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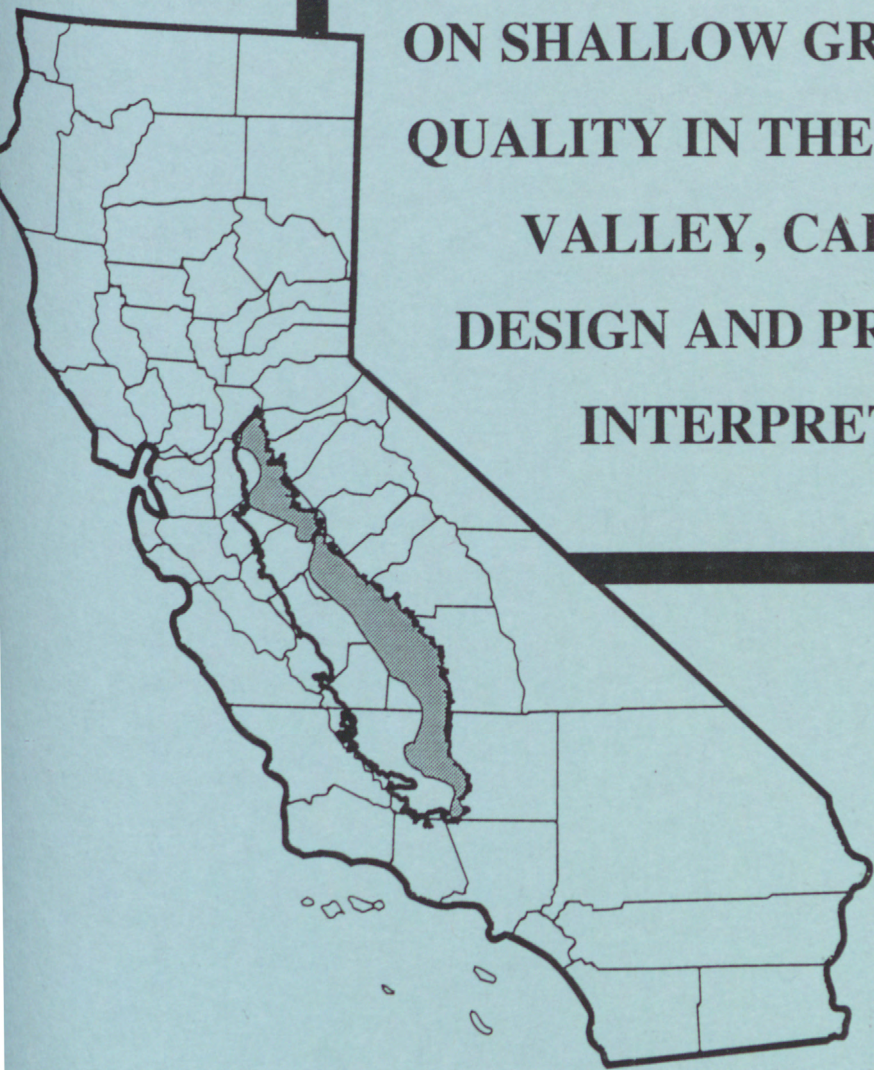

U.S. GEOLOGICAL SURVEY

Open-File Report 95-286

Prepared in cooperation with the
NATIONAL WATER-QUALITY ASSESSMENT PROGRAM

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By Neil M. Dubrovsky, Karen R. Burow, and Jo Ann M. Gronberg

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Sacramento, California
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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 a specific contamination problem; 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 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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FIGURES

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CONVERSION FACTORS

Multiply	By	To obtain
kilogram (kg)	2.2046	pound
kilogram per hectare (kg/ha)	2.2046	pound per acre
kilometer (km)	06214	mile
meter (m)	3281	foot

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Abstract

From 1992 through 1994, the San Joaquin-Tulare Basins Study team of the USGS National Water Quality Assessment program investigated the occurrence and distribution of water quality constituents in shallow groundwater underlying two areas of different agricultural land uses: almond orchards and vineyards. The study was restricted to the alluvial fans of the eastern San Joaquin Valley, the area of most groundwater use in the valley. A geographic information system (GIS) was used to delineate the distribution of the two target land uses, to evaluate ancillary data, and to select candidate wells that fit prescribed criteria. Twenty domestic water supply wells were sampled in each of the two areas. In addition, pairs of observation wells were installed and sampled at five of the sites in each area to evaluate whether the water quality in the domestic wells reflects that of the shallow groundwater underlying the target land use. A preliminary evaluation of the results shows that nitrate concentrations in the shallow groundwater are significantly higher in the almond orchard areas than in the vineyard area ($p = 0.005$). In contrast, concentrations of 1,2-dibromo-3-chloropropane (DBCP) were higher in the vineyard area than in the almond orchard area ($p = 0.032$). The most frequently detected pesticides in groundwater underlying both areas were simazine, atrazine, and desethylatrazine (an atrazine degradation product). These observations are explained, in part, by differences in chemical application and hydrogeologic factors.

INTRODUCTION

A comprehensive multidisciplinary investigation of water quality in the San Joaquin and Tulare Basins, California, was started in 1991 as part of the U.S. Geological Survey (USGS) National Water Quality Assessment (NAWQA) Program. From 1992 to 1994, the quality of shallow groundwater in a portion of the study area was investigated as part of the NAWQA Land-Use Study. The purpose of the Land-Use Study is to assess the concentration and distribution of water quality constituents in groundwater that has recently recharged through a targeted land use, and to examine the natural and human factors affecting the quality of groundwater underlying key types of land use. This paper describes the design of the two land use studies and the preliminary evaluation of the concentrations of nitrate and the four most frequently detected pesticides in shallow groundwater in areas of almond and vineyard land use.

STUDY DESIGN AND METHODS

The first step in the selection of target land use study areas was the prioritization of the groundwater system into subareas. Although the San Joaquin-Tulare Basins study area encompasses the entire drainage area, the groundwater investigations were restricted to the San Joaquin Valley part of the study area because both population and groundwater use are concentrated in this area (fig. 1 insert). The valley was subdivided into three physiographic subareas --

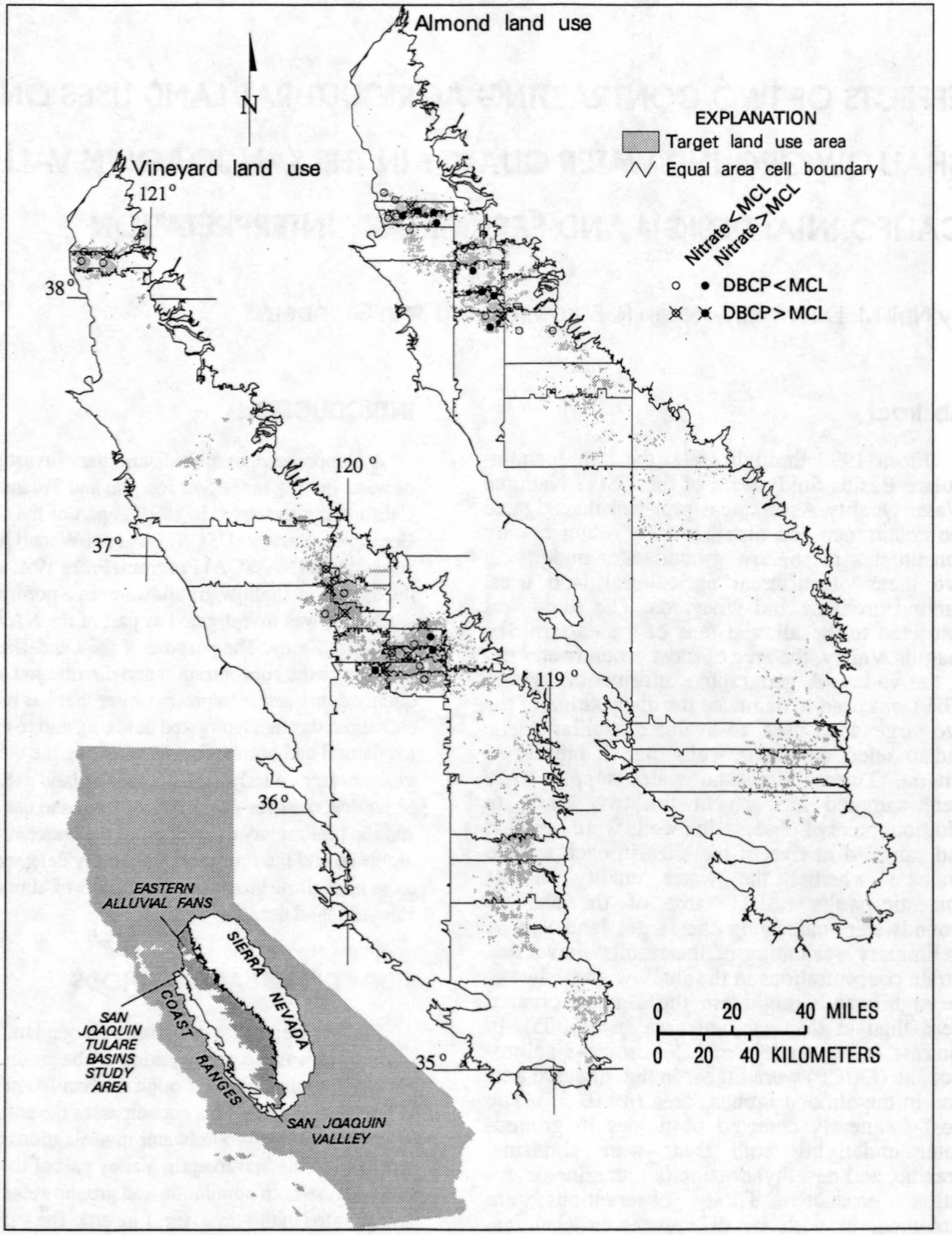

Figure 1. Vineyard and almond land use in the eastern alluvial fans subarea, with cell boundaries and wells showing nitrate and 1,2-dibromo-3-chloropropane (DBCP) concentrations. Inset map of California shows study area.

eastern alluvial fans, basin deposits, and western alluvial fans. These subareas were then evaluated for spatial distribution of groundwater use, existing information on contamination, and potential for contamination as indicated by the presence or absence of chemical and nutrient sources. Estimates based on 1988 water use data (California Department of Water Resources, 1990; Fred Stumpf, California Department of Water Resources, written commun., 1990), indicate that the eastern alluvial fans subarea accounts for about 96% of the groundwater use in the study area. In addition, existing data on groundwater quality show that there are large contrasts between the concentrations of contaminants in the three physiographic subareas, including nitrate (Dubrovsky *and others,* 1993); some trace elements (Dubrovsky *and others,* 1993; Dubrovsky 1991); and pesticides (Domagalski & Dubrovsky, 1992). Because of these considerations, the Land-Use Study was confined to the eastern alluvial fans subarea.

The eastern alluvial fans subarea contains significant acreage of five agricultural land use groups targeted by NAWQA as national priorities: vineyards; almond orchards; areas where alfalfa, corn, and vegetables are grown together or in rotation; citrus; and cotton. In aggregate, these areas represent about 67% of the total groundwater use in the study area. The vineyard, almond orchard, and alfalfa-corn-vegetable land use areas were evaluated in 1993, 1994, and 1995, respectively.

Sampling networks of 20 randomly selected domestic wells, supplemented by monitoring wells, were established in both the vineyard and almond land use areas. The shallowest existing wells in the study area -- domestic wells -- were sampled because the identification of recently recharged groundwater is difficult and beyond the scope of this study. The vineyard land use area in the eastern alluvial fan subarea was the first area selected for sampling. A geographic information system (GIS) was used to evaluate candidate wells with respect to the spatial distribution of land use and depth-to-water. Data for domestic wells less than 61 m deep were retrieved from the USGS Ground-Water Site Inventory database. Only 131 of the 1931 wells that fit this criterion were located in the vineyard area. Using the GIS, wells that had less than 50% vineyard land use acreage within a 0.8 km radius were eliminated, producing a list of 92 candidate wells. To increase the pool of wells suitable for sampling, the authors examined well logs from the California Department of Water Resources. The total area of vineyards on the eastern alluvial fan subarea was divided into 20 cells containing equal areas of vineyards using a grid-based selection program (Scott, 1990) to obtain uniform spatial coverage of the target land use (fig. 1). All candidate wells within each cell were prioritized by the percentage of vineyard land use within a 0.8 km radius and a well was selected from each cell. The ideal well for sampling would be located in a recharge area, screened near the water table, and directly downgradient from a single land use. This would lessen the influence of other land use activities and complications from upward movement of water that originated in distant areas. Candidate wells were visited prior to sampling to assess these factors, to verify the land use in the immediate vicinity of the well, and to eliminate wells potentially impacted by point sources, such as storage and handling of agricultural chemicals. Design of the almond land use study followed the same steps. The resulting networks for both the vineyard and almond areas are shown in fig. 1. Note that access to wells suitable for sampling could not be obtained in all of the cells.

Pairs of monitoring wells were installed adjacent to the domestic wells but within, or as close as possible to, the target land use, at five sites in each land use area. Each pair consists of two wells, one screened immediately below the water table and one screened at the same depth as the domestic well. Comparisons between the water quality in samples from the domestic and monitoring wells provide information on whether the water quality of the domestic wells is representative of the shallow water quality underlying the targeted land use, and whether the domestic wells are prone to point-source contamination due to factors unrelated to the land use being studied. Results from the monitoring wells are not discussed in this paper.

Sampling followed a nationally consistent set of procedures established by the NAWQA Program for obtaining groundwater samples (W. Lapham, U.S. Geological Survey, written commun., 1995). A wide variety of chemical species were analyzed to characterize groundwater quality, including major ions, nutrients, pesticides, volatile organic compounds, trace elements, selected radionuclides, and environmental isotopes (see Gilliom *and others,* 1995, tables 6 and 7 for a complete list). All chemical analyses were performed at the USGS National Water Quality Laboratory. Nitrate was analyzed by reduction to nitrite followed by colorimetric measurement (Fishman and Friedman, 1985). The samples were analyzed for 46 dissolved pesticides by solid phase extraction onto C-18 resin, followed by gas chromatography/mass spectrometry (GC/MS) analysis (Zaugg *and others,* 1995). DBCP was analyzed by extraction with hexane, followed by GC analysis using an electron capture detector (Fishman, 1993).

COMPARISON OF NITRATE CONCENTRATIONS

Comparison of the nitrate concentrations in groundwater samples from the domestic wells indicates that nitrate concentrations in the almond land use area are higher (probability p=0.005, Mann-Whitney test) than those from the vineyard land use area (table 1). The concentrations in the wells in the almond area equal or exceed the drinking water Maximum Contaminant Level (MCL) of 10 mg/l nitrate (as N) in 10 cases, whereas the concentrations in the wells in the vineyard area equal or exceed this concentration in only three cases (fig. 2). The data show that there is widespread nitrate contamination of the shallow groundwater in the almond area, whereas nitrate attains concentrations that are of concern in only a few locations in the vineyard area.

Several factors may contribute to the observed difference in nitrate concentration. It is likely that the input of nitrate to the water table derived from fertilizer application in the almond area is greater than in the vineyard area because the rate of fertilizer application is higher in almond orchards than in vineyards, 208 kg/hectare and 64 kg/hectare respectively (US Department of Agriculture, 1992). There are also a large number of dairy farms located in the vicinity of the almond orchards in the northern part of the study area. Some of the nitrate may originate from the dairy farms. Although the depth to the bottom of

Table 1. Concentrations of nitrate, 1,2-dibromo-3-chloropropane (DBCP), simazine, atrazine, and desethylatrazine in ground water samples from domestic wells in almond and vineyard land use areas, eastern San Joaquin Valley, California

[MCL, Maximum Contaminant Level]

	Maximum	Median	Minimum	No. of samples with concentration at or above the MCL	No. of samples with detectable concentrations
[1]Nitrate (as mg/l N)					
Almond	55	10	1.3	8	20
Vineyard	14	4.6	.058	3	20
[1]DBCP (µg/l)					
Almond[2]	2.6	<.03	<.03	5	7
Vineyard	3.2	.41	<.03	10	12
Atrazine (µg/l)					
Almond	.069	<.001	<.001	0	5
Vineyard	.056	<.001	<.001	0	7
Simazine (µg/l)					
Almond	.038	<.005	<.005	0	6
Vineyard	.2	<.005	<.005	0	8
[1]Desethylatrazine (µg/l)					
Almond	.019	<.002	<.002	0	9
Vineyard	.030	<.002	<.002	0	1

[1]The concentration of this constituent in the two land use areas is different at the 5% level.

[2]n=19

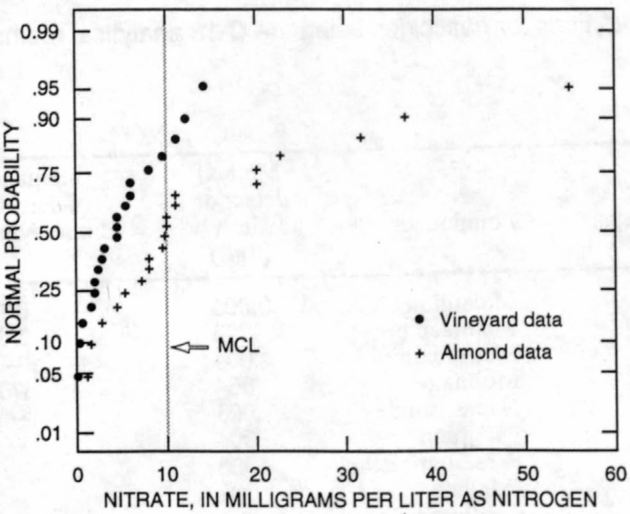

Figure 2. Normal probability plot of the nitrate concentration in samples from the almond and vineyard land use areas.

the well screens is the same in the two sets of wells, the water table is shallower in the almond area than in the vineyard area (p=0.021, Mann-Whitney test); a shallow water table means more rapid isolation from the atmosphere and less potential for nitrate removal by reactions in the unsaturated zone. Factors not yet evaluated include soil characteristics and irrigation management practices.

COMPARISON OF PESTICIDE CONCENTRATIONS

Twenty-two of the 40 wells sampled contained detectable concentrations of one or more pesticide: 12 in the vineyard land use area and 10 in the almond land use area. Nine of these detections were for single compounds, and only four wells contained more than three compounds. A total of 20 compounds were identified in the samples using this method (table 2). The same three compounds occur most frequently in both land use areas: simazine, atrazine, and desethylatrazine, an atrazine degradation product (table 1). Five other compounds were detected in samples from both areas; three compounds were detected only in samples from the vineyard area; and nine compounds were detected only in samples from the almond area (table 2). Five of the compounds -- alachlor, diazinon, fonofos, molinate, and thiobencarb -- were found only in one well in the almond area that was of note for having detections for 16 compounds, as well as having the highest concentration of nitrate (55 mg/l) in the entire data set.

Pesticide detections are associated with high nitrate concentrations in the almond area: six of eight samples that exceed the nitrate MCL also had detectable concentrations of at least one pesticide. Although this association is not significant at the 5% level (p=0.068, Chi-squared test), it does suggest that severe agricultural nitrate contamination may be accompanied by pesticide contamination in this land use area.

About 239,000 kg of the triazine herbicide simazine was applied to 34 different commodities in the San Joaquin Valley in 1991 (table 3). Application of simazine to vineyards was the second largest commodity use; use on almond orchards was about one-third of that on vineyards. By adjusting the amount of application for the approximate acreage of almond orchards and vineyards in the valley, we estimated average application rates of 0.20 kg/hectare and 0.36 kg/hectare for the almond orchards and vineyards respectively. The data also show a mode of use that greatly complicates the identification of cause-and-effect relations between agricultural use of simazine and environmental occurrence: the application of 22,900 kg to roads (rights-of-way) for weed control.

The maximum simazine concentration of 0.28 µg/l is far below the MCL of 3 µg/l. The highest single concentration, as well as the highest frequency of detection of simazine, occurs in the vineyard area, but the differences between concentrations (p=0.234, Mann-Whitney test) or frequency-of-occurrence (p=0.507, Chi-squared test) in the two areas are not significant at the 5% level. The lack of significant contrast between the simazine concentrations in the two areas may be due to groundwater contamination by simazine used on rights-of-way. This hypothesis has been suggested before to explain simazine occurrence in areas of little or no known agricultural use (Domagalski & Dubrovsky, 1992).

Table 2. Method detection limit and frequency of detections for pesticides using the C-18 analytical method (Modified from Zaugg and others, 1995).

[--, no detections in either well; µg/L, microgram per liter]

Compounds	Method detection limit (µg/l)	Frequency of detection almond/vineyard	Compounds	Method detection limit (µg/l)	Frequency of detection almond/vineyard
Alachlor	0.002	1/0	Malathion	0.005	0/1
Atrazine	.001	6/8	Metolachlor	.002	2/0
Atrazine, deathless-	.002	9/1	Metribuzin	.004	--
Azinphos-methyl	.001	--	Molinate	.004	1/0
Benfluralin	.002	--	Napropamide	.003	--
Butylate	.002	1/1	Parathion	.004	--
Carbaryl	.003	1/1	Parathion-methyl	.006	--
Carbofuran	.003	--	Pebulate	.004	--
Chlorpyrifos	.004	1/1	Pendimethalin	.004	--
Cyanazine	.004	2/0	Permethrin, cis-	.005	--
DCPA (Dacthal)	.002	1/1	Phorate	.002	--
DDE, p,p'-	.006	--	Prometon	.018	--
Diazinon	.002	1/0	Pronamide	.003	--
Dieldrin	.001	--	Propachlor	.007	--
Diethylanaline, 2,6-	.003	--	Propanil	.004	--
Disulfoton	.017	--	Propargite	.013	--
EPTC	.002	2/0	Simazine	.005	6/8
Ethalfluralin	.004	0/1	Tebuthiuron	.010	--
Ethoprop	.003	0/1	Terbacil	.007	1/0
Fonofos	.003	1/0	Terbufos	.013	--
HCH, alpha-	.002	--	Thiobencarb	.002	1/0
HCH, gamma-, (Lindane)	.004	--	Triallate	.001	--
Linuron	.002	--	Trifluralin	.002	1/2

Table 3. Application of simazine and atrazine by commodity in the San Joaquin Valley in 1991. The commodities with the 5 highest amounts of total application are given. (Data from California Department of Pesticide Regulation)

Compound	Commodity	Application (kilogram)	Percent total applied	Cumulative percent total
Simazine	Total	239,059		
	Oranges	80,171	33.5	33.5
	Grapes[1]	74,667	31.2	64.8
	Almonds	25,478	10.7	75.5
	Rights-of-way	22,865	9.6	85.1
	Walnuts	10,064	4.2	89.3
Atrazine	Total	9,936		
	Sorghum/milo	4,056	40.8	40.8
	Rights-of-way	3,428	34.5	75.3
	Corn[1]	1,221	12.3	87.6
	Sudan grass	873	8.8	96.4
	Landscaping	268	2.7	99.1

[1]. Sum of several categories in the California Department of Pesticide Regulation database.

A total of 9,936 kg of the triazine herbicide atrazine was applied to 10 different commodities in the San Joaquin Valley in 1991 (table 3). The largest agricultural use was on sorghum/milo, however 34% of the total use was for weed control on rights-of-way. Atrazine was not used in either almond orchards or vineyards. The maximum concentration of atrazine of 0.069 µg/l is almost two orders of magnitude smaller than the MCL of 3 µg/l. Although there is no difference between the concentration of atrazine in the almond and vineyard areas, the concentration of desethylatrazine, an atrazine degradation product, is higher in the almond area (p=0.008, Mann-Whitney test). The high rate of occurrence, without a similarly high rate of atrazine detection, suggests that atrazine is being more rapidly degraded in the soil zone or aquifer in the almond area than in the vineyard area. (The concentrations of desethylatrazine in table 1 are estimated, and are likely less than the true concentrations due to poor recovery efficiency of the extraction method).

Although rights-of-way application would appear to be the only source of atrazine for both land uses, a possible additional source is present in the vicinity of the almond orchards. Land use immediately west of the major concentration of almond orchards in the northern San Joaquin Valley is dominated by dairies and associated fodder crops including corn. Smaller areas of these crops are also dispersed among the almond orchards. It is possible that these crops are an additional source of atrazine to the shallow groundwater in this northern area. The high rate of desethylatrazine occurrence may be due, in this scenario, to an accelerated rate of atrazine degradation, fueled by a relatively high nutrient and organic carbon content in the groundwater impacted by dairies and manure spreading. This hypothesis cannot be tested with the existing data, and a detailed study would be required to substantiate it.

DBCP is a nematocide used from the mid-1950s until its use in California was banned in 1977 due to evidence of groundwater contamination. It has a low MCL of 0.2 µg/l, which has been exceeded in over 896 wells in the San Joaquin Valley from 1980 to 1989 (Miller and others, 1990). The concentrations of DBCP in the samples from the vineyard area are greater than those in samples from the almond area (p=0.032, Mann-Whitney test) as shown in table 1. In addition, the concentrations in the vineyard area exceed the MCL twice as frequently as in the almond area, although the difference in frequency is not significant at the 5% level (p=0.129, Chi-squared test). There is no detailed historical record of the quantity or rate of application of DBCP on various crops, but anecdotal reports indicate that vineyards received some of the heaviest applications in the San Joaquin Valley. In addition, the area of widespread ground-water contamination by DBCP identified from literally hundreds of analyses roughly corresponds to the area of vineyard cultivation. Although no rigorous analysis is possible, the evidence suggests that the difference in concentration between land use areas is due to the higher use of DBCP in the vineyard area than in the almond area.

The concentrations of DBCP are positively correlated with nitrate in the vineyard area (p=0.010, Spearman Rank correlation) as shown in fig. 3, but these constituents are not correlated in the almond area (p=0.869, Spearman Rank correlation). A strong correlation between DBCP, nitrate, and specific conductance in groundwater in the central San Joaquin Valley has been noted previously by Schmidt (1983). This observation implies that both DBCP and nitrate are not subject to rapid degradation in groundwater in this area, and instead, are transported conservatively.

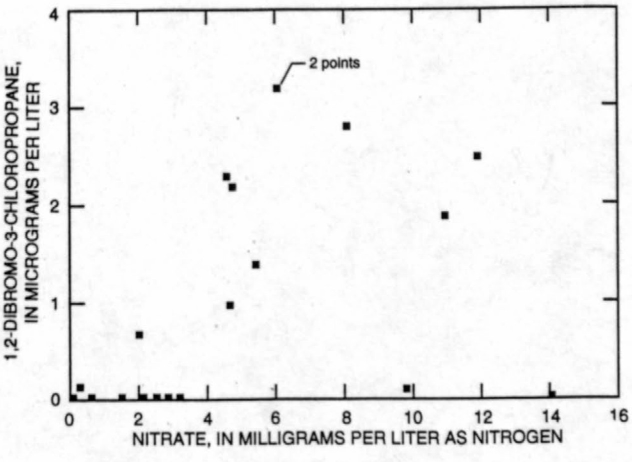

Figure 3. Scatterplot of concentrations of nitrate and 1,2-dibromo-3-chloropropane (DBCP) in samples from the vineyard land use area.

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