content at greater depths at several sites in their study area in spite of the difference in chemical properties of the two pesticides. Koterba and others (1993) observed that ground-water samples from areas with well-drained soils had a higher frequency of pesticide detections than did samples from areas with poorly drained soils. Higher frequencies of pesticide detections also have been related to well-depth characteristics, such as screen depth below the water table (Koterba and others, 1993), and to average well depth from land surface (Sievers and Fulhage, 1992). During recent studies in California (Wilkerson and others, 1985; Troiano and others, 1994), variables that could be used to predict the vulnerability of ground water to pesticide contamination were evaluated. The results of these studies indicate that the high frequencies of pesticide detections are related to shallow well depths, land use, and generally more coarse-grained soil textures.

Purpose and Scope

This report presents the results of analyses of nitrate and pesticides in ground water in the eastern alluvial fan physiographic region of the San Joaquin Valley and a preliminary evaluation of the trends in the occurrence and concentrations of nitrate and pesticides between 1986-87 and 1995. In 1995, ground-water samples were collected from 30 domestic wells; the samples were analyzed for various constituents, including nitrate, pesticides, volatile organic compounds, major ions, and tritium. One ground-water sample was

collected from each well in 1995. Twenty-three of the 30 wells sampled in 1995 also had been sampled during 1986–87 as part of the RASA Program. The relation between nitrate and pesticides and various physical and chemical characteristics was explored using the 1995 data. The characteristics explored include nitrogen fertilizer application and pesticide use; physical characteristics, such as well depth and depth to water; and water-quality characteristics, such as specific conductance, oxidation-reduction indicators, and major-ion concentrations. In addition, nitrate and pesticide concentrations and the number of pesticide detections in ground-water samples collected in 1995 were compared with the nitrate and pesticide concentrations and the number of pesticide detections in the samples collected during 1986–87.

Description of Study Area

The San Joaquin–Tulare Basins study unit in central California (fig. 1) covers about 31,250 mi². The San Joaquin Valley is a flat structural trough with thousands of feet of sediment derived from the Sierra Nevada to the east and the Coast Ranges to the west. The sediments consist of interlayered lenses of gravel, sand, silt, and clay (Bull, 1964a, b, 1972; Dale and others, 1966); Croft and Gordon, 1968; Page and LeBlanc, 1969; Hotchkiss and Balding, 1971; Miller and others, 1971; Page, 1986; Laudon and Belitz, 1991). The sediments in the eastern San Joaquin Valley have a low organic content and consist of weathered granitic rocks with smaller amounts of metasedimentary and metavolcanic rocks. These Sierra Nevada sediments interfinger near the axis of the valley with the sediments derived from the Coast Ranges.

The San Joaquin Valley consists of three physiographic regions: the eastern alluvial fan, the western alluvial fan, and the basin (Gronberg and others, in press). The eastern alluvial fan region was selected for this study because of the concentrated population and the larger amount of ground-water use in this region compared with other regions. The total population in this region was 2,052,538 in 1990; major urban areas include the cities of Fresno, Bakersfield, Stockton, and Modesto. Seventy-one percent of the land use in this region is agricultural; the primary crops are grapes, cotton, almonds, and corn. The surface water used for valley farming comes from reservoirs in the Sierra Nevada and its foothills; the water is transported using a network of Federal, State, and local irrigation canals. In

1988, ground water accounted for about one-half of the water used in the eastern alluvial fan region (Fred Stumpf, California Department of Water Resources, written commun., 1990). However, the use of ground water for irrigation is dependent on the amount of surface water available. During dry years, additional ground water is pumped to compensate for reductions in surface-water deliveries.

Throughout the San Joaquin Valley, most of the fine-grained layers are discontinuous. However, one major fine-grained layer, the Corcoran Clay Member of the Tulare Formation, has been mapped. The Corcoran Clay Member, a diatomaceous clay, is part of the modified E clay unit (Page, 1986). This clay underlies a large part of the basin and the western alluvial fan regions and, to a lesser extent, the eastern alluvial fan region. The sediments in the San Joaquin Valley are generally coarsest near the upper parts of the alluvial fans along the edge of the valley and finest near the valley trough. The regional aquifer in the San Joaquin Valley consists of an upper, unconfined to semi-confined zone separated from a lower, confined zone by the Corcoran Clay Member (Poland and Lofgren, 1984; Bertoldi and others, 1991). Many wells have been screened both above and below the Corcoran Clay Member and thus may have reduced the effectiveness of the Corcoran Clay Member as a confining unit. Williamson and others (1989) defined the regional aquifer as a single, heterogeneous aquifer with varying vertical leakance and confinement. For the purposes of this study, the upper unconfined aquifer is the zone above the Corcoran Clay Member where the Corcoran Clay is present and the zone that is as much as 250 ft below the water table where the Corcoran Clay is not present.

Prior to irrigation in the valley, the principal area of ground-water recharge was the coarse-grained, upper alluvial fan sediments along the edge of the valley. Ground water flowed toward the axis of the valley where it discharged in the basin region as evapotranspiration and to streams (Bertoldi and others, 1991). Although the ground-water recharge and discharge areas have changed owing to pumping for irrigation and public supply, ground-water movement is still toward the axis of the valley (Bertoldi and others, 1991, fig. 13). Depth to water in the eastern alluvial fan region generally ranges from about 20 ft below land surface in the north and near the rivers to as much as 400 ft below land surface in the south near Bakersfield (California Department of Water Resources, 1990a,b).

The chemistry of the ground water in the eastern alluvial fan region has been influenced by the source of the water recharged to the aquifer (Bertoldi and others, 1991). Recharge from precipitation is small compared with recharge from irrigation (derived from both surface and ground water), especially in the southern part of the region where annual rainfall averages less than 5 in. (Rantz, 1969). The concentration of dissolved solids in the shallow ground water in the eastern alluvial fan region generally is low to moderate, commonly less than 500 mg/L (Bertoldi and others, 1991). The dominant anion is bicarbonate, with lesser amounts of chloride and sulfate. Calcium and sodium proportions typically are higher than magnesium. Ground water in the basin region is generally more chemically reduced and contains higher dissolved-solids concentrations than in the eastern and western alluvial fan regions (Davis and others, 1959; Bertoldi and others, 1991). The increasing dissolved-solids concentrations result from cation exchange processes as the water moves through the sediments and from evaporative concentration in the discharge zone.

Acknowledgments

This study could not have been completed without the cooperation of landowners in the eastern San Joaquin Valley, who allowed access to their property. In addition, the California Department of Water Resources, the California Department of Pesticide Regulation, various county health departments, and local irrigation districts provided data and other services needed to complete this investigation.

STUDY DESIGN AND METHODS

Well Network

To assess the occurrence of nitrate and pesticides in the study area, 30 domestic wells, randomly distributed, were selected for sampling using NAWQA protocols and procedures as a guide (Lapham and others, 1995). The random distribution of the sampling locations (fig. 1) was designed to minimize spatial bias in the data set. The eastern alluvial fan region was divided into 30 equal-area parts or "cells" using a computer-

ized, stratified, random site-selection procedure (Scott, 1990). To evaluate temporal trends in nitrate and pesticides, wells that were sampled in 1986–87 during the RASA Program were again selected for the 1995 sampling whenever possible. Although many existing wells in the study area previously had been sampled for nitrate and pesticides, the RASA wells were targeted for resampling in 1995 because they had been sampled by the USGS and analyzed at the USGS National Water Quality Laboratory (NWQL) and, therefore, were expected to be generally comparable to the NAWQA sampling results. In addition, the well-construction information and the sampling methods were documented (Domagalski and Dubrovsky, 1991); the well-construction information was needed to develop a consistent network design for this study.

Within each equal-area cell, wells were selected for the 1995 sampling using the following criteria: (1) the well was a domestic supply well, (2) the well had a submersible pump, and (3) the well depth was documented. Domestic wells were selected for sampling because they generally are pumped at a lower rate than irrigation or municipal wells. Water samples from low-volume wells, such as the domestic wells, are more likely to represent smaller, more discrete parcels of water that can more easily be linked to specific processes affecting the ground water at each well site than would samples from high-volume wells. Wells with submersible pumps were selected to minimize the possible aeration of samples from jet pumps and the contamination of water samples from turbine pump lubricants.

During the first pass of well selection, wells were identified that were screened above the Corcoran Clay Member, where present, or less than 200 ft below the water table, where the Corcoran Clay Member was not present. If more than one well in a cell met the above criteria, wells with relatively short screened intervals were selected to minimize the effects of dilution. Wells were then randomly prioritized. After compiling a list of candidate wells, field visits were made to each well to secure permission from the landowner for sampling and to determine whether the well was accessible for sampling. In cells with no suitable wells, the selection criterion for depth was expanded to include wells that were screened at depths less than 250 ft below the water table, where the Corcoran Clay Member was not present. If no suitable wells were identified with this new depth criterion, wells near or on the boundary of an adjacent cell were chosen to represent that cell. Finally,

in cells where no wells met the above criteria, wells were selected either from other USGS well networks (Hamlin, 1993) or by going door-to-door within the area of the targeted cell and obtaining permission from the landowner to sample.

Water-Quality Data Collection and Analysis

Ground-water samples were collected from the 30 domestic wells in 1995 using sampling protocols developed by the NAWQA Program to minimize contamination during sampling and to promote the collection of high-quality, consistent ground-water data among NAWQA study units throughout the Nation (Koterba and others, 1995). Collection lines were attached to a sampling port to enable the collection of a sample before the water entered the pressure tank to minimize loss of volatile compounds and to reduce the chance of sample contamination from pressure-tank liners or from other materials that the sample water may have contacted prior to collection. The collection lines were made of Teflon to minimize cross-contamination of organic compounds; stainless steel fittings were used to attach the lines to the well head. Sample collection and preservation chambers were used to reduce contamination from airborne contaminants. Before a sample was collected, each well was purged until the readings of pH, dissolved oxygen, specific conductance, redox, turbidity, and temperature became stable (as defined in Koterba and others, 1995). Generally, at least three casing volumes of water were extracted to ensure that the sample was from ground water in the aquifer and not from water stored in the well. Sample collection, processing, storage, and shipment procedures minimized changes in water chemistry until the sample could be analyzed in the laboratory.

Ground-water samples were analyzed for a variety of constituents, including nitrate, pesticides, volatile organic compounds (VOC), major ions, and tritium (Willie Kinsey and Mark Johnson, U.S. Geological Survey, written commun., 1997). Concentrations of nitrate plus nitrite are referred to as nitrate in this report because the nitrite concentrations were very low (maximum of 0.1 mg/L) compared with the nitrate concentrations, which ranged from less than 0.05 to 34 mg/L. Nitrite accounted for a maximum of 3.8 percent of the total nitrate plus nitrite concentrations in the samples with nitrite detections. Analyses of all constituents, except tritium, were completed at the USGS NWQL in

Arvada, Colorado. Tritium was analyzed at the University of Miami Tritium Laboratory. Nitrate and major ion samples were filtered using a 0.45- μ m pleated capsule filter and analyzed using standard methods (Fishman and Friedman, 1985). Pesticide samples were filtered using a 0.7- μ m baked glass-fiber filter to obtain a 1-L sample for analysis.

Two methods were used to analyze pesticides and selected transformation products: C-18 solid-phase extraction and capillary column gas chromatography/mass spectrometry (GC/MS) (Zaug and others, 1995) was used to analyze 46 compounds, and CarboPak-B solid-phase extraction and high-performance liquid chromatography (HPLC) (Werner and others, 1996) was used to analyze 41 compounds. Three compounds (carbaryl, carbofuran, and linuron) were analyzed using both methods (table 1). Samples for a suite of 60 VOCs (table 2) were collected in 40-mL vials that were filled with unfiltered water, preserved with hydrochloric acid, and capped with lids designed to minimize loss owing to volatilization. The VOC samples were analyzed using purge and trap capillary GC/MS (Rose and Schroeder, 1995). Additional samples were collected and analyzed to detect low-level concentrations of EDB and DBCP using gas chromatography/electron-capture detection (GC/ECD) (Fishman, 1993). One liter of unfiltered water was collected for tritium samples; the samples were analyzed using electrolytic enrichment followed by gas counting (Ann Mullin, U.S. Geological Survey, written commun., 1996).

Quality-Control Data

Quality-control (QC) samples were collected during the 1995 sampling to evaluate bias and precision while obtaining environmental data. The QC-sample results were aggregated from this study and from two other NAWQA ground-water studies (Willie Kinsey and Mark Johnson, U.S. Geological Survey, written commun., 1997) that were completed in the San Joaquin Valley during the same time period. The aggregated results provided a more representative measure of bias and precision. The QC samples collected for this study were from domestic wells, but the QC samples collected for the two other studies were from both domestic and monitoring wells. The QC samples collected for all three studies were preserved and analyzed using the same methods and equipment used to collect the environmental ground-water samples.

Table 1. Pesticides analyzed in ground-water samples collected from domestic wells in the eastern San Joaquin Valley, California, 1995

[µg/L, microgram per liter]

Pesticides	Total number of samples	Method detection limit (µg/L)	Pesticides	Total number of samples	Method detection limit (µg/L)	Pesticides	Total number of samples	Method detection limit (µg/L)
Amids								
Alachlor	30	¹ 0.002	Napropamide	30	¹ 0.003	Propachlor	30	¹ 0.007
Metolachlor	30	¹ 0.002	Pronamide	30	¹ 0.003	Propanil	30	¹ 0.004
Carbamates								
Aldicarb	26	² 0.016	Carbofuran, 3-	26	² 0.014	Oxamyl	29	² 0.018
Aldicarb sulfone ³	26	² 0.016	EPTC	30	¹ 0.002	Pebulate	30	¹ 0.004
Aldicarb	26	² 0.021	Methiocarb	29	² 0.026	Propham	29	² 0.035
Butylate	30	¹ 0.002	Methomyl	26	² 0.017	Propoxur	29	² 0.035
Carbaryl	29	^{1,2} 0.003	Molinate	30	¹ 0.004	Thiobencarb	30	¹ 0.002
Carbofuran	29	^{1,2} 0.028	1-Naphthol ³	29	² 0.007	Triallate	30	¹ 0.001
Chlorophenoxy Herbicides								
2,4-D (acid)	30	² 0.035	Dichlorprop (2,4-DP)	30	² 0.032	Silvex (2,4,5-TP)	30	² 0.021
2,4-DB	30	² 0.035	MCPA	30	² 0.05	2,4,5-T	30	² 0.035
Dacthal, mono-	30	² 0.017	MCPB	30	² 0.035	Triclopyr	30	² 0.05
Dinitroanilines								
Benfluralin	30	¹ 0.002	Oryzalin	29	² 0.019	Trifluralin	30	¹ 0.002
Ethalfuralin	30	¹ 0.004	Pendimethalin	30	¹ 0.004			
Organochlorines								
Chlorothalonil	29	² 0.035	Dichlobenil	29	² 0.020	γ-HCH	30	¹ 0.004
Dacthal (DCPA)	30	¹ 0.002	Dieldrin	30	¹ 0.001			
<i>p,p'</i> -DDE ³	30	¹ 0.006	α-HCH ³	30	¹ 0.002			
Organophosphates								
Azinphos-methyl	30	¹ 0.001	Ethoprop	30	¹ 0.003	Parathion	30	¹ 0.004
Chlorpyrifos	30	¹ 0.05	Fonofos	30	¹ 0.003	Phorate	30	¹ 0.002
Diazinon	30	¹ 0.002	Malathion	30	¹ 0.005	Terbufos	30	¹ 0.013
Disulfoton	30	¹ 0.017	Methyl parathion	30	¹ 0.006			
Pyrethroids								
Esfenvalerate	29	² 0.019	<i>cis</i> -Permethrin	30	¹ 0.005			
Triazine Herbicides								
Atrazine	30	¹ 0.001	Cyanazine	30	¹ 0.004	Prometon	30	¹ 0.018
Atrazine,	30	¹ 0.002	Metribuzin	30	¹ 0.004	Simazine	30	¹ 0.005
Uracils								
Bromacil	30	² 0.035	Terbacil	30	¹ 0.007			
Ureas								
Diuron	29	² 0.02	Fluometuron	29	² 0.035	Neburon	29	² 0.015
Fenuron	26	² 0.013	Linuron	29	^{1,2} 0.018	Tebuthiuron	30	¹ 0.01
Miscellaneous								
Acifluorfen	30	² 0.035	Clopyralid	30	² 0.05	DNOC	30	² 0.035
Bentazon	30	² 0.014	Dicamba	30	² 0.035	Norflurazon	29	² 0.024
Bromoxynil	30	² 0.035	2,6-Diethylalanine ³	30	¹ 0.003	Picloram	30	² 0.05
Chloramben	29	² 0.011	Dinoseb	30	² 0.035	Propargite	30	¹ 0.013

¹Solid-phase extraction and gas chromatography/mass spectrometry (GC/MS).

²Solid-phase extraction and high performance, liquid chromatography (HPLC).

³Transformation product.

Table 2. Volatile organic compounds analyzed in ground-water samples collected from selected domestic wells in the eastern San Joaquin Valley, California, 1995

[Unless otherwise noted, total number of samples for each compound listed is 30, and the method reporting limit is 0.200 microgram per liter; purge and trap capillary column gas chromatography/mass spectrometry, GC/MS, method of analysis used]

Compound	Compound	Compound
Benzene	1,4-Dichlorobenzene	Methyl <i>tert</i> -butyl ether (MTBE)
Bromobenzene	1,1-Dichloroethane	Naphthalene
Bromochloromethane	1,2-Dichloroethane	<i>n</i> -Propylbenzene
Bromodichloromethane	1,1-Dichloroethene	Styrene
Bromomethane	<i>cis</i> -1,2-Dichloroethene	1,1,1,2-Tetrachloroethane
<i>n</i> -Butylbenzene	<i>trans</i> -1,2-Dichloroethene	1,1,2,2-Tetrachloroethane
<i>sec</i> -Butylbenzene	Dichlorodifluoromethane	Tetrachloroethene
<i>tert</i> -Butylbenzene	Dichloromethane	Tetrachloromethane
Chlorobenzene	1,2-Dichloropropane	Tribromomethane
Chlorodibromomethane	1,3-Dichloropropene	1,2,3-Trichlorobenzene
Chloroethane	2,2-Dichloropropane	1,2,4-Trichlorobenzene
Chloroethene	1,1-Dichloropropene	1,1,1-Trichloroethane
Chloromethane	<i>cis</i> -1,3-Dichloropropene	1,1,2-Trichloroethane
2-Chlorotoluene	<i>trans</i> -1,3-Dichloropropene	Trichloroethene
4-Chlorotoluene	Dimethylbenzene, total	Trichlorofluoromethane
1,2-Dibromo-3-chloropropane (DBCP) ¹	Ethylbenzene	Trichloromethane
1,2-Dibromoethane (EDB) ²	Hexachlorobutadiene	1,2,3-Trichloropropane
Dibromomethane	Isopropylbenzene	1,1,2-Trichloro-1,2,2-trifluoroethane
1,2-Dichlorobenzene	<i>p</i> -Isopropyltoluene	1,2,4-Trimethylbenzene
1,3-Dichlorobenzene	Methylbenzene	1,3,5-Trimethylbenzene

¹Method detection limit is 0.030 microgram per liter: gas chromatography/electron-capture detection, GC/ECD, method of analysis used.

²Method detection limit is 0.040 microgram per liter: gas chromatography/electron-capture detection, GC/ECD, method of analysis used.

Duplicate ground-water samples were collected to assess the combined effects of field and laboratory procedures on measurement precision. Duplicate samples were collected sequentially. Blank and field matrix spike samples (hereinafter referred to as blanks and spikes) were collected to estimate bias. The blanks were made up of blank solution water (water that is free of the analytes of interest) that had been processed, preserved, and analyzed using the same methods used for the environmental sample. Three types of blank samples were collected and analyzed for this study: equipment blanks, field blanks, and trip blanks. Equipment blanks were collected prior to each sampling season to determine whether the sampling equipment may be a source of contamination to the environmental samples. Field blanks were collected immediately following the collection of the environmental samples. The field blanks were used to determine whether the field-cleaning procedure following each sample collection was adequate for preventing cross-contamination between wells and to

determine whether the sample was exposed to atmospheric contamination during sampling. The trip blanks were collected in a controlled environment and then transported to the field to be submitted to the laboratory with the environmental samples. The trip blanks were used to determine whether the samples were contaminated during travel or shipping. Spiked samples are environmental samples fortified in the field with a spike solution containing known concentrations of method analytes.

Nitrate

Twelve pairs of duplicate ground-water samples were analyzed for nitrate (dissolved nitrate plus nitrite, expressed as elemental nitrogen) (Willie Kinsey and Mark Johnson, U.S. Geological Survey, written commun., 1997). Concentrations were identical in 8 of 12 duplicate samples and were within 0.3 mg/L in 3 of the duplicate samples and within 1 mg/L in 1 pair of samples. The mean relative deviation for all 12 samples

was 1.1 percent. The maximum deviation was 7.4 percent. The small relative percent deviation indicates a high degree of precision in the collection, the processing, and the analysis of the nitrate samples.

Pesticides

Twenty field blanks were analyzed for the GC/MS pesticide analytes: 12 samples were collected at the domestic well sites, and 8 samples were collected at the monitoring well sites. Seventeen field blanks were analyzed for the HPLC pesticide analytes: 10 samples were collected at the domestic well sites, and 7 samples were collected at the monitoring well sites. An equipment blank also was analyzed for the GC/MS and HPLC methods. No pesticides were detected in any of the blanks, which indicates that the sample-collection, processing, and field-cleaning procedures were successful in minimizing environmental sample contamination or carry-over of these pesticides.

Twelve spikes were analyzed using the GC/MS method. The mean recovery was high for most of the target analytes (Willie Kinsey and Mark Johnson, U.S. Geological Survey, written commun., 1997). All but 1 (desethyl atrazine) of the 46 analytes had mean recovery values greater than 73 percent; the mean recovery for desethyl atrazine was 48 percent. The relative standard deviation of recoveries ranged from 11 to 50 percent. The reported concentrations for pesticides with low recoveries or for those that were reported at concentrations below the detection limit are noted as "estimated" in this report. Recovery data for three surrogate analytes indicated that the extraction procedure for the GC/MS method was adequate for most samples. The mean recovery for diazinon-d₁₀ was 103 percent with a standard deviation of 34 percent. The mean recovery for alpha-HCH-d₆ was 94 percent with a standard deviation of 23 percent, and the mean recovery for terbuthylazine was 103 percent with a standard deviation of 22 percent.

NWQL precision and recovery data (Zaugg and others, 1995) also were evaluated to aid in data interpretation. Data on several analytes indicated variable performance and low recoveries; these analytes include desethyl atrazine, methyl azinphos, carbaryl, carbofuran, and terbacil. Because the concentrations of analytes with poor recoveries may be biased low, the concentrations of these pesticides should be interpreted with caution. Two of the most frequently detected pesticides, atrazine and simazine, had mean recoveries in

spikes of 102 and 101 percent, respectively, and both had a relative standard deviation of 15 percent.

Eleven spikes were collected and analyzed using the HPLC method. The mean recoveries of these analytes were highly variable and ranged from 22 to 145 percent (Willie Kinsey and Mark Johnson, U.S. Geological Survey, written commun., 1997), with a relative standard deviation ranging from 6 to 40 percent. Precision and recovery for most HPLC analytes generally were consistent enough and high enough to use confidently in the data analysis. Several analytes, however, had poor overall precision and recovery rates; these analytes include 1-naphthol, aldicarb, aldicarb sulfone, carbaryl, chlorothalonil, dichlobenil, 4,6-dinitro-*o*-cresol, esfenvalerate, 4-(4-chloro-2-methylphenoxy) butanoic acid, methiocarb, and oxamyl. These analytes have a greater chance of being reported as a "false negative" when the analyte is not detected in samples that contain concentrations at detectable levels. The HPLC analyte most frequently detected in this study was diuron. For diuron, the mean recovery in spikes was 50 percent, with a relative standard deviation of 14 percent. Recovery data for a surrogate analyte added to all the samples indicate that the overall recovery using the HPLC method was lower than the recovery using the GC/MS method. The mean recovery for BDMC was 69 percent, with a standard deviation of 28 percent.

Volatile Organic Compounds

Eighteen field blanks were analyzed for the GC/MS VOCs: 12 samples were collected at domestic well sites, and 6 samples were collected at monitoring well sites (Willie Kinsey and Mark Johnson, U.S. Geological Survey, written commun., 1997). Chloromethane was detected in four blank samples collected at the domestic well sites (concentrations ranged from 0.2 to 0.7 µg/L) and in six blank samples collected at the monitoring well sites (concentrations ranged from 0.3 to 1.0 µg/L). Chloromethane was not detected in any environmental water samples collected during this study, but it was detected in environmental samples collected during two simultaneous NAWQA ground-water studies in this area. This analyte was considered to be a result of systematic contamination likely owing to the hydrochloric acid used for VOC preservation (John Zogorski, U.S. Geological Survey, written commun., 1996).

Only two analytes (trichlorofluoromethane and trichloromethane) were detected in both the environmental samples and the blank samples. Trichlorofluo-

romethane was detected at a concentration of 0.3 µg/L in one environmental sample collected in 1995. This analyte was also detected in the 1994 equipment blank sample (0.2 µg/L), in two monitoring-well field blanks collected in 1994 (both 0.3 µg/L), and in two environmental samples (0.4 and 1.1 µg/L) collected for the two simultaneous NAWQA ground-water studies. The presence of trichlorofluoromethane may be the result of atmospheric contamination and, therefore, was not interpreted in this report. Trichloromethane was detected in one environmental sample at a concentration of 0.3 µg/L. Trichloromethane was also detected in three field blanks collected at the domestic well sites (concentrations ranged from 0.2 to 0.4 µg/L) and in one field blank collected at a monitoring well site (0.7 µg/L). The detection of trichloromethane in the environmental sample might have resulted from chlorination of well water—a common practice done to eliminate bacteria in domestic wells. The detection of trichloromethane in the field blanks is probably unrelated to the occurrence of trichloromethane in the environmental sample because the detections in the field blanks occurred in 1993 and 1994. The domestic well containing the trichloromethane detection was in a predominantly agricultural area. Because trichloromethane is not associated with agricultural land-use practices, the detection of this analyte is not interpreted in this report.

Tetrachloroethene was detected in one environmental sample at a concentration of 0.4 µg/L. Because the sample was collected from a well that was partly surrounded by urban land use (25 percent), the detection of tetrachloroethene is probably not related to pesticide use and, thus, is not interpreted in this report.

Seven other VOCs were detected in the blank samples: benzene, bromodichloromethane, chlorodibromomethane, dichloromethane, dimethylbenzene (total), methylbenzene, and tribromomethane. These analytes were not detected in the environmental samples collected during this study and, therefore, do not affect the interpretation of the data. Nineteen field blanks were collected for analysis of DBCP and EDB using the low-level GC/ECD method: 12 blank samples were collected at domestic well sites, and 7 blank samples were collected at monitoring well sites. DBCP or EDB was not detected in any of the blank samples.

Seventeen VOC spikes were collected and analyzed using the purge and trap GC/MS method. Replicate VOC spike samples were collected at 13 of the 17 domestic and monitoring well sites where the VOC

spikes were collected. Because a micropipettor was used for spiking samples, the spike recoveries were variable and biased low (Peter Rogerson, U.S. Geological Survey, written commun., 1996); the field spike data, therefore, do not accurately represent the performance of the GC/MS method. Recoveries of three surrogate analytes indicate that the overall recovery of most of the samples was good. The mean recovery for 1,2-dichloroethane-d₄ was 100 percent with a standard deviation of 6 percent. The mean recovery for toluene-d₈ was 98 percent with a standard deviation of 2 percent, and the mean recovery for 1-bromo-4-fluorobenzene was 100 percent with a standard deviation of 9 percent.

Determination of Local-Scale Nitrogen Fertilizer Applications

To evaluate the relation between local applications of nitrogen fertilizer and concentrations of nitrate in ground water, the estimated amount of nitrogen fertilizer applications was calculated for each sampling site and compared with the measured nitrate concentrations in the ground-water samples. The nitrogen contribution from septic systems was not included in this evaluation because the contribution was expected to be minor (7.5 lb of nitrogen per person per year); (Frimpter and others, 1990; Rupert, 1996) relative to the amount of nitrogen fertilizer from the surrounding land use. Most of the domestic wells sampled during this study are in sparsely populated agricultural areas and are at least 100 ft from household septic systems.

Nitrogen fertilizer applications were estimated for each well on the basis of annual application rates for nitrogen fertilizer (Rauschkolb and Mikkelsen, 1978; National Agricultural Statistics Service and Economic Research Service, 1992a, b) for each crop type within a 0.25-mi or 0.5-mi radial distance from the well. To develop a local-scale coverage of land-use distribution, land-use data at a county level were obtained from the California Department of Water Resources (1971) in various forms and compiled into a land-use coverage using the geographic information system—a computer system capable of assembling, storing, manipulating, and displaying geographically referenced information. The land-use data were created from a detailed, field-verified network for the San Joaquin Valley. The most recent (1984–93) land-use data for each county were used to determine the land use surrounding each well. To estimate the amount of nitrogen fertilizer applica-

tion to the area surrounding each well, the estimated annual rate of nitrogen fertilizer applied to each crop was multiplied by the total area of that crop within 0.25- or 0.5-mi radial distance from the well. The total application was computed as the sum of the estimated applications for all crops within the specified radial distance from the well.

Statistical Methods

Nonparametric statistical methods were used in this study because the data set is relatively small and most of the data are not normally distributed. Nonparametric statistics are robust techniques that are generally unaffected by outlying values and do not require the data to follow any particular distribution (Helsel and Hirsch, 1992). The significance level (commonly referred to as α) used for hypothesis testing in this report is 5 percent ($\alpha=0.05$). The Mann-Whitney test was used to test the difference between two groups of data, whereas the Kruskal-Wallis test, an analysis of variance, was used to test the differences among more than two groups of data (Conover, 1980). The Wilcoxon signed-rank test was used to evaluate the differences in matched pairs of data, and the Spearman's rho was used to evaluate the correlation of two variables (Lehmann, 1975). The Chi-square statistic was used to evaluate contingency tables for categorical variables (Zar, 1974). For compounds with reported concentrations that were less than the detection limit, a concentration of one-half the minimum detection limit was used in the statistical analyses.

OCCURRENCE OF NITRATE

Dissolved nitrate plus nitrite (as nitrogen) was detected in 27 of 30 ground-water samples collected in 1995. Concentrations of dissolved nitrate plus nitrite will hereinafter be referred to as nitrate, expressed as elemental nitrogen, because the maximum nitrite concentration in this study was 0.1 mg/L. Nitrite accounted for a maximum of 3.8 percent of the total nitrate plus nitrite concentrations in the samples where nitrite was detected. Nitrate concentrations ranged from less than 0.05 to 34 mg/L, with a median of 4.6 mg/L (table 3). Nitrate concentrations exceeded the MCL of 10 mg/L (U.S. Environmental Protection Agency, 1996) in 5 of the 30 ground-water samples (17 percent). Concentrations were less than 3.0 mg/L in 12 samples

(40 percent)—ground water with nitrate concentrations less than about 1.0 to 3.0 mg/L (referred to as background concentrations) likely has not been affected by human activity (Madison and Brunett, 1985; Mueller and Helsel, 1996). A concentration of 3.0 mg/L was selected as a conservative value representing background nitrate concentrations.

The median nitrate concentration calculated for water samples collected during this study was higher than the median concentration calculated for ground-water samples collected from comparable settings during a national study. Mueller and others (1995) calculated the median nitrate concentration in ground water in unconsolidated sand and gravel aquifers within agricultural settings to be 2.4 mg/L, which is lower than the median nitrate concentration calculated for the ground-water samples collected for this study. However, the percentage of wells with nitrate concentrations exceeding the MCL was 17 percent in both studies. The median nitrate concentration calculated during the national study might have been lower than the 1995 median concentration observed in this study because the samples were aggregated from a broad range of sedimentary depositional environments, hydrologic conditions, crop types, crop-management practices, and well depths.

Relation Between Nitrate and Fertilizer Applications

The nitrate concentrations in ground water in the study area probably are related to the use of fertilizer because a large percentage of the land use is agricultural. The application rates of nitrogen fertilizer vary depending on crop type, but rates in the San Joaquin Valley in 1973 ranged from 20 lb/acre for alfalfa to 175 lb/acre for crops such as corn and potatoes (Rauschkolb and Mikkelsen, 1978). All but one of the wells (well 25) are in predominantly agricultural land-use settings or in areas where agricultural land has given way to encroaching suburbs within the last 20 years (table 4).

To evaluate the relation between local nitrogen fertilizer application and nitrate concentrations in individual ground-water samples, the amount of nitrogen fertilizer applied to each sampling site was calculated and the estimate was then compared with measured concentrations of nitrate in the ground-water samples. The measured nitrate concentrations were not significantly correlated with the estimated amount of nitrogen

Table 3. Well characteristics and general water quality of 1995 ground-water samples and concentrations of nitrate and specific conductance in 1995 and 1986-87 ground-water samples in the eastern San Joaquin Valley, California

[State well No.: See well-numbering diagram on page VII. Location of wells shown on figure 1. Well depth, screened interval, and depth to water are in feet below land surface. $\mu\text{g/L}$, microgram per liter; mg/L , milligram per liter; $\mu\text{S/cm}$, microsiemen per centimeter at 25 degrees Celsius, pCi/L , picocuries per liter. —, no data available; (), estimated; <, actual value is less than value shown]

Well No.	State well No.	Well depth	Screened interval	Depth to water	Tritium (pCi/L)	Iron, dissolved ($\mu\text{g/L}$ as Fe)	Manganese, dissolved ($\mu\text{g/L}$ as Mn)	Oxygen, dissolved (mg/L)	Oxidation reduction potential (millivolts)	Sulfide (mg/L)	Nitrate (mg/L as N)		Specific conductance ($\mu\text{S/cm}$)	
											1995	1986-87	1995	1986-87
1	¹ 06S/09E-25B1	67	47-67	5	68	7.0	261	0.1	263	(0.001)	8.3	—	898	—
2	03S/09E-03N2	110	92-110	44	—	<3.0	<1	5.0	384	—	9.2	8.8	601	530
3	02S/08E-35M1	100	80-100	(30)	—	4.0	<1	6.2	360	—	19	8.6	1,020	890
4	03N/07E-22P1	215	195-215	104	.15	<3.0	<1	6.0	334	—	1.1	—	212	—
5	05N/06E-10Q2	160	none	95	13	4.0	2	7.0	343	—	3.4	—	516	—
6	¹ 03S/11E-31G2	182	162-182	77	.4	430	2,100	.2	378	<.003	<.05	—	2,270	—
7	06S/13E-04Q1	128	108-128	(92)	36	<3.0	<1	5.0	400	—	2.9	3.1	346	388
8	06S/12E-21C1	121	116-121	71	—	<3.0	<1	7.2	400	—	.19	.3	125	129
9	07S/15E-35F2	105	85-105	(25)	—	<3.0	<1	5.4	410	—	4.8	3.9	50	375
10	11S/17E-03A2	340	—	(145)	.6	14	<1	7.0	421	—	2.5	—	22	—
11	12S/18E-01P2	144	104-144	114	—	14	1	7.2	305	—	5.9	6.7	340	365
12	¹ 20S/21E-01Q1	228	180-228	65	5.9	86	109	.9	-87	odor	.06	.12	753	1,020
13	¹ 18S/20E-34L1	232	160-232	101	—	53	8	1.6	1	—	<.05	<0.1	413	306
14	14S/20E-34G1	124	64-124	57	—	3.0	<1	8.7	387	—	34	28	956	898
15	13S/19E-17H2	145	105-145	(75)	—	<3.0	<1	6.2	411	—	3.1	2.3	731	575
16	13S/21E-01G1	120	80-120	(55)	5.9	<3.0	<1	7.2	334	—	6.5	8.2	733	613
17	12S/22E-14F1	100	25-72	10	—	<3.0	<1	3.5	387	—	4.3	4.0	660	628
18	16S/24E-26M1	120	40-120	39	—	<3.0	<1	8.4	265	—	27	31	793	766
19	19S/23E-34P2	182	158-182	104	—	<3.0	<1	3.8	291	—	4.8	4.7	302	328
20	20S/24E-22C1	236	200-236	22	—	3.0	<1	10	350	—	13	2.4	448	244
21	22S/24E-02A1	310	210-310	135	48	5.0	<1	5.4	354	—	5.4	4.7	505	536
22	28S/24E-30M1	250	150-250	58	—	15	<1	6.5	317	—	8.5	<0.1	1,040	866
23	31S/27E-16D1	300	200-300	143	—	<3.0	<1	3.3	298	—	.11	.12	287	295
24	30S/28E-29P1	200	160-200	152	—	<3.0	<1	2.4	317	—	2.8	2.2	466	428
25	29S/27E-27B6	350	200-350	(175)	45	23	<1	11	240	—	1.6	1.7	298	331
26	¹ 28S/27E-06G1	702	602-702	(510)	.15	6.0	2	.2	-211	.660	<.05	<0.1	231	241
27	25S/26E-05A3	336	—	122	79	<3.0	<1	7.1	367	—	16	—	1,110	—
28	24S/26E-08A2	400	—	(150)	40	6.0	<1	12	330	—	9.8	—	497	—
29	21S/25E-26H1	280	200-280	118	27	<3.0	<1	5.0	365	—	6.8	2.1	518	714
30	18S/26E-02J1	104	38-63	13	—	<3.0	<1	4.4	351	—	.52	<0.1	177	154

¹Wells for which ground-water samples were interpreted as chemically reduced.

Table 4. Land use, nitrate concentrations, and detected pesticides in selected domestic wells in the eastern San Joaquin Valley, California

[State well No.: See well-numbering diagram on page VII. Location of wells are shown on figure 1. Land-use data are from California Department of Water Resources (1971); [], land use determined by field observation; DBCP, 1,2-dibromo-3-chloropropane; EDB, 1,2-dibromoethane. mg/L, milligram per liter; <, actual value is less than value shown]

Well No.	State well No.	Land use within 0.5-mile radius of well	Nitrate (mg/L as N)	Detected pesticides
1	06S/09E-25B1	Corn (77%), alfalfa (18%), [dairy]	8.3	
2	03S/09E-03N2	Urban (40%), peaches and nectarines (18%), grapes (14%), poultry (10%), corn and sudan grass (9%)	9.2	
3	02S/08E-35M1	Almonds (40%), walnuts (12%), alfalfa (12%), urban (10%)	19	desethyl atrazine, DBCP
4	03N/07E-22P1	Grapes (50%), mixed pasture (14%), tomatoes (13%)	1.1	
5	05N/06E-10Q2	Urban residential/urban vacant (38%), native vegetation (36%), mixed pasture (18%)	3.4	atrazine, dieldrin
6	03S/11E-31G2	Almonds (40%), walnuts (37%), corn (10%), bushberries (4%)	<.05	
7	06S/13E-04Q1	Mixed pasture (64%), native vegetation (35%), [dairy]	2.9	atrazine, desethyl atrazine
8	06S/12E-21C1	Almonds (69%), grapes (16%), plums (6%)	.19	atrazine, simazine
9	07S/15E-35F2	Grain and hay (30%), mixed pasture (27%), figs (21%), native vegetation (9%), farmsteads (5%)	4.8	atrazine, desethyl atrazine, dichlobenil
10	11S/17E-03A2	Suburban residential (70%), urban (11%), grapes (10%)	2.5	
11	12S/18E-01P2	Grapes (25%), suburban residential (18%), figs (16%), mixed pasture (14%), almonds (10%)	5.9	atrazine, desethyl atrazine, simazine
12	20S/21E-01Q1	Cotton (32%), grain and hay (17%), melons (16%), alfalfa (13%), native vegetation (9%)	.06	
13	18S/20E-34L1	Cotton (40%), urban (25%), idle (9%), corn (7%), native vegetation (6%)	<.05	diuron
14	14S/20E-34G1	Alfalfa (17%), urban (15%), corn (11%), mixed pasture (10%), plums (8%)	34	1,2,3-trichloropropane, 1,2-dichloropropane, EDB
15	13S/19E-17H2	Figs (36%), native vegetation (25%), almonds (20%), abandoned figs (10%), urban (5%)	3.1	simazine
16	13S/21E-01G1	Suburban residential (38%), native vegetation (34%), almonds (9%), truck crops (4%), mixed pasture (4%)	6.5	simazine, diuron
17	12S/22E-14F1	Grapes (25%), suburban residential (18%), figs (16%), mixed pasture (14%), almonds (11%)	4.3	
18	16S/24E-26M1	Grapes (39%), peaches and nectarines (27%), field crops (13%), plums (10%), grain and hay (4%)	27	desethyl atrazine, simazine, 1,2,3-trichloropropane
19	19S/23E-34P2	Corn (40%), cotton (30%), alfalfa (29%)	4.8	atrazine, desethyl atrazine, simazine, diuron
20	20S/24E-22C1	Corn (35%), cotton (30%), alfalfa (19%), [dairy]	13	atrazine, desethyl atrazine, simazine, diuron, cyanazine
21	22S/24E-02A1	Alfalfa (29%), peaches and nectarines (27%), cotton (21%), corn (16%), irrigated cemetery (2%)	5.4	
22	28S/24E-30M1	Cotton (73%), sugar beets (16%), tomatoes (8%)	8.5	1,2,3-trichloropropane, 1,2-dichloropropane
23	31S/27E-16D1	Cotton (40%), native vegetation (16%), suburban residential (16%), field crops (11%), corn (6%)	.11	atrazine, desethyl atrazine, simazine, prometon
24	30S/28E-29P1	Alfalfa (48%), cotton (23%), urban (7%), feed lot (7%), urban commercial (5%)	2.8	atrazine, desethyl atrazine
25	29S/27E-27B6	Native vegetation (75%), urban (25%), [oil field, commercial business]	1.6	atrazine, desethyl atrazine, simazine
26	28S/27E-06G1	Native vegetation (52%), poultry farms (25%), almonds (14%)	<.05	
27	25S/26E-05A3	Grapes (30%), alfalfa (10%), oranges (10%), beans (7%), urban (6%)	16	1,2,3-trichloropropane, DBCP
28	24S/26E-08A2	Grapes (61%), cotton (18%), alfalfa (14%)	9.8	DBCP
29	21S/25E-26H1	Cotton (44%), corn (30%), grain and hay (15%), alfalfa (8%), [feed lot]	6.8	atrazine, desethyl atrazine
30	18S/26E-02J1	Oranges (18%), native vegetation (16%), plums (12%), miscellaneous deciduous (10%), walnuts (10%)	.52	simazine, prometon

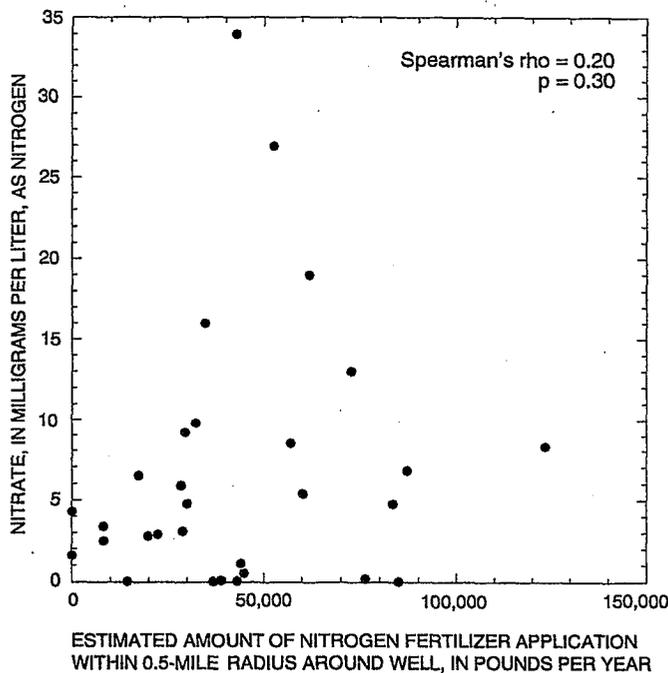


Figure 2. Nitrate concentration and estimated amount of nitrogen fertilizer application within 0.5-mi radial distance from each well in the eastern San Joaquin Valley, California. The amount of the fertilizer application is the sum of the estimated amount applied to each crop with a 0.5-mi radius of the well.

fertilizer applied within a 0.25- and a 0.5-mi radial distance from the sampled well ($p=0.25$, $\rho=0.22$ and $p=0.30$, $\rho=0.20$, respectively; Spearman's rank correlation), although nitrate concentrations have a slight tendency to increase with increasing application amounts (fig. 2). Seven wells (wells 1, 2, 7, 20, 24, 26, and 29) had either a dairy, a confined feeding operation, or a poultry farm within a 0.5-mi radial distance from the well (table 4). Of these seven wells, only one ground-water sample (well 20) had a nitrate concentration greater than the MCL. Ground-water samples from 3 of the remaining 6 wells had nitrate concentrations greater than 3.0 mg/L (wells 1, 2, and 29). Ground-water samples from the other three wells (wells 7, 24, and 26) had nitrate concentrations of less than 3.0 mg/L, indicating that there is no consistent relation between nitrate concentrations and animal sources in ground water for this small data set.

Although the estimated amount of nitrogen fertilizer applied to the area surrounding each well may not reflect the amount of nitrate that reaches ground water, the lack of a consistent correlation between the estimated amount of the nitrogen fertilizer application and the nitrate concentrations in the ground water may

be caused by other factors that affect nitrate concentrations in the aquifer. These concentrations may be controlled by factors such as soil and sediment texture, hydrogeology, well-construction characteristics, or geochemical processes acting in the aquifer.

Physical and Chemical Factors Related to Occurrence of Nitrate

Relations between nitrate concentrations and other data were examined to determine whether the occurrence of nitrate is linked to physical or chemical characteristics of the aquifer. Physical factors, such as well construction and hydrogeology, can influence the leaching rate of nitrate to shallow ground water. Chemical factors, such as dissolved-oxygen and tritium concentrations, major-ion composition, and specific conductance, may reflect geochemical processes, ground-water residence time, and the relative effect of various human activities on ground water.

Nitrate concentrations were statistically evaluated in relation to depth of well below land surface (depth to the bottom of the well casing and depth to the top, middle, and bottom of the screened interval); depth of the bottom of the well casing below the water table; and depth to water below land surface. Nitrate concentrations were inversely correlated with depth to the top (fig. 3) and depth to the middle of the screened interval ($p=0.026$, $\rho=-0.43$ and $p=0.045$, $\rho=-0.40$, respectively; Spearman's rank correlation). Nitrate concentrations generally decrease with depth because, in recharge areas, ground water that is deeper in the flow system is generally older; this older water generally has lower nitrate concentrations, which reflect lower historical application rates of nitrogen fertilizers, the effects of dispersion along longer travel paths, or a longer period of time for nitrate-removal processes to affect concentrations. A decrease in nitrate concentrations with well depth has also been noted by other investigators (Rupert, 1994; Mueller and others, 1995). None of the other well-construction characteristics, however, were significantly correlated to the nitrate concentrations.

Nitrate concentrations were inversely related to the depth to water below land surface (fig. 4); however, the correlation was not significant at $\alpha=0.05$ ($p=0.066$, $\rho=-0.34$; Spearman's rank correlation). Two of the 3 ground-water samples from wells with a shallow water table (less than 20 ft below land surface) had low nitrate concentrations (less than 5 mg/L) compared with 1 of

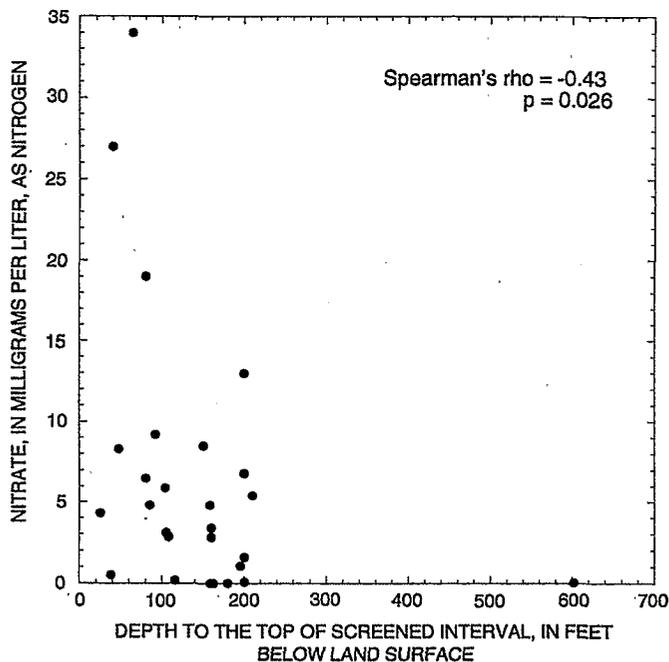


Figure 3. Relation between nitrate concentration and depth to the top of the screened interval for selected domestic wells in the eastern San Joaquin Valley, California.

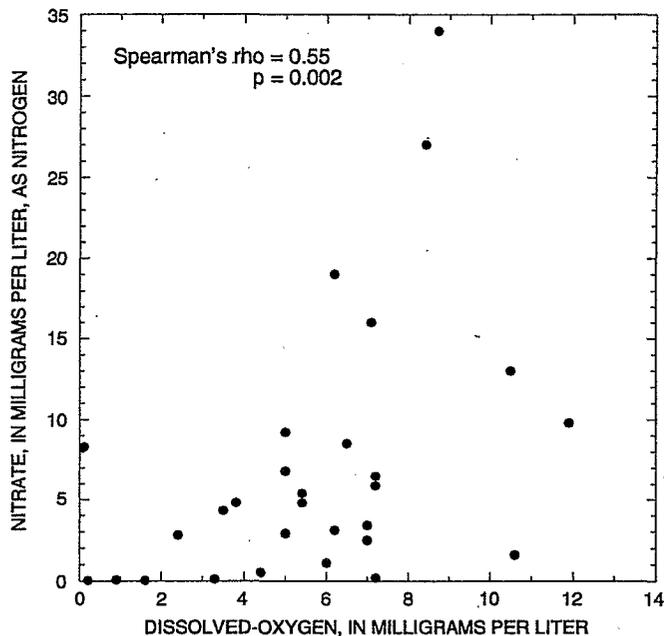


Figure 5. Relation between nitrate and dissolved-oxygen concentrations in ground-water samples from selected domestic wells in the eastern San Joaquin Valley, California.

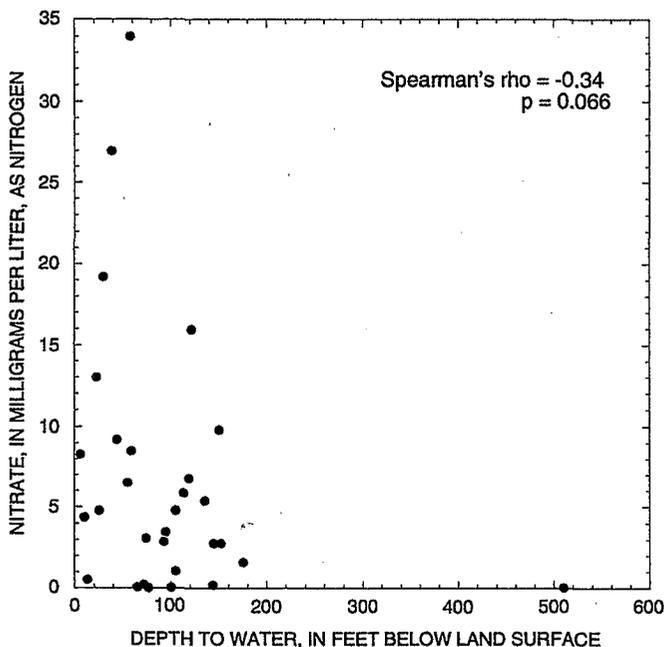


Figure 4. Relation between nitrate concentration and depth to water for selected domestic wells in the eastern San Joaquin Valley, California.

the 8 ground-water samples from wells with depths to water of 20 to 60 ft below land surface (fig. 4). The lack of a significant correlation between nitrate concentrations and the depth to water may be due to the low

nitrate concentrations in ground-water samples from the wells with shallow depths to water. Nitrate concentrations may also be influenced by differences in nitrogen fertilizer applications or by differences in soil and sediment texture.

Nitrate concentrations were evaluated in relation to water-chemistry characteristics (table 3) that indicate reduced geochemical conditions. Nitrate in anaerobic ground water can be reduced to nitrous oxide or nitrogen gas. Nitrate reduction is most likely to occur in ground water that has low dissolved-oxygen concentrations, relatively high dissolved iron or manganese concentrations, low oxidation-reduction potential, or detections of dissolved sulfide. Nitrate reduction is also likely to occur in fine-grained soils with high organic content; the soils data analyzed in this study (permeability, hardpan percent, and clay percent) are not presented in this report, however, because they were not related to nitrate concentrations.

Ground-water samples from five wells had several characteristics of reduced geochemical conditions (table 3): the samples from wells 6, 13, and 26 had nitrate concentrations below the detection limit of 0.05 mg/L; the sample from well 12 had a nitrate concentration of 0.06 mg/L; and the sample from well 1 had a nitrate concentration of 8.3 mg/L. The ground-water

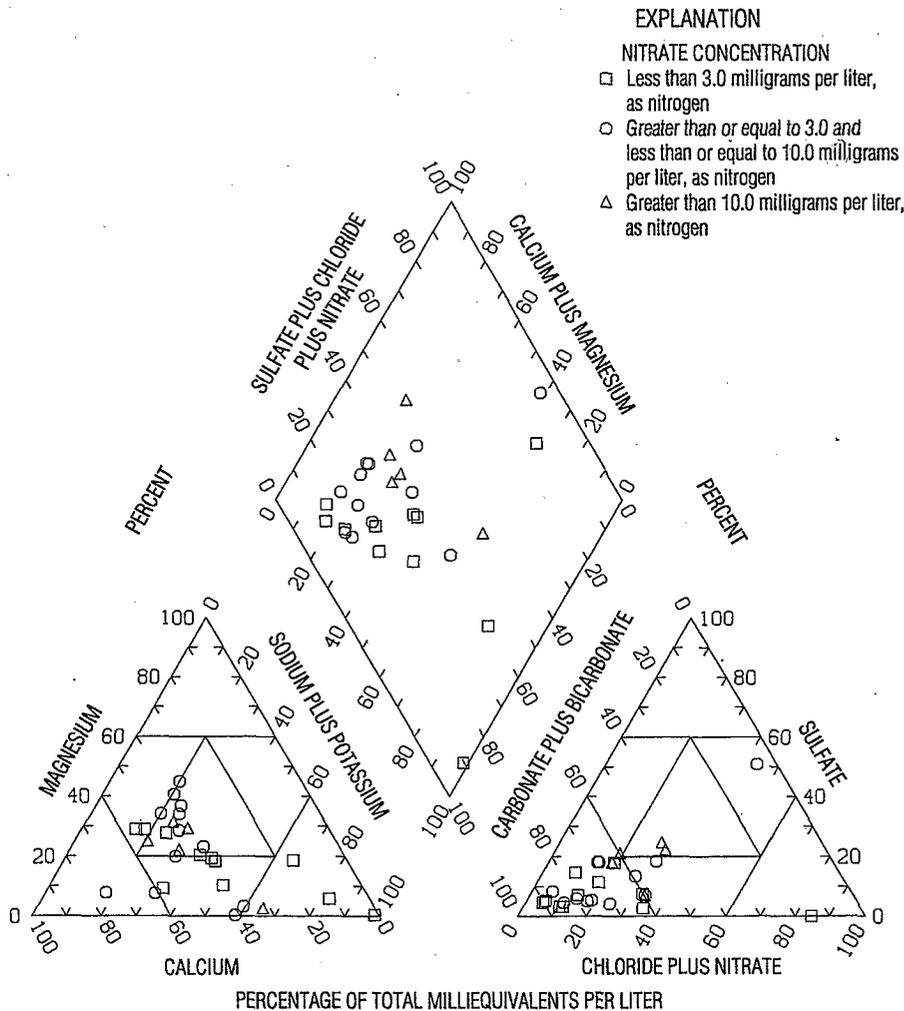


Figure 6. Major-ion composition and relation to nitrate concentration of ground-water samples from selected domestic wells in the eastern San Joaquin Valley, California.

sample from well 1 is the only sample of the five samples to have characteristics of reduced geochemical conditions and a nitrate concentration above the background level of 3.0 mg/L. Four of the five wells (wells 1, 6, 12, and 13) are near the sediments of the basin region, where ground water generally is chemically reduced (Bertoldi and others, 1991). The ground-water sample from well 26 also has characteristics of reduced geochemical conditions, but it is not located near sediments of the basin region. However, well 26 has a depth of 702 ft, indicating that the ground water sampled from this well could be relatively old. Ground-water samples from other wells located near the basin region (wells 3, 4, 20, 21, and 22) had few characteristics of reduced geochemical conditions. Of these 5 wells, only

well 22 had slightly elevated dissolved iron concentrations (table 3).

The occurrence of chemically reduced water in the wells near the boundary of the eastern alluvial fan and basin regions could be caused by the interfingering of coarse- and fine-grained sediments along the boundary of the two regions. The wells with chemically reduced ground water may be screened in sediments that more closely resemble the sediments of the basin region, although they are mapped at the land surface as eastern alluvial fan sediments. Nitrate concentrations also were positively correlated to dissolved-oxygen concentrations ($p=0.002$, $\rho=0.55$; Spearman's rank correlation) (fig. 5), indicating that the processes that caused dissolved-oxygen concentrations in ground water may influence nitrate concentrations. Well-oxy-

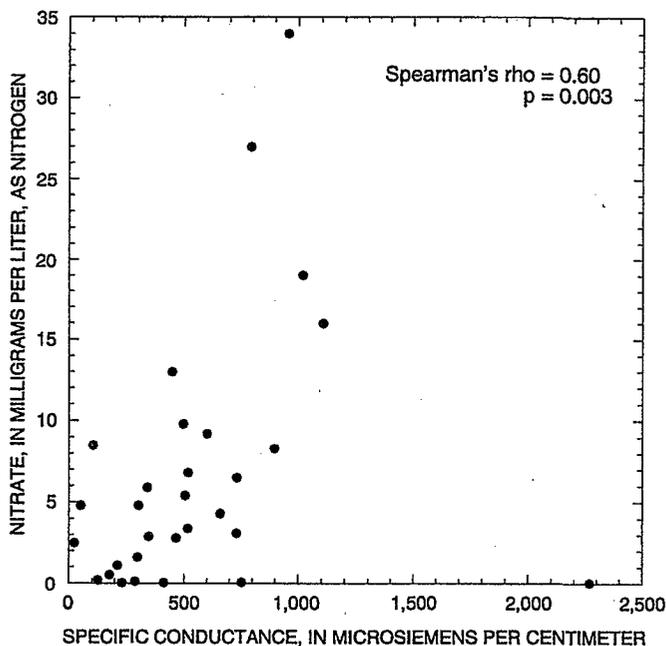


Figure 7. Relation between nitrate concentration and specific conductance in ground-water samples from selected domestic wells in the eastern San Joaquin Valley, California.

generated ground water probably occurs in areas where the water rapidly infiltrates through coarse-grained sediments with low organic content and where the ground-water residence times are relatively short.

The relation between ground-water residence time and nitrate concentrations was further evaluated using tritium analyses. Elevated tritium concentrations in ground water can be attributed to large-scale atmospheric testing of thermonuclear bombs from about 1952 to 1962. The half-life of tritium is 12.4 years; ground water that was recharged prior to 1953 is expected to have tritium concentrations below about 6.4 pCi/L (Plummer and others, 1993). Nitrate concentrations were positively correlated to tritium concentrations ($p=0.002$, $\rho=0.76$; Spearman's rank correlation); however, only 14 samples were analyzed for tritium. The positive correlation between nitrate and tritium supports the conclusion that nitrate concentrations are lower in older ground water than in ground water that was more recently recharged.

Ground water with elevated nitrate concentrations tends to have a similar major-ion composition, and, as nitrate concentrations increase, chloride increases and replaces bicarbonate as the dominant anion (fig. 6). Sulfate also increases but to a lesser degree. For this study, major-ion composition was

grouped into three categories on the basis of nitrate concentrations: nitrate concentrations of less than 3.0 mg/L, nitrate concentrations between 3.0 and 10.0 mg/L, and nitrate concentrations greater than 10.0 mg/L. These categories indicate the relative degree to which these waters are affected by human activities such as agriculture. Agriculturally affected waters may be expected to have higher salinity than do nonaffected waters and are characterized by increased concentrations of chloride and sulfate that result from the leaching of nitrogen and potash fertilizers and other agriculturally related compounds and from increased evaporation as ground water is pumped and reapplied for irrigation. Five of the 1995 ground-water samples had nitrate concentrations that exceeded 10 mg/L (table 3); 4 of the 5 samples had proportions of chloride plus sulfate of greater than 25 percent, suggesting that high concentrations of nitrate are associated with agriculturally affected waters. However, three other samples (wells 6, 12, and 13) with very high proportions of sodium plus potassium (greater than 60 percent) had nitrate concentrations less than 3.0 mg/L (fig. 6). The ground-water samples from these three wells were chemically reduced (table 3). The high salinity in the ground-water samples with low nitrate concentrations probably reflects the influence of geochemical processes rather than agricultural effects.

Nitrate concentrations were also positively correlated to specific conductance (fig. 7; $p=0.003$, $\rho=0.60$; Spearman's rank correlation). Specific conductance is related to the total ion composition of ground water and is an indicator of salinity. In the study area, increased salinity is caused, in part, by the effects of agriculture, as discussed previously. The nitrate concentration for well 6 was less than 0.05 mg/L, but the specific conductance was more than 2,000 $\mu\text{S}/\text{cm}$ (table 3). The ground-water sample from this well was chemically reduced; therefore, the low nitrate concentration may have been a result of nitrate reduction. When the ground-water samples from chemically reduced environments are removed from the data set used in the statistical analysis for this study, nitrate and specific conductance are more strongly correlated (p is less than 0.001, $\rho=0.66$; Spearman's rank correlation).

OCCURRENCE OF PESTICIDES

As mentioned earlier in this report, pesticide is a generic term for compounds used as fungicides, herbicides, insecticides, nematocides, and rodenticides. In

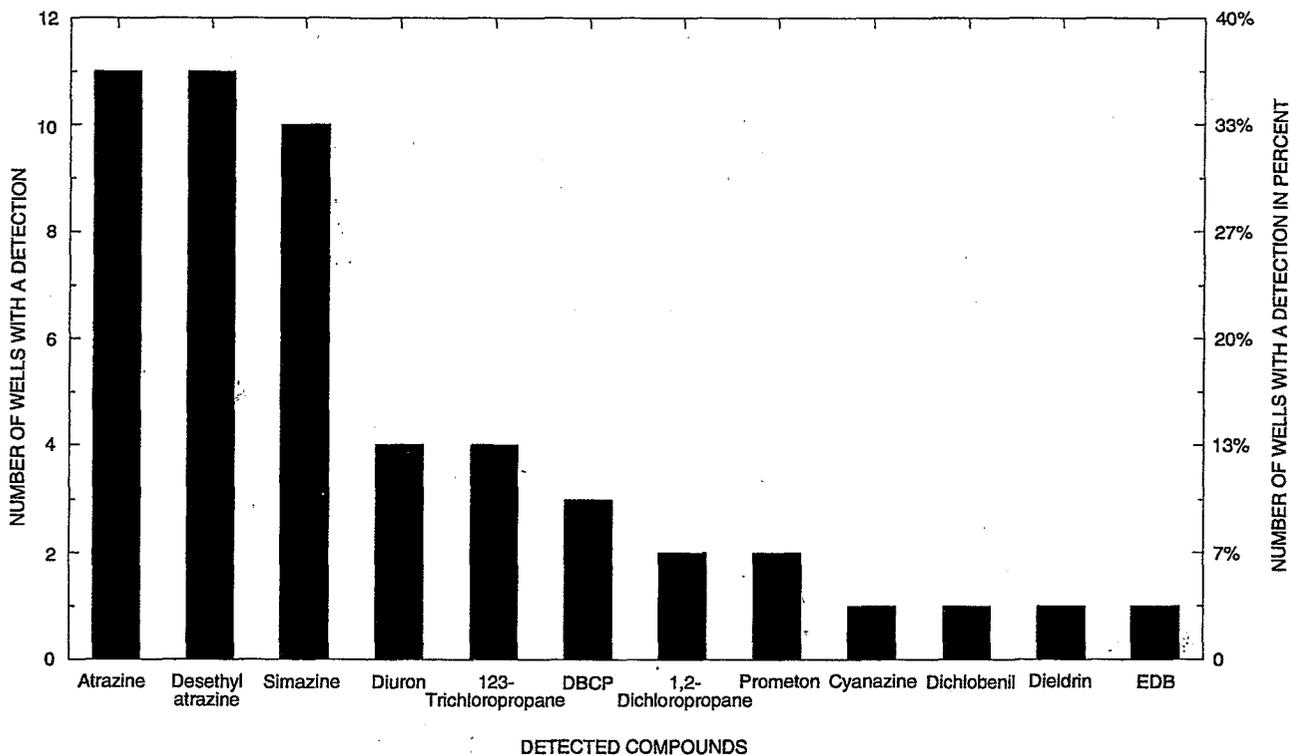


Figure 8. Pesticides detected in ground-water samples collected from selected domestic wells in the eastern San Joaquin Valley, California, 1995.

this report, the term pesticide also includes transformation products and other agriculturally related organic compounds (such as pesticide by-products or additives). Desethyl atrazine is a transformation product of atrazine. The detection of atrazine and desethyl atrazine in the same ground-water sample was counted as one detection in the data analysis and in the discussion on the number of detections in the 1995 ground-water samples.

Twenty-one of 30 ground-water samples (70 percent) collected in 1995 had at least one detected pesticide (1 sample was collected from each well) (table 4). Ground-water samples from 5 of the 21 wells (24 percent) with pesticide detections had 3 or more detected pesticides (wells 14, 18, 19, 20, and 23), and only 1 sample (well 20) (table 4) had more than 3 detected pesticides. Twelve different pesticides were detected in the 21 ground-water samples, although only 5 pesticides were detected in more than 10 percent of the samples: atrazine, desethyl atrazine, simazine, diuron, and 1,2,3-trichloropropane (fig. 8). The only pesticides in the 1995 samples detected at concentrations above the MCL for drinking water were the soil fumigants EDB and DBCP; only 5 of the 12 detected pesticides (atra-

zine, DBCP, EDB, simazine, and 1,2-dichloropropane), however, have enforceable drinking-water standards. EDB was detected at a concentration of 0.55 $\mu\text{g/L}$ in well 14 (table 5). The MCL for EDB is 0.05 $\mu\text{g/L}$ (U.S. Environmental Protection Agency, 1996). DBCP was detected in ground-water samples from wells 3, 27, and 28 at concentrations ranging from 0.35 to 1.1 $\mu\text{g/L}$ (table 5). The MCL for DBCP is 0.2 $\mu\text{g/L}$ (U.S. Environmental Protection Agency, 1996).

Atrazine and desethyl atrazine, the most frequently detected pesticides, were detected in 11 of the 30 ground-water samples (37 percent) at concentrations ranging from 0.002 to 0.12 $\mu\text{g/L}$ and 0.002 to 0.14 $\mu\text{g/L}$, respectively (table 5). Nine samples contained both pesticides. Desethyl atrazine concentrations are reported as estimated by the NWQL because the recoveries for this pesticide are low (48 percent with a relative standard deviation of 11 to 50 percent). Other pesticides that were reported at concentrations below the detection limit also are reported as estimated. The concentrations of atrazine in the 11 ground-water samples were at least one order of magnitude less than the MCL of 3 $\mu\text{g/L}$ for atrazine (U.S. Environmental Pro-

Table 5. Pesticide concentrations in 1995 and 1986-87 ground-water samples from selected domestic wells in the eastern San Joaquin Valley, California
 [State well No.: See well-numbering diagram on page VII. See figure 1 for location of wells. Data are given in micrograms per liter; E, value is estimated; <, actual value is less than value shown, which corresponds to method reporting limit, unless denoted by *, which indicates concentrations are censored at the method detection limit. —, not analyzed]

Well No.	State well No.	Atrazine		Desethyl atrazine		Simazine		Diuron		1,2,3-Trichloro-propane		1,2-Dibromo-3-chloropropane (DBCP)		1,2-Dichloro-propane	
		1995*	1986-87	1995*	1986-87	1995*	1986-87	1995*	1986-87	1995	1986-87	1995*	1986-87	1995	1986-87
2	03S/09E-03N2	<0.001	<0.1	<0.002	—	<0.005	<0.1	<0.020	—	<0.2	—	<0.03	<3.0	<0.2	<0.2
3	02S/08E-35M1	<.001	<.1	.002E	—	<.005	<.1	<.020	—	<.2	—	1.1	<3.0	<.2	<.2
5 ¹	05N/06E-10Q2	.004	—	<.002	—	<.005	—	<.020	—	<.2	—	<.03	—	<.2	—
7 ¹	06S/13E-04Q1	.025	—	.015E	—	<.005	—	<.020	—	<.2	—	<.03	—	<.2	—
8	06S/12E-21C1	.002	<.1	<.002	—	.059	<.1	<.020	—	<.2	—	<.03	<3.0	<.2	<.2
9	07S/15E-35F2	.056	<.1	.14E	—	<.005	<.1	<.020	—	<.2	—	<.03	<3.0	<.2	<.2
11	12S/18E-01P2	.007	.1	.006E	—	.01	.2	<.020	—	<.2	—	<.03	<1.0	<.2	<.2
12	20S/21E-01Q1	<.001	<.1	<.002	—	<.005	<.1	<.020	—	<.2	—	<.03	—	<.2	<3.0
13 ¹	18S/20E-34L1	<.001	—	<.002	—	<.005	—	.007E	—	<.2	—	<.03	—	<.2	—
14	14S/20E-34G1	<.001	<.1	<.002	—	<.005	<.1	<.020	—	.2	—	<.03	<1.0	.4	6.4
15	13S/19E-17H2	<.001	<.1	<.002	—	.002	<.1	<.020	—	<.2	—	<.03	<1.0	<.2	<.2
16	13S/21E-01G1	<.001	<.1	<.002	—	.095	.1	.02E	—	<.2	—	<.03	<1.0	<.2	<.2
17	12S/22E-14F1	<.001	<.1	<.002	—	<.005	<.1	<.020	—	<.2	—	<.03	<1.0	<.2	<.2
18	16S/24E-26M1	<.001	<.1	.004E	—	.006	<.1	<.020	—	.4	—	<.03	<1.0	<.2	<.2
19	19S/23E-34P2	.002	<.1	.005E	—	.11	.1	.05E	—	<.2	—	<.03	<1.0	<.2	<.2
20	20S/24E-22C1	.12	<.1	.093E	—	.049	<.1	.11	—	<.2	—	<.03	<1.0	<.2	<.2
21	22S/24E-02A1	<.001	<.1	<.002	—	<.005	<.1	<.020	—	<.2	—	<.03	—	<.2	—
22	28S/24E-30M1	<.001	<.1	<.002	—	<.005	<.1	—	—	.2	—	<.03	—	1.6	—
23	31S/27E-16D1	.081	.4	.01E	—	.009	.2	<.020	—	<.2	—	<.03	—	<.2	<3.0
24	30S/28E-29P1	.003	<.1	.004E	—	<.005	<.1	<.020	—	<.2	—	<.03	—	<.2	<3.0
25 ¹	29S/27E-27B6	.007	—	.013E	—	.006	—	<.020	—	<.2	—	<.03	—	<.2	—
27 ¹	25S/26E-05A3	<.001	—	<.002	—	<.005	—	<.020	—	.6	—	.66	—	<.2	—
28 ¹	24S/26E-08A2	<.001	—	<.002	—	<.005	—	<.020	—	<.2	—	.35	—	<.2	—
29	21S/25E-26H1	.009	.2	.005E	—	<.005	.1	<.020	—	<.2	—	<.03	—	<.2	<3.0
30	18S/26E-02J1	<.001	<.1	<.002	—	.075	.2	<.020	—	<.2	—	<.03	—	<.2	<.2

Well No.	State well No.	Prometon		Cyanazine		Dichlobenil		Dieldrin		1,2-Dibromo-ethane (EDB)		Dicamba		Dichlorprop	
		1995*	1986-87	1995*	1986-87	1995*	1986-87	1995*	1986-87	1995*	1986-87	1995*	1986-87	1995*	1986-87
2	03S/09E-03N2	<.018	<.1	<.004	<.1	<.020	—	<.001	—	<.04	<.2	<.035	<.01	<.032	0.01
3	02S/08E-35M1	<.018	<.1	<.004	<.1	<.020	—	<.001	—	<.04	<.2	<.035	<.01	<.032	<.01
5 ¹	05N/06E-10Q2	<.018	—	<.004	—	<.020	—	.004	—	<.04	—	<.035	—	<.032	—
7 ¹	06S/13E-04Q1	<.018	—	<.004	—	<.020	—	<.001	—	<.04	—	<.035	—	<.032	—
8	06S/12E-21C1	<.018	<.1	<.004	<.1	<.020	—	<.001	—	<.04	<.2	<.035	<.01	<.032	<.01
9	07S/15E-35F2	<.018	<.1	<.004	<.1	.09	—	<.001	—	<.04	<.2	<.035	<.01	<.032	<.01
11	12S/18E-01P2	<.018	<.1	<.004	<.1	<.020	—	<.001	—	<.04	<.2	<.035	<.01	<.032	<.01
12	20S/21E-01Q1	<.018	<.1	<.004	<.1	<.020	—	<.001	—	<.04	<3.0	<.035	—	<.032	—
13 ¹	18S/20E-34L1	<.018	—	<.004	—	<.020	—	<.001	—	<.04	—	<.035	—	<.032	—
14	14S/20E-34G1	<.018	<.1	<.004	<.1	<.020	—	<.001	—	.55	<.2	<.035	<.01	<.032	<.01
15	13S/19E-17H2	<.018	<.1	<.004	<.1	<.020	—	<.001	—	<.04	<.2	<.035	<.01	<.032	<.01
16	13S/21E-01G1	<.018	<.1	<.004	<.1	<.020	—	<.001	—	<.04	<.2	<.035	<.01	<.032	<.01
17	12S/22E-14F1	<.018	<.1	<.004	<.1	<.020	—	<.001	—	<.04	<.2	<.035	<.01	<.032	<.01
18	16S/24E-26M1	<.018	<.1	<.004	<.1	<.020	—	<.001	—	<.04	<.2	<.035	.01 ²	<.032	<.01
19	19S/23E-34P2	<.018	<.1	<.004	<.1	<.020	—	<.001	—	<.04	<.2	<.035	<.01	<.032	<.01
20	20S/24E-22C1	<.018	<.1	.023	<.1	<.020	—	<.001	—	<.04	<.2	<.035	<.01	<.032	<.01
21	22S/24E-02A1	<.018	<.1	<.004	<.1	<.020	—	<.001	—	<.04	—	<.035	—	<.032	—
22	28S/24E-30M1	<.018	<.1	<.004	<.1	—	—	<.001	—	<.04	—	—	—	—	—
23	31S/27E-16D1	.008E	<.1	<.004	<.1	<.020	—	<.001	—	<.04	<3.0	<.035	—	<.032	—
24	30S/28E-29P1	<.018	<.1	<.004	<.1	<.020	—	<.001	—	<.04	<3.0	<.035	—	<.032	—
25 ¹	29S/27E-27B6	<.018	—	<.004	—	<.020	—	<.001	—	<.04	—	<.035	—	—	—
27 ¹	25S/26E-05A3	<.018	—	<.004	—	<.020	—	<.001	—	<.04	—	<.035	—	<.032	—
28 ¹	24S/26E-08A2	<.018	—	<.004	—	<.020	—	<.001	—	<.04	—	<.035	—	<.032	—
29	21S/25E-26H1	<.018	<.1	<.004	<.1	<.020	—	<.001	—	<.04	<3.0	<.035	—	<.032	—
30	18S/26E-02J1	.004E	<.1	<.004	<.1	<.020	—	<.001	—	<.04	<.2	<.035	.01	—	<.01

¹Well was not sampled for pesticides in 1986-87.

²Concentration in replicate sample is <0.01 microgram per liter.

tection Agency, 1996). Simazine was detected in 10 ground-water samples at concentrations ranging from 0.002 to 0.11 $\mu\text{g/L}$. These concentrations were at least one order of magnitude lower than the MCL of 4 $\mu\text{g/L}$ for simazine (U.S. Environmental Protection Agency, 1996).

Pesticide Use

Pesticides do not occur naturally in the environment; their presence in ground water is the result of human activities, such as the application of pesticides to agricultural crops and on rights-of-way and for home and garden use. Data from the California Department of Pesticide Regulation (1993) on reported applications of pesticides on agricultural crops in the eastern San Joaquin Valley in 1993 were used during this study to examine the relation between pesticide use and the occurrence of pesticides in ground water. The data include all reported pesticide applications for which a specific location was documented (for example, township, range, and section). The amount of the reported applications may be less than the actual amount applied; however, the compiled estimate for these applications is expected to account for 90 percent of the pesticide applications in the study area. The reported applications do not necessarily correspond to the amount of pesticides applied at the time the ground water sampled for this study was being recharged, but the data do provide some indication of the relative amounts and types of pesticides used. Data on rights-of-way applications also were compiled by the California Department of Pesticide Regulation (1991); however, the rights-of-way applications of pesticides were not reported for specific locations in the San Joaquin Valley. Thus, the rights-of-way applications used in this report may be higher than the actual applications in the eastern alluvial fan region.

The total reported application of pesticides to agricultural crops in the eastern San Joaquin Valley was 83 million lb active ingredient (a.i.) in 1993 (California Department of Pesticide Regulation, 1993). Sulfur, petroleum distillates, hydrocarbons, and oils account for about 60 percent of the total applications (California Department of Pesticide Regulation, 1993). Many of the most heavily applied pesticides in 1993 were not detected in any of the ground-water samples (table 6). For example, more than 5 million lb a.i. of bromomethane was applied, but bromomethane was not detected in the ground-water samples. Therefore, other

factors, such as the chemical properties of the pesticide (transformation rate, capacity for sorption), may influence whether pesticides will be detected in ground water.

The application of atrazine in 1993 was very low (1,090 lb a.i.) (table 6); however, atrazine or desethyl atrazine or both were detected in 13 of the 30 ground-water samples (43 percent) in 1995 (table 4). At least 30 percent of the land use within a 0.5-mi radius of three wells (wells 19, 20, and 29) with detections of atrazine or desethyl atrazine was corn (table 4). Atrazine has been used on corn both recently and in the past, which may explain its occurrence in these ground-water samples. Atrazine application on rights-of-way (7,558 lb a.i.) (California Department of Pesticide Regulation, 1991) was about seven times higher than the reported agricultural applications, which may account for the high number of detections of this pesticide in the ground-water samples. Atrazine has also been detected in rain and in air in other parts of the country where the pesticide is widely used (Majewski and Capel, 1995).

Simazine, detected in 10 of the 30 ground-water samples (33 percent) in 1995, was applied primarily to grapes, citrus, and almonds in 1993. Fifteen of the 30 wells had grapes, citrus, or almonds within a 0.5-mi radius of the well (table 4); however, simazine was detected in ground-water samples from only 6 of these wells. Ground-water samples from four wells (wells 19, 20, 23, and 25) had detections of simazine, but no grapes, citrus, or almonds were grown within a 0.5-mi radius of the wells. The detections of simazine in the samples from these four wells could have been derived from applications to crops that were more than 0.5 mi from the well. Simazine applications on rights-of-way also may explain the detections in the ground-water samples from these sites, although the amount of simazine applications used on rights-of-ways was only 50,408 lb a.i. (California Department of Pesticide Regulation, 1991), about 10 percent of the reported agricultural applications.

Diuron was detected in 4 of the 30 ground-water samples (13 percent; table 4) collected in 1995 at concentrations ranging from 0.007 to 0.11 $\mu\text{g/L}$ (table 5). Diuron was applied primarily to citrus, alfalfa, grapes, and walnuts in 1993. Twenty well sites had at least one of these land uses with a 0.5-mi radius of the well; however, only 2 of the 4 detections of diuron occurred in ground-water samples collected from wells (wells 19 and 20) with citrus, alfalfa, grapes; or walnuts within a 0.5-mi radius. One well (well 16) had a citrus crop 0.5

Table 6. Pesticides applied in the eastern alluvial fan physiographic region, San Joaquin Valley, California, 1993

[Data are from California Department of Pesticide Regulation (1993). Only pesticides that were analyzed for in this study and for which a location was reported (such as township, range, and section) are listed in this table. Pesticides are listed by application, beginning with the most heavily applied; rights-of-way applications are not listed. Primary use categories are: F, fumigant; Fu, fungicide; H, herbicide; I, insecticide; M, metabolite]

Pesticide (common chemical name)	Primary use	Total pounds active ingredient applied	Major crop uses and percentage of total applied
Bromomethane (methyl bromide)	F	5,897,433	Nursery (17%), preplant soil application (17%), almonds (13%), grapes (12%), carrots (10%), uncultivated agricultural area (8%), sweet potatoes (5%).
Propargite	I	1,141,912	Grapes (36%), almonds (25%), corn (16%), cotton (10%).
Chlorpyrifos	I	774,243	Oranges (45%), almonds (24%), walnuts (12%), alfalfa (5%).
Diazinon	I	569,713	Almonds (41%), peaches (18%), nectarines (15%), plums (12%).
Simazine	H	529,814	Grapes (42%), oranges (35%), almonds (9%).
Carbaryl	I	471,828	Oranges (54%), grapes (13%), olives (9%), peaches (7%).
Oryzalin	H	376,357	Grapes (36%), almonds (30%), pistachios (9%), peaches (5%).
Diuron	H	335,940	Oranges (56%), alfalfa (16%), grapes (14%), walnuts (5%).
Trifluralin	H	335,316	Cotton (49%), alfalfa (30%), grapes (5%).
Azinphos-methyl	I	231,846	Almonds (55%), walnuts (14%), apples (12%), peaches (5%), pistachios (5%).
EPTC	H	225,108	Corn (35%), potatoes (21%), alfalfa (20%), almonds (13%).
Chlorothalonil	Fu	219,085	Peaches (22%), carrots (20%), nectarines (19%), potatoes (9%), tomatoes (9%), onions (7%), plums (7%).
Cyanazine	H	128,122	Cotton (71%), corn (28%).
2,4-D {various formulations}	H	125,304	Almonds (42%), wheat (11%), oranges (8%), grapes (7%), walnuts (6%).
Norflurazon	H	122,852	Almonds (35%), grapes (25%), oranges (16%), plums (7%).
Methomyl	I	118,284	Grapes (41%), oranges (15%), nectarines (8%), tomatoes (8%), alfalfa (6%).
Aldicarb	I	117,719	Cotton (99%).
Malathion	I	97,211	Grapes (42%), alfalfa (32%), walnuts (10%), oranges (6%).
Butylate	H	96,750	Corn (100%).
Pendimethalin	H	88,972	Cotton (76%), potatoes (8%), almonds (6%).
Metolachlor	H	82,785	Corn (61%), beans (22%), safflower (15%).
Parathion-methyl {various formulations}	I	80,024	Plums (26%), nectarines (23%), peaches (19%), grapes (14%), apples (12%).
Phorate	I	70,767	Cotton (89%).
Carbofuran	I	66,329	Grapes (83%), alfalfa (15%).
Bromacil	H	44,806	Oranges (91%), lemons (6%).
MCPA {various formulations}	H	39,515	Wheat (48%), oats (27%), barley (10%), rice (8%), beans (6%).
Linuron	H	32,279	Carrots (99%).
Bromoxynil {various formulations}	H	31,566	Wheat (34%), oats (31%), barley (12%), alfalfa (8%).

Table 6. Pesticides applied in the eastern alluvial fan physiographic region, San Joaquin Valley, California, 1993—Continued

Pesticide (common chemical name)	Primary use	Total pounds active ingredient applied	Major crop uses and percentage of total applied
Dacthal (DCPA)	H, M	30,920	Onions (78%), broccoli (9%).
Napropamide	H	29,890	Almonds (40%), nursery (17%), grapes (9%), tomatoes (9%), peaches (7%).
Permethrin, <i>cis</i> -	I	22,834	Almonds (39%), pistachios (21%), peaches (13%), corn (7%).
Molinate	H	21,575	Rice (100%).
Pebulate	H	16,637	Tomatoes (92%), sugar beets (8%).
Ethoprop	I	11,132	Sweet potatoes (61%), potatoes (39%).
Dicamba {various formulations}	H	10,933	Corn (64%), wheat (17%), oats (8%), barley (7%).
Ethalfuralin	H	8,328	Beans (86%), watermelons (12%).
Benfluralin (benefin)	H	7,490	Alfalfa (93%), lettuce (7%).
Disulfoton	I	7,474	Potatoes (61%), asparagus (9%), corn (8%), peppers (8%).
Oxamyl	I	7,219	Apples (47%), peppers (14%), tomatoes (11%), nursery (9%), melons (5%).
Esfenvalerate	I	6,916	Almonds (20%), cherries (18%), potatoes (14%), peaches (11%), tomatoes (10%), walnuts (7%), corn (5%), cotton (5%).
1,3-Dichloropropene	F	3,050	Onions (68%), almonds (12%), corn (12%), grapes (8%).
Alachlor	H	2,916	Corn (47%), cotton (27%), beans (26%).
2,4-DB	H	2,756	Alfalfa (100%).
Pronamide (propyzamide)	H	2,620	Clover (90%), lettuce (7%).
Propanil	H	2,452	Rice (100%).
Parathion {various formulations}	I	1,768	Grapes (64%), oranges (10%), alfalfa (8%), walnuts (8%).
Fonofos	I	1,402	Tomatoes (58%), peppers (42%).
Thiobencarb	H	1,193	Rice (100%).
Metribuzin	H	1,183	Tomatoes (97%).
Atrazine {various formulations}	H	1,090	Sudan grass (60%), sorghum (18%), corn (13%), uncultivated non-agricultural areas (9%).
Dinoseb {various formulations}	H, I	1,051	Grapes (78%), peaches (15%), almonds (7%).
HCH, <i>gamma</i> - (lindane)	I	343	Peppers (47%), corn (30%), beans (12%), tomatoes (7%).
1,2-Dichloropropane {1,2 Dichloropropane, 1,3 Dichloropropene, and related C3 compounds}	F	279	Grapes (97%).
Triclopyr {various formulations}	H	131	Uncultivated non-agricultural areas (37%), pasture (32%), nursery (22%), commercial (8%).
Methiocarb	I	35	Nursery (100%).
Terbacil	H	9	Peaches (100%).
Dichlobenil	H	8	Nursery (100%).
Bentazon {various formulations}	H	1	Nursery (100%).

to 1.5 mi upgradient, which may explain the occurrence of diuron in the ground-water sample collected from this well. Diuron was a large component of rights-of-way applications (313,754 lb a.i.) (California Department of Pesticide Regulation, 1991), about 93 percent of the reported agricultural applications.

Prometon was detected in 2 of the 30 ground-water samples (7 percent) collected in 1995 at estimated concentrations of 0.004 and 0.008 $\mu\text{g/L}$ (wells 30 and 23, respectively) (table 5). Prometon was used primarily for landscape maintenance and rights-of-way and is not considered an agricultural pesticide. Although the predominant land use surrounding these two wells was agricultural, the detection of this nonagricultural chemical may be associated with nearby residential landscaping or rights-of-way. Cyanazine was detected in one ground-water sample at a concentration of 0.023 $\mu\text{g/L}$ (well 20) (table 5); its occurrence is consistent with the reported application of this pesticide on cotton and corn. Land use within a 0.5-mi radius of well 20 was 35 percent corn and 30 percent cotton (table 4). Dichlobenil was detected in one ground-water sample (well 9) at a concentration of 0.09 $\mu\text{g/L}$, and dieldrin was detected in one ground-water sample (well 5) at a concentration of 0.004 $\mu\text{g/L}$ (table 5). Only 8 lb a.i. of dichlobenil were applied in the study area in 1993, and dieldrin was not applied at all. The occurrence of these two pesticides may be because dichlobenil was a small component of rights-of-way application in 1991 in the San Joaquin Valley (434 lb a.i.) (California Department of Pesticide Regulation, 1991), and dieldrin has frequently been detected in air or in rain throughout the country (Majewski and Capel, 1995).

1,2,3-Trichloropropane was detected in 4 of the 30 ground-water samples (13 percent) collected in 1995 at concentrations ranging from 0.2 to 0.6 $\mu\text{g/L}$ (table 5). Two of the samples with 1,2,3-trichloropropane also contained 1,2-dichloropropane at concentrations of 0.4 $\mu\text{g/L}$ (well 14) and 1.6 $\mu\text{g/L}$ (well 22). 1,2-Dichloropropane (often formulated with 1,3-dichloropropene) was heavily used as a nematocide (California Department of Food and Agriculture, 1983) until its use was restricted in California in the 1980's. 1,2,3-Trichloropropane was a manufacturing byproduct of 1,2-dichloropropane and 1,3-dichloropropene formulations; therefore, the co-occurrence of 1,2-dichloropropane, 1,2,3-trichloropropane, and 1,3-dichloropropene might be expected. 1,3-Dichloropropene was not

detected in any ground-water samples in this study, but past applications of 1,3-dichloropropene on row crops, grapes, and orchards (8,012,452 lb a.i.) (California Department of Food and Agriculture, 1986) may account for the detections of 1,2,3-trichloropropane in the samples. Three of four ground-water samples with detections of 1,2,3-trichloropropane were detected in wells with row crops, grapes, and orchards within a 0.5-mi radius of the well (wells 18, 22, and 27) (table 4).

DBCP was detected in 3 of the 30 ground-water samples (10 percent) collected in 1995 at concentrations of 1.1, 0.66, and 0.35 $\mu\text{g/L}$ for wells 3, 27, and 28, respectively (table 5). The occurrence of DBCP is consistent with past use of this pesticide on deciduous fruit and nut crops and on grapes. The land uses within a 0.5-mi radius of these three wells are predominantly almonds and walnuts (well 3; 40 and 12 percent, respectively) and grapes (wells 27 and 28; 30 and 61 percent, respectively) (table 4). DBCP, a persistent and mobile nematocide, was banned from agricultural use in California in 1977. DBCP has been detected at concentrations above the MCL across a large part of the eastern San Joaquin Valley, prompting many studies (Weaver and others, 1983; California Department of Pesticide Regulation, 1992; California State University, Fresno Foundation, 1994). EDB, another banned soil fumigant, was detected in one ground-water sample at a concentration of 0.55 $\mu\text{g/L}$ (well 14) (table 5). The detections of EDB are not as widespread in the study area as are the detections of DBCP (California Department of Pesticide Regulation, 1992) because EDB was not as widely used and because the higher vapor pressure of EDB may have resulted in greater losses owing to volatilization.

Physical and Chemical Factors Related to Occurrence of Pesticides

Although the occurrence of many of the pesticides detected in ground-water samples collected during this study can be explained by pesticide use on adjacent crops, additional evaluation was done to determine the physical and chemical factors related to the occurrence of these pesticides. These factors were evaluated to determine whether characteristics of the aquifer or well-construction data may help identify areas that are more susceptible to pesticide contamination. Pesticide occurrence was examined in relation to well

depth and depth to water and various water-chemistry characteristics to help identify processes in the aquifer that can affect pesticide transport and fate, including characteristics that indicate agricultural effects on water quality and on the length of ground-water residence time.

Physical characteristics—depth of well below land surface (depth to the bottom of the well casing and depth to the top, middle, and bottom of the screened interval), depth to water below land surface, and depth of well below the water table—were not significantly different between groups of ground-water samples with at least one pesticide detection compared with groups of samples with no pesticide detections. Furthermore, the number of pesticides detected in each ground-water sample was not correlated to any of these depth characteristics. Soils and sediment texture and organic content may influence the leaching of pesticides to ground water; however, these variables were not statistically related to pesticide occurrence.

Pesticide occurrence was analyzed in relation to specific conductance and concentrations of major ions, dissolved oxygen, and tritium. Dissolved-oxygen concentration was the only characteristic that was significantly higher in ground-water samples with at least one pesticide detection compared with samples with no pesticide detections ($p=0.008$; Mann-Whitney test). Furthermore, dissolved-oxygen concentrations were positively correlated to the number of pesticide detections ($p=0.002$ and $\rho=0.54$; Spearman's rank correlation). Therefore, processes that promote high numbers of pesticide detections may also promote high dissolved-oxygen concentrations; these factors may include rapid recharge rates and relatively short ground-water residence times.

RELATION BETWEEN NITRATE AND PESTICIDES

The occurrence of nitrate and pesticides in ground water in the study area was compared to physical and chemical factors to determine if certain characteristics or processes affect concentrations in the aquifer. In the study area, nitrate and pesticide occurrence in ground water is associated primarily with agricultural land use. Although the use of nitrogen fertilizers and pesticides is highly variable, some of the processes that control the occurrence of nitrate may also control the occurrence of pesticides, and the co-

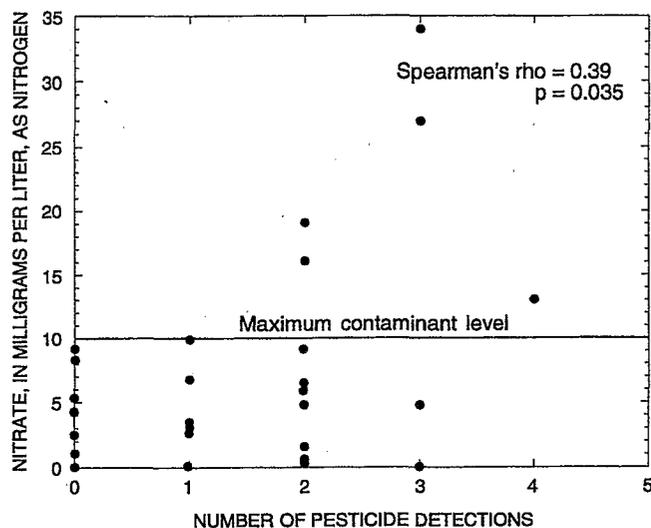


Figure 9. Relation between nitrate concentration and the number of pesticide detections in ground-water samples from selected domestic wells in the eastern San Joaquin Valley, California. Maximum contaminant level for nitrate is from U.S. Environmental Protection Agency (1996).

occurrence of nitrate and pesticides may indicate greater susceptibility to ground-water contamination.

Nitrate concentrations were positively correlated with the number of pesticides detected in each ground-water sample ($p=0.035$, $\rho=0.39$; Spearman's rank correlation). All five samples with nitrate concentrations greater than the MCL of 10 mg/L also had more than one pesticide detection (fig. 9). These relations indicate that ground water that is susceptible to nitrate contamination may also be susceptible to contamination by pesticides. This susceptibility may result from rapid infiltration through relatively coarse-grained sediments. However, the relation between nitrate and pesticide occurrence was not supported by further analysis of the data. Nitrate concentrations were not significantly different between groups of ground-water samples with at least one pesticide detection and groups of ground-water samples with no pesticide detections ($p=0.12$; Mann-Whitney test). Overall, this suggests that ground water that is susceptible to nitrate contamination could be susceptible to contamination by pesticides, but the relation may be influenced more by the differences in fertilizer and pesticide applications, or the chemical properties of the compounds, than by the physical characteristics of the sediments.

TRENDS IN NITRATE AND PESTICIDES

Twenty-three wells sampled in 1986–87 were resampled in 1995 during a preliminary evaluation of temporal trends in nitrate and pesticides. In 1986–87, ground-water samples from all 23 wells were analyzed for nitrate, 19 samples were analyzed for pesticides, 17 samples were analyzed for VOCs (including EDB), and 12 samples were analyzed for DBCP. Nitrate and pesticide concentrations and the number of pesticide detections were compared between the two data sets.

Nitrate Trends

The median nitrate concentration in the 1995 ground-water samples from the 23 resampled wells was 4.8 mg/L, compared with the median concentration in the 1986–87 samples of 2.4 mg/L. Nitrate concentrations in ground-water samples collected in 1995 were higher than nitrate concentrations in the samples collected in 1986–87 in 13 of the 23 resampled wells (56 percent) (table 3, fig. 10). Of three wells sampled in both 1995 and 1986–87 that had reduced geochemical conditions, the ground-water sample from one well (well 12) had a slightly higher nitrate concentration in 1986–87 than in 1995; whereas, the other two wells (wells 13 and 26) had no detections of nitrate in either the 1995 or the 1986–87 samples. If these 3 wells are excluded from the data set, nitrate concentrations in the samples collected in 1995 were higher in 13 of the remaining 20 wells (65 percent) than concentrations in the samples collected in 1986–87. The 13 wells with higher nitrate concentrations in the ground-water samples in 1995 were located throughout the study area and had a variety of land uses within a 0.5-mi radius of the well. In a pairwise comparison of the 1995 and 1986–87 data, nitrate concentrations were significantly higher in the 1995 ground-water samples ($p=0.05$; Wilcoxon signed-rank test) than the concentrations in the 1986–87 samples.

Nitrate concentrations were positively correlated to specific conductance in the 1995 and the 1986–87 ground-water samples ($p=0.004$, $\rho=0.51$ and $p=0.033$, $\rho=0.44$, respectively; Spearman's rank correlation). However, unlike the increase in nitrate concentrations, specific conductance was not significantly higher in the 1995 ground-water samples than in the 1986–87 samples ($p=0.30$; Wilcoxon signed-rank test).

In an earlier study (1950 through 1967), Nightingale (1970) evaluated trends in nitrate concentrations

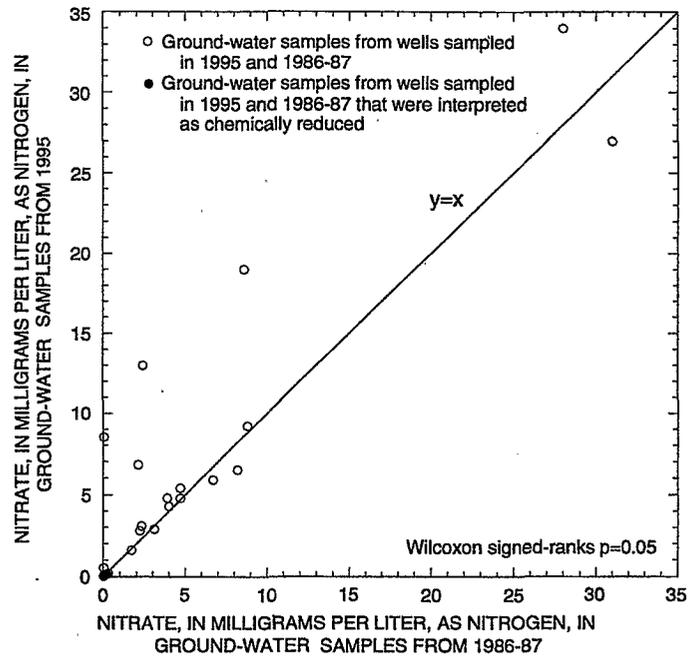


Figure 10. Nitrate concentrations in ground-water samples from 1995 and 1986–87 in the eastern San Joaquin Valley, California.

and specific conductance (electrical conductivity) in ground water in the eastern San Joaquin Valley, near Fresno. Nightingale (1970) determined that mean nitrate concentrations in an urban land-use area increased from 2.4 mg/L in 1950–55 to 3.7 mg/L in 1962–67, whereas mean nitrate concentrations in an agricultural land-use area increased from 1.2 mg/L in 1950–56 to 3.6 mg/L in 1962–67. Mean specific conductance in the urban land-use area increased from 262 $\mu\text{S}/\text{cm}$ in 1950–56 to 362 $\mu\text{S}/\text{cm}$ in 1962–67. However, mean specific conductance did not increase in the agricultural land-use area, and Nightingale (1970) did not identify a correlation between nitrate concentrations and specific conductance.

The lack of an increase in specific conductance in the agricultural land-use area in the Nightingale (1970) study and in the predominantly agricultural area in this report indicates that nitrate concentrations and salinity (as indicated by specific conductance) may be controlled by different factors. This concept is contradictory to the positive correlation between nitrate concentrations and specific conductance in this current study. One explanation for the lack of an increase in specific conductance is that the contribution of agricultural chemicals to salinity has been buffered by irrigation recharge with low-salinity surface water in the

Table 7. Summary of pesticide detections in 1995 and 1986–87 ground-water samples from selected domestic wells in the eastern San Joaquin Valley, California

[MRL, method reporting limit; MDL, method detection limit; NA, not analyzed; (), number of samples collected from wells in both 1995 and 1986-87; [], number of samples collected with indicated concentration for MRL; µg/L, microgram per liter; <, actual value less than value shown]

Pesticide	Number of detections in 1995 ¹	Number of detections in 1995 censored at or above the highest MRL or MDL	Number of detections in 1986-87	Number of detections in 1986-87 censored at or above the highest MRL or MDL	1986 MRL (µg/L)	1987 MRL (µg/L)	1995 MRL or MDL (µg/L)
Atrazine (19)	8	2	3	3	<0.1	<0.1	0.001 ²
Simazine (19)	9	3	6	6	<.1	<.1	.005 ²
1,2-Dibromo-3-chloropropane (DBCP) (12)	1	0	0	0	NA	<1.0 [8] <3.0 [4]	.03
1,2-Dichloropropane (17)	1	1	1	1	<3.0 [4]	<.2 [13]	.2
Prometon (19)	2	0	0	0	<.1	<.1	.018 ²
Cyanazine (19)	1	0	0	0	<.1	<.1	.004 ²
1,2-Dibromoethane (EDB) (17)	1	1	0	0	<3.0 [4]	<.2 [13]	.04
Dicamba (13)	0	0	2	0	<.01	<.01	.035 ²
Dichlorprop (13)	0	0	1	0	<.01	<.01	.032 ²
Total	23	7	13	10			

¹ Corresponds to samples collected from wells in both 1995 and 1986-87.

² Compounds that were not detected are reported as less than the MDL.

study area. The relative amount of ground and surface water supplied for irrigation is dependent on highly variable climatic conditions, and hence, on variable reservoir storage, making this hypothesis difficult to evaluate.

Pesticide Trends

Twenty-one of the 30 ground-water samples (70 percent) collected in 1995 contained at least one detected pesticide (table 4); 16 of the 21 samples were collected from wells that also had been sampled in 1986–87 (table 5). Although the 1995 and 1986–87 samples were analyzed by the same laboratory, the 1995 and the 1986–87 samples were not analyzed for all of the same pesticides. Of the 84 pesticides listed in table 1, 63 were analyzed in 1995 that were not analyzed in 1986–87. Therefore, both the 1995 and the 1986–87 ground-water samples were analyzed for 21 pesticides listed in table 1. Similarly, of the 60 volatile organic compounds listed in table 2, thirty-seven were analyzed in both 1995 and 1986–87. For ground-water samples collected from the same wells and analyzed for the same pesticides in 1995 and in 1986-87, seven different pesticides were detected in the 1995 ground-water samples for a total of 23 pesticide detections (table 7). Only five different pesticides were detected in

the 1986–87 ground-water samples for a total of 13 pesticide detections.

The difference in the number of detections between 1995 and 1986–87 can be attributed partly to the difference in the reporting levels between the two data sets. In 1995, the method detection limit (MDL) was at least one order of magnitude lower than the 1986–87 method reporting limit (MRL) for atrazine, simazine, DBCP, prometon, cyanazine, and EDB (table 5). Conversely, the MRLs in 1986–87 for dicamba and dichlorprop were lower than the 1995 MDLs. To account for the differences in the reporting levels of the 1995 and 1986–87 analytical methods, the concentrations were rounded to the same number of significant figures and censored at the highest MDL or MRL (table 7). Using the censored values, the 1995 ground-water samples had 7 pesticide detections compared with 10 detections in the 1986–87 ground-water samples, indicating that the number of detections has not increased.

To evaluate the relative concentrations of the pesticides, the uncensored data were used. Nine of the 13 pesticide detections in the 1986–87 ground-water samples (table 7) also occurred in the 1995 ground-water samples collected from the same wells (wells 11, 14, 16, 19, 23, 29, and 30) (table 5). Seven of the 9 pesticide detections had a concentration in 1995 that was less than one-half of the concentration in 1986–87.

Concentrations of 2 of the 9 detections were nearly equivalent (simazine, wells 16 and 19). These results indicate that pesticide concentrations have not increased between 1986–87 and 1995 for those pesticides detected in both the 1986–87 and the 1995 ground-water samples.

Four of the 13 pesticide detections in the 1986–87 ground-water samples did not occur in the 1995 samples. Three of the four detections were of dicamba and dichlorprop. These pesticides were detected in 1986–87 at concentrations below the 1995 MDL. The lack of detection of these pesticides in 1995 indicates that their concentrations have not increased significantly over time; however, it was not possible to determine whether the concentrations have decreased or remained stable. In one well (well 29), simazine was not detected above the MDL of 0.005 µg/L, even though it was detected at a concentration of 0.1 µg/L in the 1986–87 sample.

Only two pesticides (atrazine [well 20] and EDB [well 14]) were detected in the 1995 ground-water samples at concentrations above the 1986–87 MRL that were not detected in the corresponding 1986–87 ground-water samples (table 5). Atrazine use is currently restricted, and EDB has been banned from use since the 1980's; the "new" detections of these pesticides may be related to past use and, therefore, does not necessarily indicate increased degradation of the ground water between 1986–87 and 1995. Finally, no pesticides were detected in either the 1995 or the 1986–87 samples from wells 12, 17, and 21; wells 5, 7, 13, 25, 27, and 28 had pesticide detections in the 1995 ground-water samples, but these wells had not been sampled in 1986–87.

Although the number of wells resampled for selected pesticides was relatively small, the number of pesticide detections (at comparable detection limits) did not increase between 1986–87 and 1995. The high number of pesticide detections in the 1995 ground-water samples, relative to the number of detections in the 1986–87 ground-water samples, does not reflect increasing degradation of the ground-water resource, but rather an improvement in the analytical methods for detection of these pesticides. Furthermore, concentrations of most of the pesticides detected in 1986–87 seem to have decreased during this period. However, it is important to recognize that because of the depth of the sampled wells, ground water sampled in 1995 may represent land-use practices 10 to 30 years prior to sampling. Therefore, attributing the apparent decrease

in concentrations and the lack of new detections to current land-use practices could be misleading.

SUMMARY AND CONCLUSIONS

To assess the occurrence of nitrate and pesticides in ground water in the eastern San Joaquin Valley, ground-water samples were collected from 30 domestic wells in 1995 (one sample was collected from each well). The results of the analyses were related to various physical and chemical factors in an attempt to understand the processes that control the occurrence and concentrations of nitrate and pesticides in ground water. A preliminary analysis of temporal trends in the occurrence and concentrations of nitrate and pesticides was examined by comparing chemical data for the 1995 ground-water samples from 23 of the wells sampled in 1995 with the chemical data for the samples collected from the same wells during 1986–87.

Nitrate (dissolved nitrate plus nitrite, as nitrogen) was detected in 27 of the 30 ground-water samples collected in 1995. Concentrations ranged from less than 0.05 to 34 mg/L, as nitrogen, with a median of 4.6 mg/L. Nitrate concentrations exceeded the MCL of 10 mg/L in 5 of the 30 ground-water samples (17 percent). Nitrate concentrations were not significantly correlated to the estimated amount of nitrogen fertilizer applications in a 0.25- or 0.5-mi radius of each sampled well. Nitrate concentrations were inversely correlated to the depth to the screened interval of the wells sampled. Nitrate concentrations generally decrease with depth because, in recharge areas, ground water that is deeper in the flow system is generally older, which reflect lower historical application rates of nitrogen fertilizers, the effects of dispersion along longer travel paths, or a longer period of time for nitrate-removal processes to affect concentrations. Low nitrate concentrations in older ground water are consistent with a positive correlation between nitrate and dissolved-oxygen concentrations and nitrate and tritium concentrations, indicating that high concentrations of nitrate could be associated with recently recharged, well-oxygenated water. Elevated nitrate concentrations also were associated with elevated chloride and sulfate concentrations, reflecting increased agricultural effects. Agriculturally affected waters have elevated salinity as a result of the leaching of fertilizers and the increased evaporation of ground water as it is pumped and reapplied for irrigation. A positive correlation between specific conductance, an

indicator of salinity, and nitrate concentrations supports the relation between elevated nitrate concentrations and agriculturally affected ground water.

Twenty-one ground-water samples collected in 1995 (70 percent) had at least one detected pesticide. Twelve different pesticides were detected in these 21 samples, although only five pesticides were detected in more than 10 percent of the samples. The only pesticides that were detected at concentrations above the MCL for drinking water were EDB and DBCP, pesticides that are no longer used. Only 5 of the 12 detected pesticides, however, have enforceable drinking-water standards. DBCP was detected in three ground-water samples at concentrations above the MCL of 0.2 µg/L, and EDB was detected in one ground-water sample at a concentration above the MCL of 0.05 µg/L. Atrazine or desethyl atrazine (a transformation product of atrazine) was detected in 11 ground-water samples; they were the most frequently detected pesticides. The reported use of atrazine on agricultural crops in 1993 is relatively low (1,090 lb a.i.); however, the number of detections of atrazine was relatively high. The frequent detections of atrazine may be related either to past use or to its recent application on rights-of-way. Simazine was detected in 10 ground-water samples; its occurrence is generally consistent with its reported use on crops near the sampled wells. Diuron was detected in four ground-water samples. Land use at most of the wells with diuron detections was associated with diuron application. 1,2,3-trichloropropane was detected in four ground-water samples. The occurrence of 1,2,3-trichloropropane, a manufacturing by-product of 1,2-dichloropropane and 1,3-dichloropropene formulations, may be linked to past use of these pesticides.

Pesticide occurrence was linked to dissolved-oxygen concentrations, indicating that areas with relatively high dissolved-oxygen concentrations may be more susceptible to pesticide contamination. High dissolved-oxygen concentrations may be associated with relatively young ground water that has been rapidly recharged. The number of pesticides detected in each sample also was correlated to elevated nitrate concentrations, indicating that similar processes may control the concentrations and the occurrence of nitrate and pesticides in ground water in this study area.

Nitrate and pesticide concentrations and occurrence were compared between samples collected in 1995 and 1986–87 from the same wells. The median nitrate concentration in 1995 was 4.8 mg/L in the ground-water samples from the 23 resampled wells; the

median concentration in 1986–87 was 2.4 mg/L. Nitrate concentrations were significantly higher in 1995 than in 1986–87, using a pairwise comparison. Specific conductance, which was correlated to nitrate concentrations in the 1995 and the 1986–87 data sets, was not significantly higher in 1995 than in 1986–87.

Seven different pesticides were detected in the 1995 ground-water samples for a total of 23 pesticide detections in the ground-water samples collected from the same wells and analyzed for the same compounds in 1995 and 1986–87. Five different pesticides were detected in 1986–87 ground-water samples for a total of 13 pesticide detections. However, the analytical detection limits in 1995 were generally at least one order of magnitude lower than the reporting levels in 1986–87. With the detections censored at the highest MRL or MDL, the number of pesticide detections were similar between the two data sets: 7 pesticide detections in 1995 and 10 pesticide detections in 1986–87. Nine of the 13 pesticide detections in the 1986–87 ground-water samples also occurred in the 1995 ground-water samples collected from the same wells, although 7 of the 9 detections had a concentration in 1995 that was less than one-half the concentration in 1986–87. Only two pesticides (atrazine and EDB) were detected in the 1995 ground-water samples at concentrations above the 1986–87 MRL that were not detected in the corresponding 1986–87 ground-water samples. Although these two detections constitute “new” pesticide detections, the occurrence of atrazine and EDB may be related to past use and, therefore, does not necessarily indicate increased degradation of the ground-water resource between 1986–87 and 1995.

In conclusion, these data indicate that nitrate may pose a greater threat to the quality of ground water in the eastern alluvial fan region of the San Joaquin Valley than pesticides, in the context of current drinking-water standards. Nitrate concentrations exceeded the MCL in 5 of the 30 ground-water samples (17 percent) and nitrate concentrations have significantly increased between 1986–87 and 1995. Although four ground-water samples had pesticide detections at concentrations above the MCL, the pesticides that were detected (DBCP and EDB) have been banned from use. Furthermore, the number of pesticide detections did not increase significantly between 1986–87 and 1995 and the concentrations of the detected pesticides seem to have decreased. The difference in the overall effect of nitrate and pesticides on ground water may be caused by the large spatial variability in the application

of pesticides or by differences in their chemical properties. The number of wells resampled for nitrate and pesticides was small; therefore, the results of the comparison between 1986-87 and 1995 must be interpreted with caution.

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