

In cooperation with the Central Valley Regional Water Quality Control Board

# Occurrence, Distribution, Instantaneous Loads, and Yields of Dissolved Pesticides in the San Joaquin River Basin, California, During Summer Conditions, 1994 and 2001

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Scientific Investigations Report 2004-5083

*Cover photo: Orestimba Creek at River Road Bridge near Crows Landing. (Effluent emerging from pipe can be seen near the center of the top photograph. A hydrologic technician measures stream depth near the effluent.) Photographed by Jason T. May, U.S. Geological Survey.*

# **Occurrence, Distribution, Instantaneous Loads, and Yields of Dissolved Pesticides in the San Joaquin River Basin, California, During Summer Conditions, 1994 and 2001**

By Larry R. Brown, Sandra Y. Panshin, Charles R. Kratzer, Celia Zamora, and JoAnn M. Gronberg

Prepared in cooperation with the Central Valley Regional Water Quality Control Board

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# Conversion Factors, Datum, and Abbreviations

## CONVERSION FACTORS

	<b>Multiply</b>	<b>By</b>	<b>To obtain</b>
cubic foot per second (ft <sup>3</sup> /s)		0.02832	cubic meter per second
liter (L)		1.057	quart
mile (mi)		1.609	kilometers
square mile (mi <sup>2</sup> )		2.590	square kilometers
pound, avoirdupois (lb)		0.4536	kilogram

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

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

Specific conductance is given in microsiemens per centimeter at 25 degrees Celsius ( $\mu\text{S}/\text{cm}$  at 25°C).

Concentrations of chemical constituents in water are given either in milligrams per liter (mg/L) or micrograms per liter ( $\mu\text{g}/\text{L}$ ).

## DATUM

Vertical coordinate information is referenced to the North American Vertical Datum of 1988 (NAVD 88). Horizontal coordinate information is referenced to the North American Datum of 1983 (NAD 83).

## ABBREVIATIONS

CMC	criterion maximum concentration
GC/MS	gas chromatography/mass spectrometry
>	greater than
$K_{oc}$	organic carbon normalized adsorption coefficient
LRL	laboratory reporting level
<	less than
LT/MDL	long-term method detection limit
mg	milligram
MDL	method detection limit
$\mu\text{m}$	micrometer
$\mu\text{g}/\text{L}$	microgram per liter
PCA	principal components analysis
RPD	relative percent difference
NWQL	National Water Quality Laboratory
TMDL	total maximum daily load
USGS	U.S. Geological Survey
WSID	Westside Irrigation District



# Occurrence, Distribution, Instantaneous Loads, and Yields of Dissolved Pesticides in the San Joaquin River Basin, California, During Summer Conditions, 1994 and 2001

By Larry R. Brown, Sandra Y. Panshin, Charles R. Kratzer, Celia Zamora, and JoAnn M. Gronberg

## Abstract

Water samples were collected from 22 drainage basins for analysis of 48 dissolved pesticides during summer flow conditions in 1994 and 2001. Of the 48 pesticides, 31 were reported applied in the basin in the 28 days preceding the June 1994 sampling, 25 in the 28 days preceding the June 2001 sampling, and 24 in the 28 days preceding the August 2001 sampling. The number of dissolved pesticides detected was similar among sampling periods: 26 were detected in June 1994, 28 in June 2001, and 27 in August 2001. Concentrations of chlorpyrifos exceeded the California criterion for the protection of aquatic life from acute exposure at six sites in June 1994 and at five sites in June 2001. There was a single exceedance of the criterion for diazinon in June 1994. The number of pesticides applied in tributary basins was highly correlated with basin area during each sampling period (Spearman's  $r = 0.85, 0.70,$  and  $0.84$  in June 1994, June 2001, and August 2001, respectively, and  $p < 0.01$  in all cases). Larger areas likely include a wider variety of crops, resulting in more varied pesticide use. Jaccard's similarities, cluster analysis, principal components analysis, and instantaneous load calculations generally indicate that west-side tributary basins were different from east-side tributary basins. In general, west-side basins had higher concentrations, instantaneous loads, and instantaneous yields of dissolved pesticides than east-side basins, although there were a number of exceptions. These differences may be related to a number of factors, including differences in basin size, soil texture, land use, irrigation practices, and stream discharge.

## Introduction

Agriculture in the San Joaquin Valley of California is both productive and valuable. The availability of water for irrigation, the Mediterranean climate, and the long growing season have combined to make it one of the most intensively farmed and economically important agricultural regions in the United States. In 2000, the agricultural industry of California produced a gross cash income of 27 billion dollars and supplied more than half the nation's fruits, nuts, and vegetables (California Department of Food and Agriculture 2001). Much of this production occurred in the San Joaquin Valley.

This intensive agricultural activity includes widespread and intensive use of various pesticides. The occurrence and concentrations of these pesticides and their effects on water quality have been a long-standing concern in the region, especially their potential toxicity to aquatic organisms (Foe and Connor, 1991; Foe, 1995; de Vlaming and others, 2000; Werner and others, 2000). Many recent studies have focused on storm transport of pesticides applied to orchard crops during the winter (Kuivila and Foe, 1995; Kratzer, 1997; Domagalski and others, 1997; Kratzer, 1999; Kratzer and others, 2002), providing important insights into pesticide transport processes and effects on water quality, especially during winter storms. Other studies have conducted periodic sampling at a limited number of sites (MacCoy and others, 1995; Domagalski, 1997; Panshin and others, 1998; Domagalski and Munday, 2003), documenting temporal variability in the occurrence and concentrations of dissolved pesticides. However, these studies have not sufficiently documented geographic variability in the occurrence of dissolved pesticides during the summer irrigation season (April–August), a period of high pesticide use. Understanding geographic variability is important, particularly in the context of understanding source loads with regard to total maximum daily loads (TMDLs).

## 2 Occurrence, Distribution, Instantaneous Loads, and Yields of Dissolved Pesticides, San Joaquin River Basin, Calif.

### Purpose and Scope

This report documents the occurrence, distribution, and instantaneous loads of dissolved pesticides in the surface waters of the San Joaquin River Basin during summer flow conditions in 1994 and 2001. Distribution was assessed by evaluating patterns in pesticide concentrations, instantaneous loads, and instantaneous yields among the sites sampled. To the extent possible, the occurrence, distribution, and instantaneous loads of dissolved pesticides were compared with available data on land use and pesticide applications in order to provide insights into sources and transport mechanisms for the chemicals detected. Samples were collected at 22 sites in June 1994 (*table 1*) and at 22 sites in June and August 2001 (*table 1*) for analysis of 48 dissolved pesticides (*table 2*).

These sites included various tributaries and several nested subbasins of the perennial mainstem San Joaquin River. The tributaries were selected to characterize water inputs from subbasins with physiography, land use, and pesticide applications typical of tributary inputs to the San Joaquin River. Subbasins of the San Joaquin River were selected to characterize changes in water quality resulting from surface water inputs (*fig. 1*). The site at the San Joaquin near Vernalis integrates the effects of all upstream inputs. This study focuses on geographic variability of pesticide application, occurrence, distribution, instantaneous loads, and instantaneous yields. Information on temporal variability in pesticides during the April to August, 2001 sampling period is available in Domagalski and Munday (2003).

**Table 1.** Sites sampled in 1994 and 2001 in the San Joaquin River Basin, California.

[Site codes are the sampling sites shown in *fig. 1*; WSID, Westside Irrigation District; mi<sup>2</sup>, square mile]

USGS station number	Site code	Station name	Drainage basin area—valley floor (mi <sup>2</sup> )	Year sampled
371521120390800	E1	Bear Creek at Bert Crane Road near Merced	317	1994, 2001
11260815	S1	San Joaquin River near Stevinson	866	1994, 2001
11261100	G1	Salt Slough at Highway 165 near Stevinson	492a	1994, 2001
371636120575200	G2	Los Banos Creek at Highway 140	198	2001
11262900	G3	Mud Slough near Gustine	492 <sup>a</sup>	1994, 2001
372424120432800	E2	Livingston Canal at Livingston Treatment Plant near Livingston	44	1994, 2001
372323120481700	E3	Highline Canal Spill near Hilmar	46	1994, 2001
11270900	E4	Merced River below Merced Falls Dam near Snelling	0	1994
11273500	E5	Merced River at River Road Bridge near Newman	321	1994, 2001
371903120585400	W1	Newman Wasteway at Highway 33 near Gustine	9	1994, 2001
11274538	W2	Orestimba Creek at River Road near Crows Landing	11	1994, 2001
11274554	W3	Spanish Grant Combined Drain near Patterson	22	1994, 2001
11274560	E6	Harding Drain at Carpenter Road near Patterson	84	1994, 2001
11274570	S2	San Joaquin River at Patterson Bridge near Patterson	3,770	1994, 2001
373232121053900	E7	Westport Drain near Modesto	79	1994, 2001
373027121051401	W4	Olive Avenue Drain near Patterson	8	1994, 2001
11274653	W5	Del Puerto Creek at Vineyard Road near Patterson	8	1994, 2001
373621121102801	S3	San Joaquin River below WSID pump above Tuolumne River near Westley	4,145	1994, 2001
11290000	E8	Tuolumne River at Modesto	299	1994
11290200	E9	Tuolumne River at Shiloh Road Bridge near Grayson	319	2001
373842121131800	W6	Hospital Creek at River Road near Patterson	5	1994, 2001
373747121125200	W7	Ingram Creek at River Road near Patterson	11	1994, 2001
11303000	E10	Stanislaus River at Ripon near Patterson	127	1994
374209121103800	E11	Stanislaus River at Caswell State Park near Ripon	160	2001
11303500	S4	San Joaquin River near Vernalis	7,395	1994, 2001

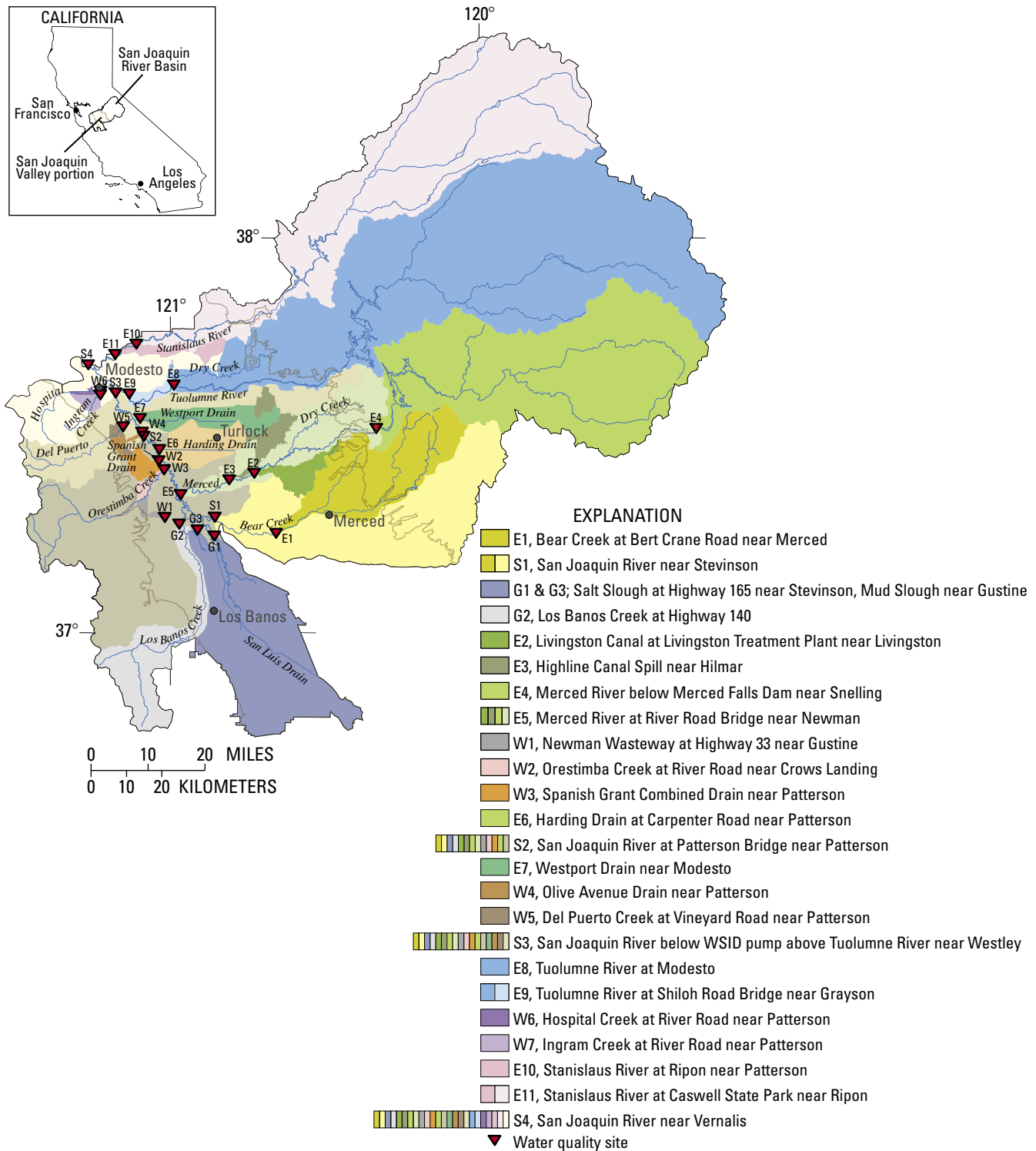
<sup>a</sup>Salt Slough and Mud Slough are interconnected by manmade structures, and so, share the same drainage.

**Table 2.** Pesticide, CAS number, and reporting limits.

[CAS, Chemical Abstracts Service; LRL, Laboratory Reporting Level; m, only method reporting limit available; MRL, Method Detection Limit; NA, not analyzed; µg/L, microgram per liter]

Pesticide	CAS number	LRL 2001 (µg/L)	MRL 1994 (µg/L)
2,6-Diethylaniline	579-66-8	0.002	0.003
Acetochlor	34256-82-1	.004	.002
Alachlor	15972-60-8	.002	.002
Atrazine	1912-24-9	.007	.001
Atrazine, deethyl	6190-65-4	.006	.002
Azinphos-methyl	86-50-0	.05	.001
Benfluralin	1861-40-1	.01	.002
Butylate	2008-41-5	.002 m	.002
Carbaryl	63-25-2	.041	.003
Carbofuran	1563-66-2	.02	.003
Chlorpyrifos	2921-88-2	.005	.004
Cyanazine	21725-46-2	.018	.004
Dacthal (DCPA)	1861-32-1	.003	.002
DDE, <i>p,p'</i> -	72-55-9	.003	.006
Diazinon	333-41-5	.005	.002
Dieldrin	60-57-1	.005	.001
Disulfoton	298-04-4	.021	.017
EPTC	759-94-4	.002	.002
Ethalfuralin	55283-68-6	.009	.004
Ethoprophos	13194-48-4	.005	.003
Fonofos	944-22-9	.003	.003
HCH, alpha- (alpha-BHC)	319-84-6	.005	.002
HCH, gamma- (Lindane)	58-89-9	.004	.004
Linuron	330-55-2	.035	.002
Malathion	121-75-5	.027	.005
Methyl parathion	298-00-0	.006	.006
Metolachlor	51218-45-2	.013	.002
Metribuzin	21087-64-9	.006	.004
Molinate	2212-67-1	.002	.004
Napropamide	15299-99-7	.007	.003
Parathion	56-38-2	.007	.004
Pebulate	1114-71-2	.002	.004
Pendimethalin	40487-42-1	.01	.004
Permethrin, <i>cis</i> -	54774-45-7	.006	.005
Phorate	298-02-2	.011	.002
Prometon	1610-18-0	.015	.018
Propachlor	1918-16-7	.01	.007
Propanil	709-98-8	.011	.004
Propargite	2312-35-8	.023	.013
Pronamide	23950-58-5	.004	.003
Simazine	122-34-9	.011	.005
Tebuthiuron	34014-18-1	.016	.01
Terbacil	5902-51-2	.034	.007
Terbufos	13071-79-9	.017	.013
Terbuthylazine	5915-41-3	.1 m	NA
Thiobencarb	28249-77-6	.005	.002
Triallate	2303-17-5	.002	.001
Trifluralin	1582-09-8	.009	.002

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**Figure 1.** Basins and sites sampled in June 1994 and June and August 2001, in the lower San Joaquin River Basin. See *table 1* for site codes.

## Study Area

The perennial San Joaquin River Basin drains an area of 19,023 km<sup>2</sup> (7,345 mi<sup>2</sup>). Of this area, 59 percent is in the Sierra Nevada, 11 percent is in the Coast Ranges, and 30 percent is in the San Joaquin Valley. The Sierra Nevada and Coast Ranges portions of the drainage are predominantly forested land. Virtually all irrigated agriculture and most pesticide applications occur in the San Joaquin Valley portion of the drainage; thus, this study focuses on the San Joaquin Valley portion of the perennial San Joaquin River Basin (*fig. 2*). The water distribution system within the valley floor area is complex. As of the late 1980s, there were at least 86 agricultural diversions and 104 agricultural discharges to the San Joaquin River (Kratzer and Shelton, 1998).

Climate in the San Joaquin Valley is arid-to-semiarid. Precipitation, which falls primarily as snow in the Sierra Nevada during November through April, is highly variable from year to year. The years sampled in this study, 1994 and 2001, were considered critically dry and dry, respectively, due to limited precipitation (California Department of Water Resources, accessed January 20, 2004). The surface hydrology of the San Joaquin River drainage has been altered substantially to store and distribute surface water derived from snowmelt in the Sierra Nevada. Every major river system in the study area has one or more reservoirs. This water is subsequently used for irrigated agriculture and a variety of other urban and environmental uses. On the basis of U.S. Geological Survey (USGS) streamflow records for 1951 to 1990, 67 percent of the flow of the perennial San Joaquin River is from the three large eastern tributaries: the Merced River (15 percent), the Tuolumne River (30 percent), and the Stanislaus River (22 percent). Bear Creek, Mud and Salt Sloughs, ephemeral streams draining the Coast Ranges, and drainage canals that flow directly to the San Joaquin River, contribute the remaining 33 percent of streamflow.

Because of geological differences between the Sierra Nevada and Coast Ranges, the texture of the soils is different between the east side and west side of the valley (Gronberg and others, 1998; Panshin and others, 1998). Sediments on the eastern side of the valley are generally highly permeable, medium- to coarse-grained sands with low total organic carbon. Soils on the eastern side of the valley tend to be finest near the valley trough and coarser near the upper parts of the alluvial fans. Soils on the western side of the valley tend to be finer textured with higher clay content and lower permeability than soils on the eastern side of the valley. The west side of the valley also tends to be steeper on average than the east side of the valley, resulting in steeper gradient in creeks and agricultural drains.

These differences in soils and topography have contributed to differences in agricultural land use (*table 3*). The west side of the valley is dominated by row crops (48 percent)

along with relatively small percentages of orchards (7 percent) and vineyards (<1 percent). In contrast, orchards are the dominant agricultural land use on the east side of the valley (24 percent) and row crops constitute only about 18 percent. The soils, topography, and related cropping patterns also seem to influence irrigation practices and potential agricultural return flows. Drip and flood irrigation tend to be more common on the east side of the valley, where they are used primarily on orchards and vineyards. These methods allow water to percolate into the soil and generally produce little irrigation return flow. Furrow irrigation tends to be more common on the west side of the valley, where it is used on row crops. This method produces more irrigation return flow because all of the applied water does not percolate into the soil. Suspended sediment concentrations can be fairly high in irrigation return flow from furrow irrigation. Unfortunately, irrigation practices and associated return flows are not quantified, so any relation between irrigation practices and pesticide transport is somewhat speculative.

The southernmost part of the basin differs from the remainder of the basin in several important ways. This area includes extensive managed wetlands in addition to agricultural uses. Even though the tributaries in this area are considered to be on the west side of the valley, they are very low gradient. For these reasons, these tributaries (Salt Slough, Mud Slough, and Los Banos Creek) are coded differently than the other west-side tributaries (*figs. 1 and 2, table 1*).

## Methods

### Sampling Design

Pesticide sampling in June 1994 occurred from 18 to 24 June in conjunction with a dye study (Kratzer and Biagittin, 1997) resulting in a Lagrangian design. This means that each parcel of water sampled was estimated to reach the San Joaquin near Vernalis (site code S4) at the same time. Sampling in 2001 was not Lagrangian, but was completed within two days on each occasion. In both years, water samples were collected from each of 22 sites. Of these, 19 sites were common to both years (*table 1*). Additional water samples (replicates) were collected at some sites as described in the section on quality assurance procedures. The 18 tributary sites sampled each year (sites not on the San Joaquin River in *table 1*) were selected to characterize water inputs from subbasins having physiography, land use, and pesticide applications typical of tributary inputs to the San Joaquin River. The four sites on the San Joaquin River were the same both years and were selected to characterize changes in water quality related to tributary inputs.

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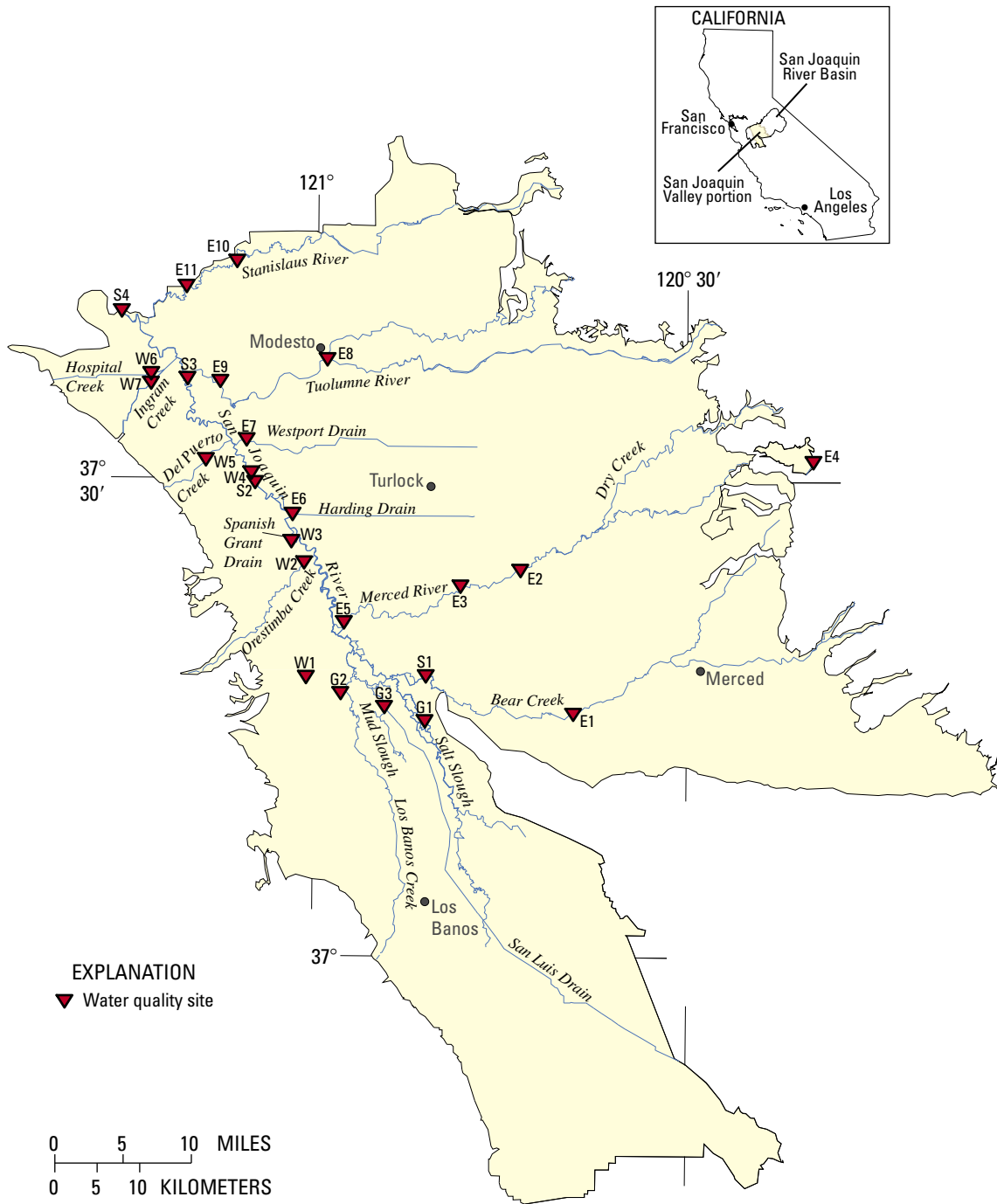


Figure 2. Sites sampled in the valley portion of the lower San Joaquin River Basin. See table 1 for site codes.

**Table 3.** Percentages of land use on the east side and west side of the study area in the mid-1990s.

[Data obtained from the California Department of Water Resources 1995, 1996, 1997a,b. Data for the basins in the southern part of the study area are included in the west side. Percentages do not total 100 because of rounding. <, smaller than]

Land use	East side basins	West side basins
Idle agricultural land	2	1
Native vegetation	23	24
Orchards—citrus	<1	<1
Orchards—other	24	7
Pasture	16	14
Rice	1	1
Row crops	18	48
Semiagricultural <sup>1</sup>	3	1
Urban	10	3
Vineyards	4	<1

<sup>1</sup>Farmsteads, livestock feed lots, dairies, and poultry farms.

## Field Method and Sample Processing

Discrete water samples were collected for analyses of pesticides. Most samples were collected as either flow- and width-integrated samples using a D-77 isokinetic sampler with Teflon nozzle and 3-L Teflon bottle (Shelton, 1994) or as equally spaced three-point integrated samples collected with a 3-L Teflon bottle strapped into a metal cage and suspended from a rope. Exceptions included wide channels where five points were integrated rather than three (S3 and S4); Del Puerto Creek (W5), which was only wide enough for a mid-point grab with a 3-L Teflon bottle; and the Stanislaus River at Caswell State Park near Ripon (E11), where a dip sample was collected from the part of the channel carrying most of the flow. Data collected using these other methods have been compared with data from integrated samples, and the data are comparable (Domagalski and Munday, 2003; Zamora and others, 2003). Samples were stored on ice and processed (filtered and extracted) within three days of collection.

A 1-L aliquot was processed from each water sample. All aliquots were filtered (0.7  $\mu\text{m}$ , glass fiber filter) to remove suspended solids. Pesticides were extracted from the 1-L aliquot by passing the sample through a 500-mg C-18 solid-phase extraction cartridge. The cartridge was then dried by passing carbon dioxide or nitrogen gas through it. In 1994, samples were filtered and extracted at the USGS California District laboratory. In 2001, whole water was sent to the USGS, National Water Quality Laboratory (NWQL) in Denver, Colorado where filtering and extraction were conducted. The cartridges were analyzed for extracted pesticides at NWQL.

## Analytical Methods

The samples extracted using the C-18 cartridge were analyzed for 48 pesticides and pesticide metabolites (table 2) by gas chromatography/mass spectrometry (GC/MS). The pesticides were eluted from the C-18 cartridge using

hexane-isopropanol (in a ratio of 3:1). The eluate was analyzed by GC/MS in the selected ion-monitoring mode using three characteristic ions for each pesticide. Zaugg and others (1995) and Lindley and others (1996) provide a complete description of the method.

Most analytical results were reported as laboratory reporting level (LRL). The LRL is generally equal to twice the annually determined long-term method detection limit (LT-MDL). The LRL controls false negative error. The probability of falsely reporting a nondetection for a sample that contained an analyte at a concentration equal to or greater than the LRL is predicted to be no more than 1 percent (Childress and others, 1999). The remaining analytes are reported in terms of the method detection limit (MDL) defined as the smallest measured concentration of a constituent that may be reliably measured (<1 percent chance of a false positive) by a given analytical method.

## Quality Control Procedures

Quality control samples were collected and analyzed to evaluate possible contamination of samples and recovery efficiency and reproducibility of the pesticide analyses, given the sampling, transport, and analytical procedures. A total of 22 environmental samples were collected in 1994 and a total of 22 environmental samples were collected in 2001. Two types of field quality control samples were evaluated: field blanks (1 in 1994 and 3 in 2001) and field replicates (2 in 1994 and 5 in 2001). Laboratory quality control samples consisted of spiked environmental samples (1 in 1994 and 3 in 2001) (Mueller and others, 1997).

Two quality control samples were collected by the California Regional Water Quality Control Board in June 1994 in conjunction with this study, but could not be used. The spiked sample collected used a spiking solution that was too concentrated, and this spiking solution contaminated the associated blank.

## Field Blank Samples

Field blanks were collected to estimate bias from contamination of the samples. Field blanks were processed in the field after an environmental sample was processed and equipment was cleaned in the field to determine whether the cleaning procedure following each sample collection was adequate to prevent cross-contamination and to determine whether the sample was exposed to atmospheric contamination during sampling. Field blanks consisted of certified organic-free water that was poured from the 3-L Teflon bottle, through the sample splitting device, into a 1-L glass sample bottle. The blanks were then extracted and analyzed in the same manner as a regular sample.

One field blank was analyzed in 1994, and three were analyzed in 2001. The field blank from 1994 contained no pesticides at detectable levels. One of the field blanks from 2001 contained metolachlor at an estimated concentration of 0.005 µg/L. This concentration is much lower than the LRL of 0.013 µg/L. No other pesticides were detected in any of the 2001 field blanks. The low rate of detection in the data from the four field blanks indicates that no systematic contamination was caused by the sampling or cleaning procedures.

## Replicate Samples

Replicate samples were collected to assess the variability caused by sample collection, field processing, and laboratory analysis procedures. The replicates were sequential, duplicate samples; that is, one sample (the environmental sample) was collected, then a second sample (the replicate) was collected while the first sample was being processed. The replicate was processed in a manner identical to the environmental sample. Two pairs of replicates were analyzed in 1994, and five pairs were analyzed in 2001 (*table 4*). Because multiple pesticides were analyzed in each environmental sample, there was a total of 92 individual pesticide analyses performed in 1994 and a total of 235 individual pesticide analyses performed in 2001.

The simplest level of analysis of these replicates addresses the issue of detection or nondetection of a specific pesticide in the environmental sample and its corresponding replicate. Ideally, if a pesticide is not detected in the environmental sample, it should not be detected in the paired replicate. This pairing of nondetections occurred in 82 percent of the 1994 analyses, and in 75 percent of the 2001 analyses. Conversely, if the pesticide is detected in the environmental sample, it should also be detected in the paired replicate. This pairing of detections occurred in 15 percent of the 1994 analyses, and in 24 percent of the 2001 analyses. In 1994, 3 percent of the analyses (3 pesticides in 1 sample, out of 92 analyses performed) detected a pesticide in either the environmental sample or the replicate, but not in both. In 2001, this value was

less than 1 percent (2 pesticides in 1 sample, out of 235 analyses performed). In all of these cases of pairing a detection with a nondetection, the detected value was relatively low (less than 0.016 µg/L) relative to the LRL, and in two of the cases, the detected concentration was less than the MDL.

For cases where the pesticide is detected in the environmental sample and the replicate, assessment of the difference in concentration between the environmental sample and the paired replicate is important. This assessment is performed by calculating the absolute difference and the relative percent difference between the two values. The relative percent difference (RPD) is defined as:

$$RPD = |C_{Sample} - C_{Replicate}| / [(C_{Sample} + C_{Replicate}) / 2] \times 100\%$$

where

$C_{Sample}$  = concentration of pesticide in the environmental sample,

$C_{Replicate}$  = concentration of pesticide in the replicate.

When the pesticide was detected in both the replicate and the environmental sample, a median RPD of 8 percent was calculated for both the 1994 ( $n = 14$ ) and the 2001 ( $n = 56$ ) data. Thus, when a pesticide was detected in both the environmental sample and the replicate, the values were very close. For all the replicate data, it is important to remember that most of these concentrations are very low; therefore, a small absolute difference in the concentrations of the environmental sample and the replicate sample can lead to a large relative percent difference between the two values. Minimum, maximum, and median values for the absolute difference and relative percent difference of all pesticides are presented in *table 4*.

## Spiked Samples

Spiked samples are used to measure bias caused by analyte degradation or sample matrix interference on the analyses of specific constituents. Spiked samples (spikes) consisted of an environmental sample to which a known amount of certain analytes had been added. Each spike had a corresponding environmental sample, collected at the same time, to which nothing was added. The June 1994 spiked sample had the solution added in the field. The June and August 2001 spikes had the analytes added at NWQL. The percentage recovery of each pesticide in the spikes was determined by calculating the concentration of that pesticide in the spiked sample, subtracting the amount in the environmental sample, and dividing by the expected concentration in the spiked sample and multiplying by 100. The expected concentration was what would be detected if the pesticide were not present in the environmental sample, assuming 100 percent recovery from the spiked sample.



**Table 4.** Relative percent difference (RPD) and absolute difference (in micrograms per liter) for pesticides collected in environmental and replicate samples in 1994 and 2001.

[For 1994, n = 2 pair; for 2001, n = 5 pairs; ND, not detected in either sample; DET, detected in both samples; E, concentration estimated in both samples]

Pesticide	Year	Comments	Minimum RPD	Maximum RPD	Median RPD	Minimum absolute difference	Maximum absolute difference	Median absolute difference
Alachlor	1994	1 ND, 1 DET	0	20.7	10.3	0	0.006	0.003
Atrazine	1994	1 ND, 1 DET	0	3.2	1.6	0	.002	.001
	2001	1 ND, 3 DET	0	13.3	7.7	0	.002	.001
Atrazine, deethyl	1994	1 ND	0	0	0	0	0	0
	2001	3 ND, 1 E	0	40	0	0	.001	0
Azinphos-methyl	1994	1 ND, 1 E	0	8.3	4.2	0	.02	.01
Carbaryl	1994	1 ND, 1 E	0	19.2	9.6	0	.007	.0035
	2001	1 ND, 4 E	0	19.2	8	0	.007	.001
Chlorpyrifos	1994	1 ND, 1 DET	0	11.8	5.9	0	.03	.015
	2001	2 ND, 3 DET	0	25	4.7	0	.002	.001
Diazinon	1994	1 ND	0	0	0	0	0	0
	2001	1, ND, 2 DET, 2 E	0	9.2	0	0	.007	0
Dieldrin	2001	2 ND, 3 DET	0	38.7	0	0	.012	0
EPTC	1994	2 DET	4	111.9	57.9	.02	.033	.0265
	2001	1 ND, 4 DET	0	8.9	3.5	0	.004	.003
Ethalfuralin	2001	4 ND, 1 DET	0	5.9	0	0	.004	0
Fonofos	2001	4 ND, 1 E	0	0	0	0	0	0
Lindane	2001	4 ND, 1 E	0	0	0	0	0	0
Malathion	2001	3 ND, 2 E	0	18.2	0	0	.001	0
Metolachlor	1994	2 DET	2.9	7.7	5.3	.001	.004	.0025
	2001	5 DET	1.9	14.9	6.7	.002	.141	.005
Metribuzin	1994	1 ND	0	0	0	0	0	0
	2001	2 ND, 3 DET	0	25	6.5	0	.005	.001
Molinate	2001	3 ND, 2 DET	0	9.1	0	0	.002	0
Napropamide	2001	2 ND, 3 DET	0	30.7	5.1	0	.231	.001
DDE, <i>p,p'</i>	1994	1 ND, 1 DET	0	11.8	5.9	0	.001	.0005
	2001	2 ND, 2 DET, 1 E	0	37.5	10.5	0	.006	.001
Pendimethalin	2001	4 ND, 1 DET	0	12.2	0	0	.01	0
Prometon	2001	4 ND, 1 E	0	22.2	0	0	.001	0
Propargite	1994	1 ND, 1 DET	0	19.8	9.9	0	.018	.009
	2001	1 ND, 4 DET	0	29.5	1.6	0	.054	.002
Simazine	1994	2 DET	6	6.5	6.2	.001	.004	.0025
	2001	1 ND, 3 DET, 1 E	0	16.7	7.4	0	.002	.001
Trifluralin	1994	1 ND, 1 DET	0	6.1	3	0	.03	.015
	2001	2 ND, 3 DET	0	14.6	1.5	0	.152	.006

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One spike was analyzed in 1994; however, data from this spike were unusable because of an error in recording the lot number of the spiking solution. Three spikes were analyzed in 2001 (*table 5*). For these spikes, the median percentage recoveries range from 79 to 119 percent, with the exception of *p,p'*-DDE (52 percent) and *cis*-permethrin (59 percent). Recoveries were not calculated for pesticides that had estimated concentrations (carbaryl, carbofuran, deethylatrazine, azinphos-methyl, and terbacyl).

NWQL regularly performs quality control checks on analytical procedures. These checks consist of spiking each of the measured pesticides into pesticide-grade purified water to a concentration of 0.1 µg/L. The results from these checks are listed in *table 6*. In general, the results were similar to those obtained from the spiked environmental samples (*table 5*). Both *p,p'*-DDE and *cis*-permethrin were biased low in the laboratory quality control checks and in the spiked environmental samples. Recoveries of most of the other pesticides (34) ranged from 80 to 108 percent. However, there were a number of notable results. Carbofuran and carbaryl had relatively good mean and median recoveries (87–110 percent), but had very high standard deviations (79 and 110, respectively) (*table 6*). Low recoveries (44–78 percent) were found for several pesticides (*table 6*) that had estimated concentrations or median recoveries of 79 percent or less in the spiked environmental samples (*table 5*). The pesticides that had estimated values in the spiked environmental samples included deethylatrazine (44 percent), azinphos-methyl (73 percent), and terbacyl (78 percent). The pesticides that had median recoveries of 79 percent or less in the spiked environmental samples included benfluralin (65 percent), disulfoton (43 percent), ethalfluralin (76 percent), pendimethalin (66 percent), phorate (67 percent), propargite (66 percent), and trifluralin (66 percent). Although recoveries for these pesticides were biased low, the standard deviations for these pesticides also were low indicating limited variability (*table 6*).

For most pesticides, the analytical method generally yields consistent results for spiked samples. Low spike recoveries indicate that the pesticide has an increased chance of not being detected in environmental samples when it is present at low, but nominally detectable concentrations.

**Table 5.** Summary of quality control data in 2001 for three spiked samples.

[E, recovery not calculated because concentration was reported as an estimate]

Pesticide	Minimum recovery	Maximum recovery	Median recovery
2,6-Diethylaniline	88	101	97
Acetochlor	106	127	119
Alachlor	104	128	107
Atrazine	107	118	116
Atrazine, deethyl	E	E	E
Azinphos-methyl	E	E	E
Benfluralin	69	103	79
Butylate	86	96	87
Carbaryl	E	E	E
Carbofuran	E	E	E
Chlorpyrifos	90	106	102
Cyanazine	113	123	119
Dacthal (DCPA)	105	113	111
DDE, <i>p,p'</i> -	46	76	52
Diazinon	96	102	98
Dieldrin	74	114	80
Disulfoton	77	100	94
EPTC	79	115	98
Ethalfluralin	102	135	104
Ethoprophos	93	124	113
Fonofos	88	100	95
HCH, alpha- (alpha-BHC)	92	115	113
HCH, gamma- (Lindane)	96	118	112
Linuron	95	117	107
Malathion	95	102	100
Methyl parathion	80	88	83
Metolachlor	83	117	108
Metribuzin	101	115	108
Molinate	91	98	92
Napropamide	107	133	109
Parathion	109	116	111
Pebulate	91	97	95
Pendimethalin	82	115	104
Permethrin, <i>cis</i> -	55	80	59
Phorate	87	114	96
Prometon	106	118	111
Propachlor	102	111	110
Propanil	97	115	114
Propargite	94	139	105
Pronamide	101	112	108
Simazine	98	105	99
Tebuthiuron	105	134	114
Terbacil	E	E	E
Terbufos	92	103	94
Thiobencarb	98	104	100
Triallate	92	101	92
Trifluralin	78	128	79

**Table 6.** Mean, median, and standard deviation of recoveries of laboratory spikes in pesticide-grade purified water.

[µg/L, microgram per liter]

Pesticide	Amount spiked (µg/L)	Total number of samples	Mean	Median	Standard deviation
2,6-Diethylaniline	0.1	295	94	92	12
Acetochlor	.1	295	97	96	11
Alachlor	.1	295	95	95	10
Atrazine	.1	295	96	95	11
Atrazine, deethyl	.1	295	45	44	15
Azinphos-methyl	.1	295	78	73	33
Benfluralin	.1	295	66	65	11
Butylate	.1	295	90	88	10
Carbaryl	.1	295	109	87	110
Carbofuran	.1	295	110	94	79
Chlorpyrifos	.1	295	90	90	11
Cyanazine	.1	295	93	93	24
Dacthal (DCPA)	.1	295	100	99	11
DDE, <i>p,p'</i> -	.1	295	63	64	8
Diazinon	.1	295	95	95	8
Dieldrin	.1	295	91	89	11
Disulfoton	.1	295	41	43	27
EPTC	.1	295	91	91	13
Ethalfuralin	.1	295	76	76	13
Ethoprophos	.1	295	83	83	14
Fonofos	.1	295	87	90	15
HCH, alpha (alpha-BHC)	.1	295	90	91	13
HCH, gamma- (Lindane)	.1	295	97	97	12
Linuron	.1	295	103	100	27
Malathion	.1	295	87	84	16
Methyl parathion	.1	295	87	84	19
Metolachlor	.1	295	99	97	12
Metribuzin	.1	295	84	84	12
Molinate	.1	295	92	91	10
Napropamide	.1	295	88	86	15
Parathion	.1	295	89	85	21
Pebulate	.1	295	93	91	10
Pendimethalin	.1	295	69	66	15
Permethrin, <i>cis</i> -	.1	295	42	42	8
Phorate	.1	295	66	67	18
Prometon	.1	295	92	92	12
Pronamide	.1	295	90	90	15
Propachlor	.1	295	99	97	15
Propanil	.1	295	100	99	15
Propargite	.1	295	74	66	28
Simazine	.1	295	87	88	15
Tebuthiuron	.1	295	110	108	22
Terbacil	.1	295	77	78	23
Terbufos	.1	295	70	73	16
Thiobencarb	.1	295	94	95	8
Triallate	.1	295	89	89	8
Trifluralin	.1	295	66	66	13

## Assessment of Quality Assurance

Overall, the quality control samples showed that no systematic contamination was caused by the sampling or cleaning procedures. The results are reproducible on the basis of results from replicate samples. Measured concentrations are likely biased low for a number of pesticides that are based on spiked environmental samples and laboratory spikes into pesticide-grade purified water. However, variability in concentration is low for these potentially biased analyses so that the relative concentrations when compared among sites (that is, which sites are higher or lower than others) are likely correct. Finally, high variability for carbofuran and carbaryl, despite good mean and median recoveries, suggests caution in interpreting results for those chemicals. All quality control results should be considered when interpreting the concentration data.

## Statistical Methods for Assessing Patterns in Application, Occurrence, and Distribution of Pesticides

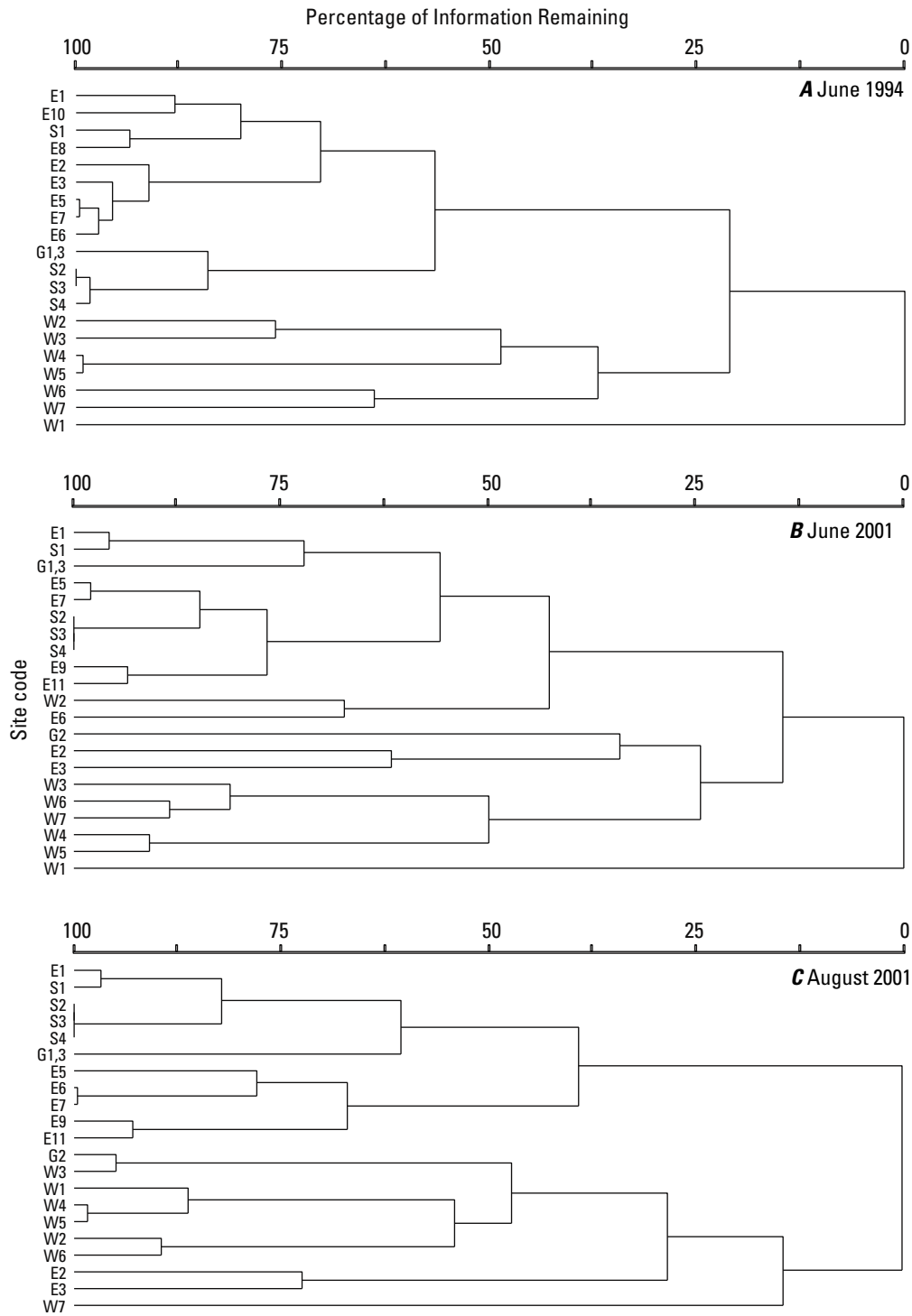
Cluster analysis and principal components analysis (PCA) were utilized to determine if there were patterns in pesticide application, occurrence and distribution among the study basins (statistical techniques explained below). Pesticide application data (California Department of Pesticide Regulation, 2002) were obtained for each study basin (*table 1*) for the 28 days preceding the first day of sampling for each sample period. The 28-day time period was determined by the most measurable precipitation preceding any sampling period. Applications were analyzed as both presence/absence and application intensity (pounds active ingredient per square mile). Basin areas for large east-side tributary rivers were based on basin areas in the valley. Because Salt Slough and Mud Slough are interconnected, this basin was analyzed as a single site. Merced River below Merced Falls (E4) was omitted from the analysis because it was sampled as a reference site, above the valley, and thus was considered to have no upstream basin area for the purposes of this analysis.

Occurrence and distribution data were obtained from the chemical analysis of the water samples. A pesticide was considered present if it was detected at a concentration above the reporting level (MDL in 1994 and LRL in 2001). Pesticides that had reported estimated concentrations below the reporting level were not considered present. Concentrations of dissolved pesticides were compared to several water quality criteria (*table 2*). Pesticide presence/absence data were analyzed by cluster analysis. Concentration data, instantaneous load data, and instantaneous yield data were analyzed with PCA.

Presence/absence data were analyzed using Jaccards similarities followed by a group average linkage method cluster analysis. Jaccards similarity is calculated as,  $2C/(A+B+C)$ , where A is the number of pesticides found only at site 1, B is the number of pesticides found only at site 2, and C is the number of pesticides found at both sites. Jaccards similarity varies from 1 (all pesticides shared) to 0 (no pesticides shared). Clustering, in general, is a group of methods that produce a hierarchical arrangement of sites on the basis of their similarity (see Gauch, 1982). The method starts with each sample assigned to a cluster with a single member, and then uses a distance measure to group similar clusters into larger clusters until a final single cluster contains all the samples. In this analysis the distance is  $1 - (\text{Jaccards similarity})$ . Thus, more similar sites are closer in distance and cluster together. The results are portrayed graphically as a dendrogram (see *fig. 3* as an example). The similarity of different groups can be assessed by observing the "percentage information remaining" at branching points. All information is present when individual sites are considered and no information remains when all sites have been combined into a single group.

Application intensity was analyzed using PCA. The basic purpose of PCA is to produce a reduced number of independent composite variables (principal component axes) that summarize the relations of a larger number of correlated variables (Gauch, 1982). The associations of the original variables to the derived composite variables are known as loadings and are analogous to correlations. So, variables with high loadings on a principal component axis are highly correlated with each other, increasing or decreasing together. The eigenvalue is a calculated value for each axis that represents the percentage of variance in the data explained by that axis. The first few principal component axes usually summarize most of the variation in a data set. In this study, only principal component axes with eigenvalues greater than one are interpreted. This cutoff is commonly used to identify the PCA axes with the greatest explanatory value (McCune and Grace, 2002).

Principal components analysis is most appropriate for data meeting certain statistical assumptions. The analysis assumes that the data are normally distributed (bell-shaped curve around the mean). When data do not satisfy this assumption, the data can be transformed to better meet the assumption of normality. The data in this study were characterized by many low and moderate values and a few high values. The data values were transformed with the function  $\log_{10}(\text{value} + 1)$ , to improve normality.



**Figure 3.** Cluster analysis of Jaccard distances, which are based on the presence or absence of pesticide applications in the study basins in (A) June 1994, (B) June 2001, and (C) August 2001. See *table 1* for site codes. Percentage information remaining varies from 100, starting with the individual sites, and decreases to 0 as the sites are clustered into a single group.

Only pesticides applied in more than seven basins (more than one-third) were used in the PCA. PCA was also used to analyze concentrations, instantaneous loads, and instantaneous yields. Instantaneous loads were calculated by multiplying the concentration at a site by the discharge. This gives the mass of pesticide being transported by the stream at the time the sample was taken. It was not possible to calculate cumulative loads because continuous discharge data and periodic pesticide data were not available for many of the sites. Instantaneous yields were calculated by dividing the instantaneous load by the basin area. Standardizing by area provides a more meaningful comparison of basins of widely differing sizes. As for application intensities, only pesticides detected in more than seven basins were used in the PCA. However, the San Joaquin mainstem sites (S1–4) were not included in the PCA analyses of instantaneous loads and instantaneous yields. The high discharges at the mainstem sites resulted in very high calculated instantaneous loads that obscured patterns among the tributary sites. Also, nondetections were assigned a value of zero for the analyses of instantaneous loads and instantaneous yields because assigning a value of one-half the detection limit to a site having high discharge sometimes resulted in values higher than at sites where pesticides were actually detected. This added source of variation is undesirable for PCA. For the analysis of concentrations, nondetections were assigned a value of one-half the reporting limit, and the data were transformed, as in the application intensity analysis.

The low bias for some pesticides noted in the quality control procedures (*tables 5 and 6*) should not have a significant effect on the results of PCA. PCA is being used in this study to evaluate patterns of correlation among pesticides. Therefore, the relative value at a site—which sites have high values and which sites have low values—is more important than the absolute concentration in determining the resulting patterns.

### Instantaneous Pesticide Loads

The data were used to address two objectives. First, we determined the major sources of pesticides detected at the San Joaquin River near Vernalis (S4) during the June 1994 study period. Second, we compared the instantaneous loads from upstream tributaries with the instantaneous loads at the San Joaquin River near Vernalis to determine if the total basin

instantaneous load could be estimated from instantaneous loads in the tributaries during the June 1994 study period. These types of analyses are most appropriately applied to data collected in a Lagrangian manner. This means that the same parcel of water is sampled as it moves downstream through the system. Because only the 1994 sampling was conducted in a Lagrangian manner, only the 1994 data are analyzed in this fashion.

The first objective was addressed by examining and comparing the instantaneous loads from each of the tributaries. The second objective was addressed by summing the instantaneous loads from the San Joaquin River near Stevinson (S1) with instantaneous loads from the east-side tributaries and the west-side tributaries. The east-side tributaries included the Merced River (E5), Harding Drain (E6), Westport Drain (E7), Tuolumne River (E8), and Stanislaus River (E10). The west-side sites included Newman Wasteway (W1), Orestimba Creek (W2), Spanish Grant Drain (W3), Olive Avenue Drain (W4), Del Puerto Creek (W5), Hospital Creek (W6), and Ingram Creek (W7). The southern tributaries were included with the west-side sites for this analysis and included Salt Slough (G1) and Mud Slough (G3). Los Banos Creek (G2) was not included because it was dry at the time of sampling. For the purposes of these calculations, samples which did not have detections of a particular pesticide were assigned a concentration value equal to one-half the MDL.

Instantaneous loads were calculated for all pesticides at each site. The data were screened to determine which pesticides to examine in more detail. The pesticides that were examined in detail met all three of the following criteria: (1) the pesticide was detected at San Joaquin River near Vernalis (the integrator site); (2) the pesticide was detected at five or more sites; and (3) at least one sample had a concentration greater than or equal to 0.1 µg/L. Five pesticides met all the criteria: alachlor, EPTC, metolachlor, molinate, and trifluralin. These pesticides exhibited good recoveries in spiked samples, except trifluralin (*tables 5 and 6*), which was biased low. Despite the bias, calculation of instantaneous loads should still be useful in identifying the basins contributing more or less of the pesticide to the San Joaquin River near Vernalis. The bias primarily affects calculations of the actual mass of the pesticide present, not the relative importance of the different sources.

## Results and Discussion

### Patterns in Application

Of the 48 pesticides analyzed, 31 were reported applied in the San Joaquin River Basin upstream of Vernalis in 1994 (*table 7*). Fewer pesticides were applied preceding the June (25 pesticides) and August (24 pesticides) 2001 sampling periods. The amounts applied varied between years and between the two sampling periods in 2001 (*table 7*). More than 1,000 lb of active ingredient were applied for 19 pesticides in June 1994, 15 in June 2001, and 12 in August 2001. The number of pesticides applied in individual tributary basins ranged from 5 to 19 in 1994, from 4 to 16 in June 2001, and from 3 to 14 in August 2001. Newman Wasteway (W1) always had the minimum number of pesticides applied. The maximum number of pesticides was applied in the Westport Drain (E7) and Tuolumne River at Modesto (E8) basins in 1994 and in the Tuolumne River at Shiloh Road (E9) (June) and Stanislaus River at Caswell State Park (E11) (June and August) in 2001. The number of pesticides applied in tributary basins was highly correlated with basin area during each sampling period (Spearman's  $r = 0.85, 0.70, \text{ and } 0.84$  in June 1994, June 2001, and August 2001, respectively  $p < 0.01$  in all cases). Larger areas likely include a wider variety of crops, resulting in more varied pesticide use.

Jaccards similarities ranged widely in June 1994 (0.16–0.96), June 2001 (0.08 and 0.96), and August 2001 (0.13–1.00). The results of the cluster analysis (*fig. 3*) reflected the relation between basin size and number of pesticides applied. In June 1994 and June 2001, the mainstem San Joaquin River sites and large east-side and southern tributary sites occurred together in clusters with greater than 50 percent of the information remaining (*fig. 3*). June 1994 differed from June 2001 in that all of the smaller east-side drains also occurred in the cluster (*fig. 3*). In June 1994, Jaccards similarities between sites in the cluster ranged from a minimum of 0.42 (E1 and S4) to a maximum of 0.96 (S2 and S3). In June 2001, only Westport Drain (E7) of the smaller tributaries, clustered with the larger basins (*fig. 3*). In June 2001, Jaccards similarities between sites in the cluster ranged from a minimum of 0.36 (E7 and S1) to a maximum of 0.96 (S3 and S4). In August 2001, the mainstem San Joaquin River basins clustered with some of the southern basins, but the large east-side basins formed a separate cluster with Harding Drain (E6) and Westport Drain (E7) (*fig. 3*). Jaccards similarities ranged from 0.50 to 1.00 in the mainstem cluster and from 0.50 to

0.90 in the cluster of east-side sites. Most of the smaller basins exhibited no obvious pattern between sampling periods, with the following exceptions: Del Puerto Creek (W4) and Olive Avenue Drain (W5) were always very similar to each other (Jaccards similarity from 0.67 to 0.89) as were Livingston Canal (E2) and Highline Canal (E3) (Jaccards similarity from 0.50 to 0.75).

These patterns in similarity are not surprising given the correlation between basin size and number of pesticides applied. The larger basins cluster together because the larger basins tend to have at least small applications of a wide variety of pesticides. The mainstem San Joaquin River basins are expected to cluster closely because they are nested within each other and only gain or lose a few pesticides between the upstream and downstream sites. The smaller basins cluster less regularly because fewer pesticides were applied and not all the same pesticides were applied in each basin, during the preceding 28 days. This variability presumably relates to the specific land uses and needs within those basins. Some of these differences might become less obvious if longer application periods were considered, assuming that there is some probability of small applications of additional pesticides within a longer time period.

The results of the principal components analyses (*table 8* and *figs. 4–6*) provided information regarding similarities in application intensity among sites. In 1994, the first seven principal component (PC) axes had eigenvalues that were greater than one, but only the first three principal component axes had high loadings ( $>0.50$ ) for more than two pesticides (*table 8*). Plots of basin scores on the first three PC axes (*fig. 4*) gave results similar to the cluster analysis (*fig. 3A*). The mainstem, southern, and east-side basins tended to have PC axis 1 scores of around zero or greater with a fairly restricted range of scores on PC axis 2. The small west-side basins had negative scores on PC axis 1 and a wide range of scores on PC axis 2. The separation of sites on PC axis 1 was mainly due to higher applications of pebulate and trifluralin combined with no or lower applications of butylate, cyanazine, methyl parathion, pendimethalin, *cis*-permethrin, and simazine in west-side basins compared with the other basins. PC axis 2 separated basins having higher applications of propargite from basins having higher applications of carbaryl, chlorpyrifos, and gamma-HCH. PC axis 3 mainly separated basins having higher applications of azinphos-methyl, ethalfluralin, and metolachlor from basins having lower applications of those chemicals. Neither PC axis 2 nor PC axis 3 exhibited any strong geographic pattern.

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**Table 7.** Number of basins in which a pesticide was applied, the total amount applied in the 28 days before water samples were collected, and the number of basins for which the pesticide was detected in the water sample.

[A total of 22 basins were sampled during each sampling period. D, number of samples with concentrations above the MDL (Method Detection Limit) in 1994 and LRL (Laboratory Reporting Level) in 2001; E, number of samples with estimated concentrations below the reporting limit; lb, pound; <, less than]

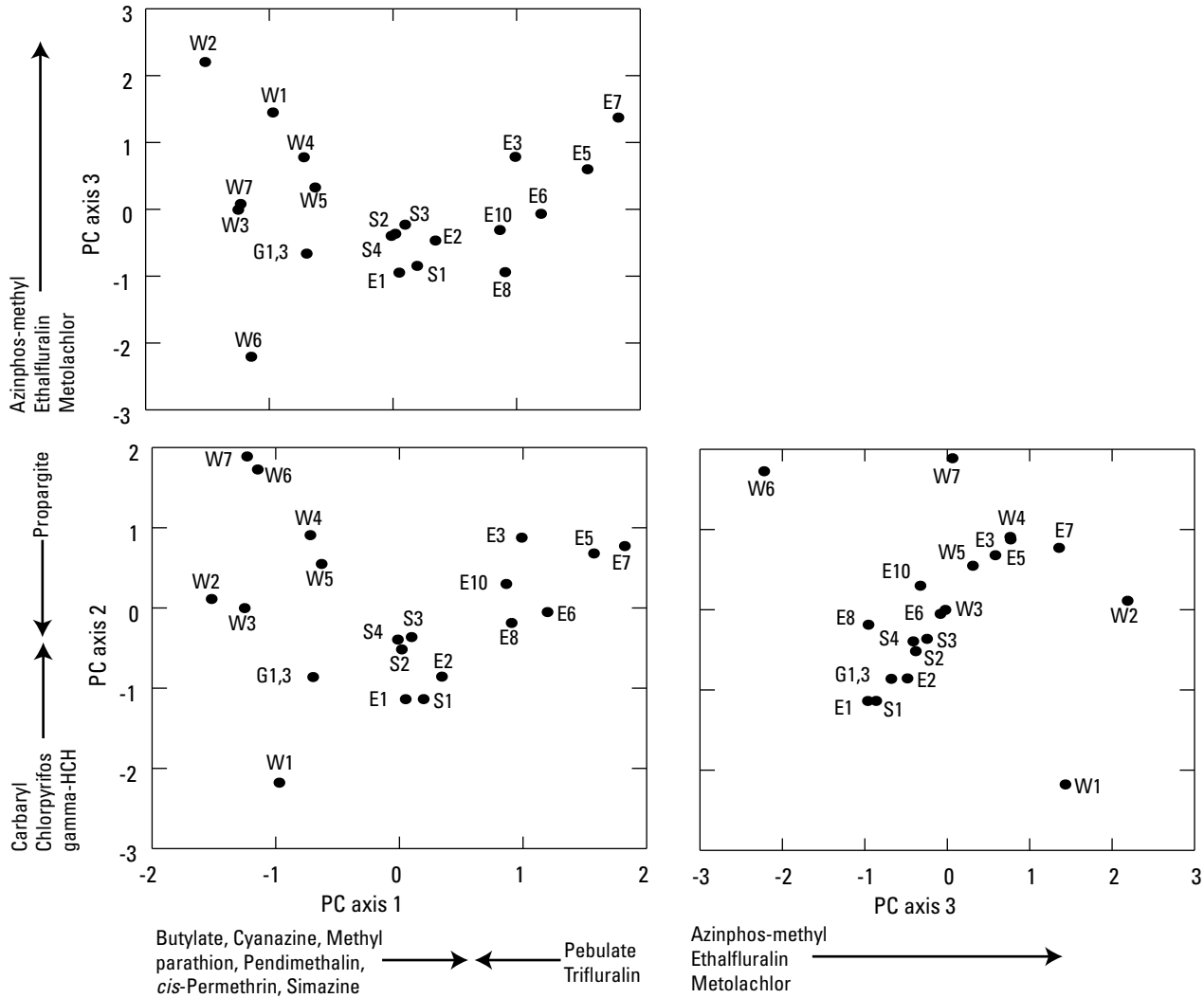
Pesticide	June 1994			June 2001			August 2001		
	Basins where applied	Total amount applied (lb)	Basins where detected	Basins where applied	Total amount applied (lb)	Basins where detected	Basins where applied	Total amount applied (lb)	Basins where detected
Alachlor	4	927	7D	5	691	0	0	0	1D
Atrazine	0	0	14D	0	0	12D, 5E	0	0	8D, 9E
Azinphos-methyl	18	4,054	6D	9	295	2E	12	4,002	0
Butylate	12	25,577	4D	7	3,657	0	7	528	0
Carbaryl	18	7,726	9D	18	12,332	1D, 12E	13	1,772	11E
Carbofuran	2	78	1D	0	0	0	5	88	0
Chlorpyrifos	19	15,793	11D, 1E	19	13,386	13D, 2E	20	34,289	15D, 1E
Cyanazine	13	5,542	5D	0	0	0	4	117	9D, 2E
Dacthal (DCPA)	0	0	1D, 1E	0	0	0	0	0	1D
DDE, <i>p,p'</i> -	0		5D, 1E	0	0	6D, 3E	0	0	6D
Diazinon	20	7,952	10D	12	916	11D, 10E	14	2,561	15D, 2E
Dieldrin	0	0	3D	0	0	4D	0	0	4D
Disulfoton	4	172	0	0	0	0	4	117	0
EPTC	13	28,548	17D	9	3,297	17D, 2E	9	2,264	16D
Ethalfuralin	13	3,093	5D	7	229	1D	0	0	1D
Ethoprophos	0	0	0	0	0	1D, 1E	0	0	1D
Fonofos	7	970	0	0	0	1D, 1E	0	0	0
HCH, alpha- (alpha-BHC)	0	0	0	0	0	1D	0	0	1D
HCH, gamma- (Lindane)	10	27	0	6	72	3D, 1E	4	<1	2D, 2E
Linuron	4	25	0	0	0	0	0	0	0
Malathion	7	217	0	11	1,647	1E	12	5,279	12E
Methyl parathion	10	1,854	0	11	3,590	1D, 1E	7	625	0
Metolachlor	17	18,137	15D	17	9,958	16D, 5E	9	1,448	16D, 5E
Metribuzin	3	14	2D	5	373	2D	3	43	1D
Molinate	8	8,550	12D	7	8,251	10D, 2E	0	0	3D
Napropamide	11	191	4D	4	130	5D, 1E	6	165	1D, 1E
Parathion	5	50	0	0	0	0	0	0	0
Pebulate	9	9,755	5D	5	590	0	4	96	0
Pendimethalin	9	1,307	0	10	1,002	0	6	83	3D
Permethrin, <i>cis</i> -	13	1,035	0	16	2,410	0	20	4,225	0
Phorate	5	1,713	0	6	329	0	5	465	0
Prometon	0	0	0	0	0	5E	0	0	0
Pronamide	1	7	0	3	16	1D	2	13	0
Propachlor	0	0	0	0	0	1E	0	0	1E
Propanil	2	891	0	7	6,494	0	6	2,941	0
Propargite	17	11,653	4D, 1E	20	28,394	5D	21	135,686	13D, 2E
Simazine	11	2,823	22D	12	1,554	10D, 9E	12	2,395	6D, 10E
Tebuthiuron	0	0	1E	0	0	1E	0	0	1E
Thiobencarb	6	6,520	4D	6	10,700	1D, 2E	0	0	1D
Trifluralin	20	13,856	13D	18	9,682	11D, 4E	14	2,563	10D, 2E



**Table 8.** Loadings of pesticides on axes from principal component analysis (PCA) of pesticide application intensity (pounds per square mile).

[—, loading &lt;0.5]

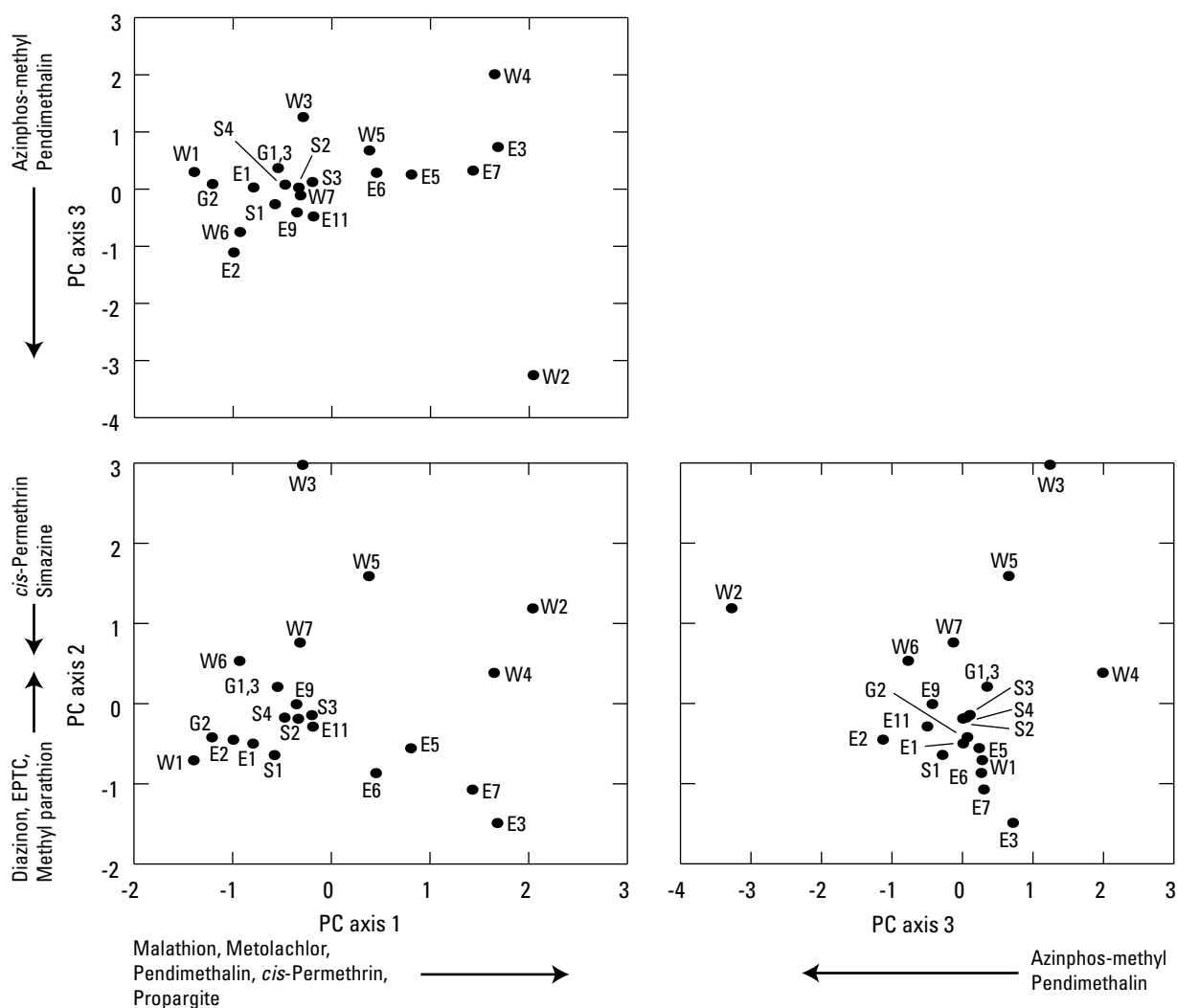
	PCA axis 1	PCA axis 2	PCA axis 3	PCA axis 4	PCA axis 5	PCA axis 6	PCA axis 7
<b>June 1994</b>							
Azinphos-methyl	—	—	0.60	—	—	—	—
Butylate	0.81	—	—	—	—	—	—
Carbaryl	—	0.56	—	—	—	—	—
Chlorpyrifos	—	.78	—	—	—	– 0.50	—
Cyanazine	.70	—	—	—	—	—	—
Diazinon	—	—	—	—	—	—	—
EPTC	—	—	—	0.59	—	—	—
Ethalfuralin	—	—	.51	—	—	—	—
HCH, gamma- (Lindane)	—	.51	—	—	—	—	—
Methyl parathion-	.60	—	—	—	—	.53	—
Metolachlor	—	—	.72	—	—	—	—
Molinate	—	—	—	—	0.54	—	—
Napropamide	—	—	—	—	.51	—	—
Pebulate	–.70	—	—	—	—	—	—
Pendimethalin	.64	—	—	—	—	—	0.54
Permethrin, <i>cis</i> -	.88	—	—	—	—	—	—
Propargite	—	–.69	—	—	—	—	—
Simazine	.71	—	—	—	—	—	—
Trifluralin	–.80	—	—	—	—	—	—
Percent variance explained:	27.2	15.5	14.6	10.0	7.7	6.3	5.5
<b>June 2001</b>							
Azinphos-methyl	—	—	–.66	—	—	—	—
Carbaryl	—	—	—	.57	—	—	—
Chlorpyrifos	—	—	—	.54	—	—	—
Diazinon	—	.69	—	—	—	—	—
EPTC	—	.67	—	—	—	—	—
Malathion	.69	—	—	—	—	—	—
Methyl parathion	—	.56	—	—	—	—	—
Metolachlor	.68	—	—	—	—	—	—
Pendimethalin	.50	—	–.75	—	—	—	—
Permethrin, <i>cis</i> -	.55	–.57	—	—	—	—	—
Propargite	.76	—	—	—	—	—	—
Simazine	—	–.55	—	—	—	—	—
Trifluralin	—	—	—	—	—	—	—
Percent variance explained:	24.1	18.8	14.8	12.8	9.3	—	—
<b>August 2001</b>							
Azinphos-methyl	—	—	.67	—	—	—	—
Carbaryl	—	.69	.67	—	—	—	—
Chlorpyrifos	.89	—	—	—	—	—	—
Diazinon	—	—	—	.72	—	—	—
EPTC	—	.77	—	—	—	—	—
Malathion	—	—	—	–.84	—	—	—
Metolachlor	—	—	—	—	—	—	—
Permethrin, <i>cis</i> -	.93	—	—	—	—	—	—
Propargite	.87	—	—	—	—	—	—
Simazine	.78	—	—	—	—	—	—
Trifluralin	.79	—	—	—	—	—	—
Percent variance explained:	34.3	18.0	15.4	14.1	—	—	—



**Figure 4.** Site scores on the first three axes from a principal components analysis of pesticide application in the 28 days preceding sampling in June 1994. See *table 1* for site codes. The arrows indicate the direction of increasing application of particular pesticides.

The PCA of June 2001 application intensity (*table 8*, *fig. 5*) largely reflected the results of the cluster analysis (*fig. 3B*) but also exhibited differences because of the amounts applied. Five of the PC axes had eigenvalues greater than one, but only the first two were loaded highly for more than two pesticides. No pesticides were highly loaded on PC axis 5. A plot of PC axes 1 and 2 showed a tight group of basins with negative scores on both axes. This group included most of the basins in the cluster of mainstem, southern, and large east-side tributary basins identified by cluster analysis (*fig. 3B*). The main differences in the PCA grouping were the inclusion of Newman Wasteway (W1) and Livingston Canal (E2) in the group and the absence of the Merced River at River Road (E5). There were few applications of any pesticides in the Newman Wasteway and Livingston Canal basins, which tended to group them with the large cluster that had low application intensities for many pesticides. The Merced River at River Road varied from the other mainstem and large east-side

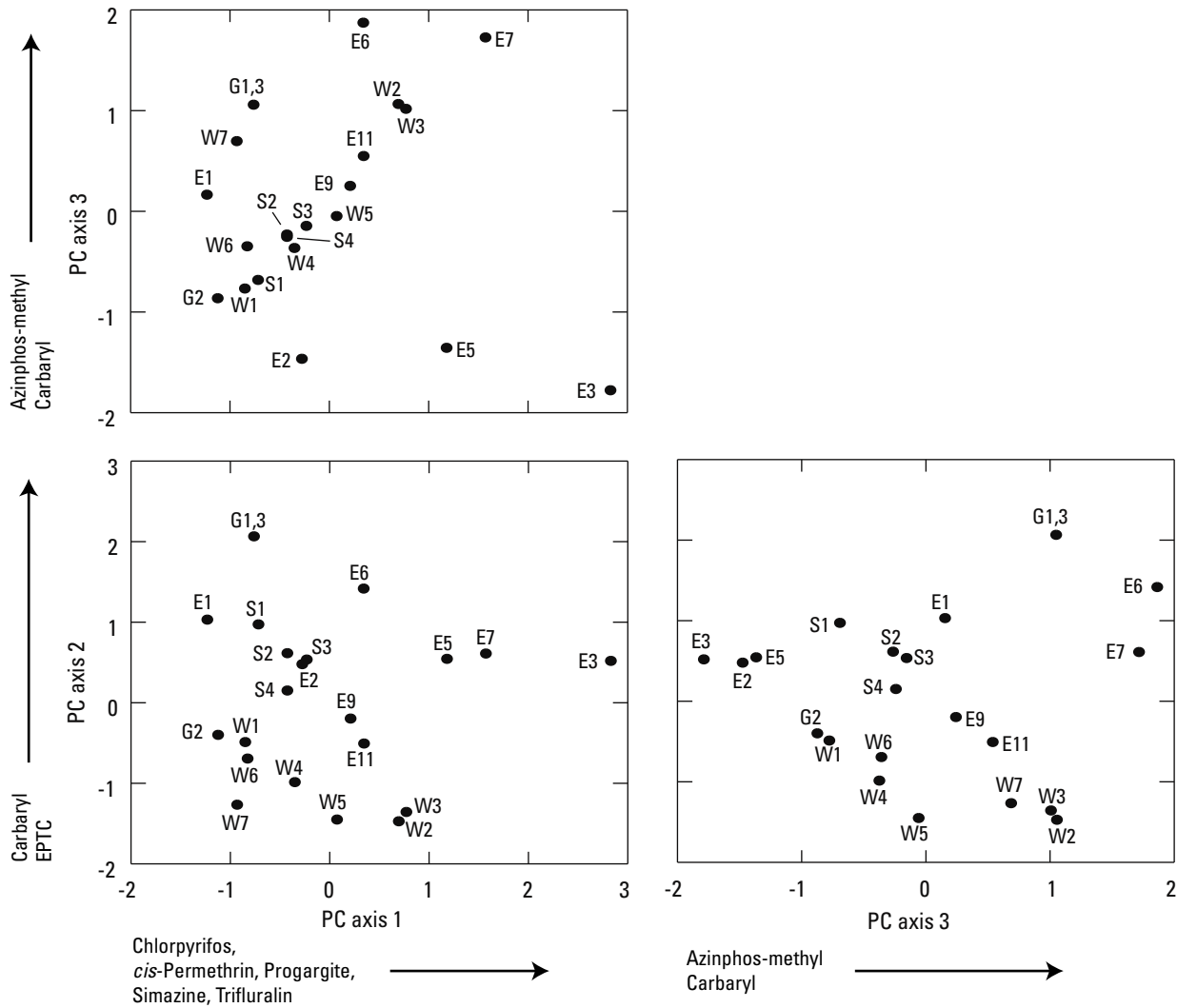
basins mainly because of heavy application of propargite. PC axis 3 mainly separates the Orestimba Creek Basin from the others because it had the highest applications of pendimethalin and azinphos-methyl. In contrast to June 1994, PC axis 1 did not separate west-side basins from the others. The main geographic separation occurred on PC axis 2, which shows west-side basins having higher scores than the other basins. This relationship corresponds to higher applications of diazinon, EPTC, and methyl parathion and lower applications of *cis*-permethrin and simazine in west-side basins compared with the other basins. Although there is some overlap in the pesticides contributing to the geographic separation (*cis*-permethrin, simazine, and methyl parathion), there are differences as well. In June 1994, butylate, cyanazine, pendimethalin, pebulate, and trifluralin were also important (*fig. 4*). These pesticides were not important in June 2001, but diazinon and EPTC were important.



**Figure 5.** Site scores on the first three axes from a principal components analysis of pesticide application in the 28 days preceding sampling in June 2001. See *table 1* for site codes. The arrows indicate the direction of increasing application of particular pesticides.

Just as the cluster analysis did not show a single large cluster in August 2001 (*fig. 3C*), the PCA of application intensity did not reveal any closely associated groups of similar basins (*fig. 6*). Only the first four PC axes had eigenvalues greater than one and only the first PC axis was loaded heavily for more than two pesticides (*table 8*). PC axis 1 separated basins on the basis of application intensity of five pesticides used in nearly all of the basins. There seemed to be no strong geographic pattern; however, the three highest scores are all for east-side basins (E3, E5, E7). In contrast, PC axis 2 scores showed a strong geographic pattern with six west-side basins (W2–W7) having no or little application of carbaryl and EPTC. Neither of these pesticides were important in geographic differences in June 1994. EPTC contributed to geographic variation in June 2001, but carbaryl did not. PC axis 3 separated basins on the basis of applications of azinphos-methyl and carbaryl, but similar to PC axes 1 and 2, there was no strong grouping of sites.

There were not any consistent strong patterns in application intensity. Although the June 1994 analysis showed a clear separation of east-side and west-side sites on PCA axis 1, which explains the greatest proportion of variance in the data (*table 8*), a similar pattern was not apparent in 2001. East-side and west-side basins had widely overlapping distributions of scores on PCA axis 1 in both June and August 2001. There was separation of west-side basins from other basins in 2001 on the basis of PC axis 2 scores; however, PC axis 2 explains less of the variance of the data (*table 8*) suggesting that other factors were more important than geography in determining application rates. Also, the pesticides that were important in separating the west-side basins from the other basins varied among sample periods. The lack of a consistent strong pattern between years and between months should not be surprising given the wide variety of factors likely affecting application patterns. Such factors include changing cropping patterns in different basins, changing price and availability of specific pesticides, and outbreaks of different pests.



**Figure 6.** Site scores on the first three axes from a principal components analysis of pesticide application in the 28 days preceding sampling in August 2001. See *table 1* for site codes. The arrows indicate the direction of increasing application of particular pesticides.

**Patterns in Occurrence and Distribution**

In 1994, 26 pesticides were detected at least once, including pesticides having estimated concentrations below the reporting level (*tables 7 and 9*). In June 2001, 28 pesticides were detected at least once, including pesticides having estimated concentrations below the reporting level (*tables 7 and 10*). In August 2001, 27 pesticides were detected at least once, including pesticides having estimated concentrations below the reporting level (*tables 7 and 11*). Two pesticides detected during each sampling period are breakdown products of pesticides. Deethylatrazine is derived from atrazine and *p,p'*-DDE is derived from DDT (these chemicals are included in the term pesticide throughout this report).

Only chlorpyrifos exceeded any of the water quality criteria considered in this study (*table 2*), except for one exceedance of the California CMC (criterion maximum concentration) for diazinon during June 2001 at Hospital Creek (W6). In June 1994, four (W2, W3, W4, and W5) of seven west-side sites exceeded the California CMC for chlorpyrifos of 0.020 µg/L. Hospital Creek (W6) and one site on the San Joaquin River (S3) were at the CMC. In June 2001, there were five exceedances of the chlorpyrifos CMC, including three east-side tributaries (E5, E9, and E11) and two west-side tributaries (W2 and W7). There were no exceedances in August 2001.

**Table 9.** Streamflow and dissolved pesticide concentrations for sites sampled during June 1994 in the San Joaquin River Basin.[E, estimated concentration; WSID, Westside Irrigation District; ft<sup>3</sup>/s, cubic feet per second; µg/L, microgram per liter; <, less than]

Site code	Station name	Date	Time	Stream-flow (ft <sup>3</sup> /s)	Aalachlor concentration (µg/L)	Atrazine concentration (µg/L)	Atrazine, deethyl concentration (µg/L)	Azinphos-methyl concentration (µg/L)	Butylate concentration (µg/L)	Carbaryl concentration (µg/L)
E1	Bear Creek at Bert Crane Road near Merced	06/18/1994	1100	68.2	<0.002	<0.001	<0.002	<0.001	0.007	<0.003
S1	San Joaquin River near Stevinson	06/20/1994	1830	17.3	<.002	.008	<.002	<.001	<.002	<.003
G1	Salt Slough at Highway 165 near Stevinson	06/21/1994	0600	187	<.002	<.001	<.002	<.001	<.002	<.003
G3	Mud Slough near Gustine	06/21/1994	0400	28	<.002	.022	E.010	<.001	<.002	E.015
E2	Livingston Canal at Livingston Treatment Plant near Livingston	06/20/1994	1300	44.2	<.002	<.001	<.002	<.001	<.002	<.003
E3	Highline Canal Spill near Hilmar	06/21/1994	0220	15.3	<.002	<.001	<.002	<.001	<.002	<.003
E4	Merced River below Merced Falls Dam near Snelling	06/18/1994	0900	1,680	<.002	<.001	<.002	<.001	<.002	<.003
E5	Merced River at River Road Bridge near Newman	06/22/1994	0400	141	<.002	<.001	<.002	<.001	<.002	<.003
W1	Newman Wasteway at Highway 33 near Gustine	06/22/1994	0100	10	.009	.036	E.005	E.013	<.002	E.170
W2	Orestimba Creek at River Road near Crows Landing	06/22/1994	1645	9.6	<.002	.017	E.005	E.079	<.002	<.003
W3	Spanish Grant Combined Drain near Patterson	06/22/1994	2100	35	<.002	.022	E.005	E1.000	<.002	E.021
E6	Harding Drain at Carpenter Road near Patterson	06/22/1994	2300	35	<.002	.008	E.012	<.001	.008	E.390
S2	San Joaquin River at Patterson Bridge near Patterson	06/23/1994	0530	487	<.002	.011	E.008	E.077	<.002	E.150
E7	Westport Drain near Modesto	06/23/1994	1100	15.2	<.002	<.001	<.002	<.001	.002	<.003
W4	Olive Avenue Drain near Patterson	06/23/1994	0630	6.2	.032	.063	<.002	E.250	<.002	E.040
W5	Del Puerto Creek at Vineyard Road near Patterson	06/23/1994	0830	7.8	.520	.040	E.006	<.001	<.002	<.003
S3	San Joaquin River below WSID pump above Tuolumne River near Westley	06/23/1994	2200	347	.021	.013	E.005	E.046	<.002	E.028
E8	Tuolumne River at Modesto	06/23/1994	0400	121	<.002	.007	<.002	<.001	.004	E.010
W6	Hospital Creek at River Road near Patterson	06/23/1994	2330	32.1	.240	.048	<.002	<.001	<.002	<.003
W7	Ingram Creek at River Road near Patterson	06/24/1994	0030	11.1	.130	.023	E.008	<.001	<.002	E.053
E10	Stanislaus River at Ripon near Patterson	06/23/1994	1800	499	<.002	<.001	<.002	<.001	<.002	<.003
S4	San Joaquin River near Vernalis	06/24/1994	1100	1,110	.014	.009	E.004	<.001	<.002	<.003

**Table 9.** Streamflow and dissolved pesticide concentrations for sites sampled during June 1994 in the San Joaquin River Basin—Continued.[E, estimated concentration; WSID, Westside Irrigation District; ft<sup>3</sup>/s, cubic feet per second; µg/L, microgram per liter; <, less than]

Site code	Station name	Date	Time	Carbofuran concentration (µg/L)	Chlorpyrifos concentration (µg/L)	Cyanazine concentration (µg/L)	Dacthal concentration (µg/L)	DDE, p,p'-concentration (µg/L)	Diazinon concentration (µg/L)
E1	Bear Creek at Bert Crane Road near Merced	06/18/1994	1100	<0.003	E0.003	<0.004	<0.002	<0.006	0.005
S1	San Joaquin River near Stevinson	06/20/1994	1830	<.003	<.004	.130	<.002	<.006	<.002
G1	Salt Slough at Highway 165 near Stevinson	06/21/1994	0600	<.003	<.004	<.004	<.002	<.006	<.002
G3	Mud Slough near Gustine	06/21/1994	0400	<.003	<.004	.150	.006	<.006	.012
E2	Livingston Canal at Livingston Treatment Plant near Livingston	06/20/1994	1300	<.003	<.004	<.004	<.002	<.006	<.002
E3	Highline Canal Spill near Hilmar	06/21/1994	0220	<.003	<.004	<.004	<.002	<.006	<.002
E4	Merced River below Merced Falls Dam near Snelling	06/18/1994	0900	<.003	<.004	<.004	E.001	<.006	<.002
E5	Merced River at River Road Bridge near Newman	06/22/1994	0400	<.003	<.004	<.004	<.002	<.006	<.002
W1	Newman Wasteway at Highway 33 near Gustine	06/22/1994	0100	<.003	<.004	.026	<.002	<.006	.011
W2	Orestimba Creek at River Road near Crows Landing	06/22/1994	1645	<.003	.270	<.004	<.002	.018	<.002
W3	Spanish Grant Combined Drain near Patterson	06/22/1994	2100	E.01	.029	<.004	<.002	.006	.016
E6	Harding Drain at Carpenter Road near Patterson	06/22/1994	2300	<.003	.014	<.004	<.002	<.006	.030
S2	San Joaquin River at Patterson Bridge near Patterson	06/23/1994	0530	<.003	.030	.049	<.002	<.006	.011
E7	Westport Drain near Modesto	06/23/1994	1100	<.003	.015	<.004	<.002	<.006	<.002
W4	Olive Avenue Drain near Patterson	06/23/1994	0630	<.003	.270	<.004	<.002	.009	<.002
W5	Del Puerto Creek at Vineyard Road near Patterson	06/23/1994	0830	<.003	.037	<.004	<.002	E.003	.019
S3	San Joaquin River below WSID pump above Tuolumne River near Westley	06/23/1994	2200	<.003	.020	<.004	<.002	<.006	.009
E8	Tuolumne River at Modesto	06/23/1994	0400	<.003	.012	.049	<.002	<.006	<.002
W6	Hospital Creek at River Road near Patterson	06/23/1994	2330	<.003	.020	<.004	<.002	.027	.009
W7	Ingram Creek at River Road near Patterson	06/24/1994	0030	<.003	.007	<.004	<.002	.012	.009
E10	Stanislaus River at Ripon near Patterson	06/23/1994	1800	<.003	<.004	<.004	<.002	<.006	<.002
S4	San Joaquin River near Vernalis	06/24/1994	1100	<.003	<.004	<.004	<.002	<.006	<.002

**Table 9.** Streamflow and dissolved pesticide concentrations for sites sampled during June 1994 in the San Joaquin River Basin—Continued.[E, estimated concentration; WSID, Westside Irrigation District; ft<sup>3</sup>/s, cubic feet per second; µg/L, microgram per liter; <, less than]

Site code	Station name	Date	Time	Dieldrin concentration (µg/L)	EPTC concentration (µg/L)	Ethalfluralin concentration (µg/L)	Fonofos concentration (µg/L)	Metolachlor concentration (µg/L)	Metribuzin concentration (µg/L)	Molinate concentration (µg/L)
E1	Bear Creek at Bert Crane Road near Merced	06/18/1994	1100	<0.001	E40.000	<0.004	<0.003	0.004	<0.004	0.006
S1	San Joaquin River near Stevinson	06/20/1994	1830	<.001	.130	<.004	<.003	.110	<.004	.100
G1	Salt Slough at Highway 165 near Stevinson	06/21/1994	0600	<.001	<.002	<.004	<.003	<.002	<.004	<.004
G3	Mud Slough near Gustine	06/21/1994	0400	<.001	.012	<.004	<.003	<.002	<.004	.690
E2	Livingston Canal at Livingston Treatment Plant near Livingston	06/20/1994	1300	<.001	<.002	<.004	<.003	<.002	<.004	<.004
E3	Highline Canal Spill near Hilmar	06/21/1994	0220	<.001	<.002	<.004	<.003	<.002	<.004	<.004
E4	Merced River below Merced Falls Dam near Snelling	06/18/1994	0900	<.001	<.002	<.004	<.003	<.002	<.004	.016
E5	Merced River at River Road Bridge near Newman	06/22/1994	0400	<.001	.013	<.004	<.003	.034	<.004	<.004
W1	Newman Wasteway at Highway 33 near Gustine	06/22/1994	0100	<.001	.180	<.004	<.003	.180	<.004	<.004
W2	Orestimba Creek at River Road near Crows Landing	06/22/1994	1645	.012	.340	.120	.120	.560	.012	<.004
W3	Spanish Grant Combined Drain near Patterson	06/22/1994	2100	<.001	.140	.018	.028	.170	<.004	.015
E6	Harding Drain at Carpenter Road near Patterson	06/22/1994	2300	<.001	.022	<.004	<.003	.005	<.004	<.004
S2	San Joaquin River at Patterson Bridge near Patterson	06/23/1994	0530	<.001	.110	<.004	.005	.071	<.004	.099
E7	Westport Drain near Modesto	06/23/1994	1100	<.001	.051	<.004	<.003	<.002	<.004	<.004
W4	Olive Avenue Drain near Patterson	06/23/1994	0630	<.001	.510	<.004	<.003	.054	<.004	<.004
W5	Del Puerto Creek at Vineyard Road near Patterson	06/23/1994	0830	<.001	.320	.036	<.003	.110	<.004	.008
S3	San Joaquin River below WSID pump above Tuolumne River near Westley	06/23/1994	2200	<.001	.100	<.004	.006	.087	<.004	.079
E8	Tuolumne River at Modesto	06/23/1994	0400	<.001	.020	<.004	<.003	.280	<.004	.027
W6	Hospital Creek at River Road near Patterson	06/23/1994	2330	.013	.660	.073	.017	.053	.032	.090
W7	Ingram Creek at River Road near Patterson	06/24/1994	0030	.012	.140	.190	.006	.076	<.004	.041
E10	Stanislaus River at Ripon near Patterson	06/23/1994	1800	<.001	<.002	<.004	<.003	<.002	<.004	<.004
S4	San Joaquin River near Vernalis	06/24/1994	1100	<.001	.034	<.004	<.003	.064	<.004	.030

**24 Occurrence, Distribution, Instantaneous Loads, and Yields of Dissolved Pesticides, San Joaquin River Basin, Calif.**

**Table 9.** Streamflow and dissolved pesticide concentrations for sites sampled during June 1994 in the San Joaquin River Basin—Continued.

[E, estimated concentration; WSID, Westside Irrigation District; ft<sup>3</sup>/s, cubic feet per second; µg/L, microgram per liter; <, less than]

Site code	Station name	Date	Time	Napro pamide concentration (µg/L)	Pebulate concentration (µg/L)	Propargite concentration (µg/L)	Simazine concentration (µg/L)	Tebu- thiuron concentration (µg/L)	Thio- bencarb concentration (µg/L)	Tri- fluralin concentration (µg/L)
E1	Bear Creek at Bert Crane Road near Merced	06/18/1994	1100	<0.003	<0.004	<0.013	0.008	<0.010	<0.002	0.006
S1	San Joaquin River near Stevinson	06/20/1994	1830	<.003	<.004	<.013	.043	<.010	<.002	<.002
G1	Salt Slough at Highway 165 near Stevinson	06/21/1994	0600	<.003	<.004	E.006	.053	<.010	<.002	<.002
G3	Mud Slough near Gustine	06/21/1994	0400	<.003	<.004	<.013	.061	<.010	.077	.018
E2	Livingston Canal at Livingston Treatment Plant near Livingston	06/20/1994	1300	<.003	<.004	<.013	.007	<.010	<.002	<.002
E3	Highline Canal Spill near Hilmar	06/21/1994	0220	<.003	<.004	<.013	.035	<.010	<.002	<.002
E4	Merced River below Merced Falls Dam near Snelling	06/18/1994	0900	<.003	<.004	<.013	.007	<.010	.004	<.002
E5	Merced River at River Road Bridge near Newman	06/22/1994	0400	<.003	<.004	<.013	.016	<.010	<.002	<.002
W1	Newman Wasteway at Highway 33 near Gustine	06/22/1994	0100	<.003	<.004	<.013	.073	<.010	<.002	.010
W2	Orestimba Creek at River Road near Crows Landing	06/22/1994	1645	.033	.098	.430	.054	<.010	<.002	.140
W3	Spanish Grant Combined Drain near Patterson	06/22/1994	2100	.019	.054	1.100	.069	<.010	<.002	.100
E6	Harding Drain at Carpenter Road near Patterson	06/22/1994	2300	<.003	<.004	<.013	.024	<.010	<.002	<.002
S2	San Joaquin River at Patterson Bridge near Patterson	06/23/1994	0530	<.003	<.004	.031	.039	<.010	.007	.013
E7	Westport Drain near Modesto	06/23/1994	1100	<.003	<.004	<.013	.030	<.010	<.002	.016
W4	Olive Avenue Drain near Patterson	06/23/1994	0630	<.003	<.004	.100	.065	<.010	<.002	.510
W5	Del Puerto Creek at Vineyard Road near Patterson	06/23/1994	0830	<.003	<.004	<.013	.050	<.010	<.002	.035
S3	San Joaquin River below WSID pump above Tuolumne River near Westley	06/23/1994	2200	<.003	.016	<.013	.042	<.010	.004	.018
E8	Tuolumne River at Modesto	06/23/1994	0400	<.003	<.004	<.013	.030	<.010	<.002	<.002
W6	Hospital Creek at River Road near Patterson	06/23/1994	2330	.056	.033	<.013	.059	E.006	<.002	.350
W7	Ingram Creek at River Road near Patterson	06/24/1994	0030	.069	.053	<.013	.037	<.010	<.002	.430
E10	Stanislaus River at Ripon near Patterson	06/23/1994	1800	<.003	<.004	<.013	.024	<.010	<.002	<.002
S4	San Joaquin River near Vernalis	06/24/1994	1100	<.003	<.004	<.013	.033	<.010	<.002	.019



**Table 10.** Streamflow and dissolved pesticide concentrations for sites sampled during June 2001 in the San Joaquin River Basin.[E, estimated concentration; ft<sup>3</sup>/s, cubic feet per second; M, deleted due to interferences; µg/L, microgram per liter; <, less than; ND, no data]

Site code	Station name	Date	Time	Stream-flow (ft <sup>3</sup> /s)	Atrazine concentration (µg/L)	Atrazine, deethyl concentration (µg/L)	Azin-phos-methyl concentration (µg/L)	Carbaryl concentration (µg/L)	Chlor-pyrifos concentration (µg/L)
E1	Bear Creek at Bert Crane Road near Merced	06/20/2001	0830	2.9	<0.007	<0.006	<0.050	<0.041	0.018
S1	San Joaquin River near Stevinson	06/20/2001	1110	1.3	.008	<.006	<.050	<.041	<.005
G1	Salt Slough at Highway 165 near Stevinson	06/20/2001	1040	201	.014	E.002	<.050	E.022	.008
G2	Los Banos Creek at Highway 140	06/20/2001	0910	7.4	.015	<.006	<.050	E.015	<.005
G3	Mud Slough near Gustine	06/20/2001	0950	62.0	.016	<.006	<.050	<.041	E.004
E2	Livingston Canal at Livingston Treatment Plant near Livingston	06/20/2001	1010	0	<.007	<.006	<.050	<.041	<.005
E3	Highline Canal Spill near Hilmar	06/20/2001	1110	4.25	E.001	<.006	E.019	<.041	E.003
E5	Merced River at River Road Bridge near Newman	06/20/2001	1340	180	<.007	<.006	<.050	<.041	.025
W1	Newman Wasteway at Highway 33 near Gustine	06/20/2001	1200	6.1	E.006	<.006	<.050	E.002	.013
W2	Orestimba Creek at River Road near Crows Landing	06/20/2001	1150	12.9	.013	<.006	<.050	E.004	.149
W3	Spanish Grant Combined Drain near Patterson	06/20/2001	1350	21.0	.018	<.006	E.013	E.310	.009
E6	Harding Drain at Carpenter Road near Patterson	06/21/2001	1120	61.5	E.004	E.004	<.050	E.007	.012
S2	San Joaquin River at Patterson Bridge near Patterson	06/20/2001	0910	336	.009	E.003	<.050	E.002	<.005
E7	Westport Drain near Modesto	06/21/2001	0940	21.2	<.007	<.006	<.050	E.002	<.005
W4	Olive Avenue Drain near Patterson	06/21/2001	0950	ND	.021	E.003	<.050	E.004	.007
W5	Del Puerto Creek at Vineyard Road near Patterson	06/20/2001	1440	6.4	.013	E.004	<.050	E.013	<.005
S3	San Joaquin River below WSID pump above Tuolumne River near Westley	06/21/2001	1120	502	.008	<.006	<.050	<.041	.009
E9	Tuolumne River at Shiloh Road Bridge near Grayson	06/21/2001	1230	177	E.004	<.006	<.050	E.002	.021
W6	Hospital Creek at River Road near Patterson	06/21/2001	1400	4.1	.016	E.003	<.050	E.012	<.005
W7	Ingram Creek at River Road near Patterson	06/21/2001	1310	15	.027	<.006	<.050	E.040	0.021
E11	Stanislaus River at Caswell State Park near Ripon	06/21/2001	1300	550	<.007	<.006	<.050	.041	.100
S4	San Joaquin River near Vernalis	06/21/2001	1220	1,368	E.005	<.006	<.050	<.041	.010

**26 Occurrence, Distribution, Instantaneous Loads, and Yields of Dissolved Pesticides, San Joaquin River Basin, Calif.**

**Table 10.** Streamflow and dissolved pesticide concentrations for sites sampled during June 2001 in the San Joaquin River Basin—Continued.

[E, estimated concentration; ft<sup>3</sup>/s, cubic feet per second; M, deleted due to interferences; µg/L, microgram per liter; <, less than; ND, no data]

Site code	Station name	Date	Time	DDE, <i>p,p'</i> -concentration (µg/L)	Diazinon concentration (µg/L)	Dieldrin concentration (µg/L)	EPTC concentration (µg/L)	Ethalfluralin concentration (µg/L)	Ethoprophos concentration (µg/L)
E1	Bear Creek at Bert Crane Road near Merced	06/20/2001	0830	<0.003	E0.002	<0.005	0.003	<0.009	<0.005
S1	San Joaquin River near Stevinson	06/20/2001	1110	E.001	E.003	<.005	.007	<.009	<.005
G1	Salt Slough at Highway 165 near Stevinson	06/20/2001	1040	<.003	.006	<.005	.015	<.009	<.005
G2	Los Banos Creek at Highway 140	06/20/2001	0910	<.003	E.003	<.005	.035	<.009	<.005
G3	Mud Slough near Gustine	06/20/2001	0950	<.003	E.003	<.005	.003	<.009	<.005
E2	Livingston Canal at Livingston Treatment Plant near Livingston	06/20/2001	1010	<.003	<.005	<.005	<.002	<.009	<.005
E3	Highline Canal Spill near Hilmar	06/20/2001	1110	<.003	E.001	<.005	<.002	<.009	<.005
E5	Merced River at River Road Bridge near Newman	06/20/2001	1340	<.003	.007	<.005	.002	<.009	<.005
W1	Newman Wasteway at Highway 33 near Gustine	06/20/2001	1200	.003	E.004	<.005	.011	<.009	<.005
W2	Orestimba Creek at River Road near Crows Landing	06/20/2001	1150	.009	E.004	.007	.048	<.009	E.003
W3	Spanish Grant Combined Drain near Patterson	06/20/2001	1350	.010	.029	.007	.072	<.009	.033
E6	Harding Drain at Carpenter Road near Patterson	06/21/2001	1120	<.003	.038	<.005	.010	<.009	<.005
S2	San Joaquin River at Patterson Bridge near Patterson	06/20/2001	0910	E.002	.007	<.005	.008	<.009	<.005
E7	Westport Drain near Modesto	06/21/2001	0940	M	E.002	<.005	E.001	<.009	<.005
W4	Olive Avenue Drain near Patterson	06/21/2001	0950	<.003	.006	<.005	.053	<.009	<.005
W5	Del Puerto Creek at Vineyard Road near Patterson	06/20/2001	1440	.005	.008	<.005	.047	<.009	<.005
S3	San Joaquin River below WSID pump above Tuolumne River near Westley	06/21/2001	1120	E.001	.007	<.005	.011	<.009	<.005
E9	Tuolumne River at Shiloh Road Bridge near Grayson	06/21/2001	1230	<.003	.026	<.005	E.002	<.009	<.005
W6	Hospital Creek at River Road near Patterson	06/21/2001	1400	.019	.180	.037	.077	<.009	<.005
W7	Ingram Creek at River Road near Patterson	06/21/2001	1310	.013	E.004	.009	.116	.070	<.005
E11	Stanislaus River at Caswell State Park near Ripon	06/21/2001	1300	<.003	.030	<.005	<.002	<.009	<.005
S4	San Joaquin River near Vernalis	06/21/2001	1220	<.003	E.004	<.005	.004	<.009	<.005

**Table 10.** Streamflow and dissolved pesticide concentrations for sites sampled during June 2001 in the San Joaquin River Basin—Continued.[E, estimated concentration; ft<sup>3</sup>/s, cubic feet per second; M, deleted due to interferences; µg/L, microgram per liter; <, less than; ND, no data]

Site code	Station name	Date	Time	Fonofos concentration (µg/L)	HCH, alpha-concentration (µg/L)	HCH, gamma-concentration (µg/L)	Malathion concentration (µg/L)	Methyl parathion concentration (µg/L)	Metolachlor concentration (µg/L)
E1	Bear Creek at Bert Crane Road near Merced	06/20/2001	0830	<0.003	<0.005	<0.004	<.027	<0.006	E0.009
S1	San Joaquin River near Stevinson	06/20/2001	1110	<.003	<.005	<.004	<.027	<.006	.329
G1	Salt Slough at Highway 165 near Stevinson	06/20/2001	1040	<.003	<.005	<.004	<.027	<.006	.119
G2	Los Banos Creek at Highway 140	06/20/2001	0910	<.003	<.005	<.004	<.027	<.006	.051
G3	Mud Slough near Gustine	06/20/2001	0950	<.003	<.005	<.004	<.027	<.006	.088
E2	Livingston Canal at Livingston Treatment Plant near Livingston	06/20/2001	1010	<.003	<.005	<.004	<.027	<.006	<.013
E3	Highline Canal Spill near Hilmar	06/20/2001	1110	<.003	<.005	<.004	<.027	<.006	E.002
E5	Merced River at River Road Bridge near Newman	06/20/2001	1340	<.003	<.005	<.004	<.027	<.006	E.005
W1	Newman Wasteway at Highway 33 near Gustine	06/20/2001	1200	<.003	<.005	<.004	<.027	<.006	.044
W2	Orestimba Creek at River Road near Crows Landing	06/20/2001	1150	<.003	<.005	<.004	<.027	E.004	.271
W3	Spanish Grant Combined Drain near Patterson	06/20/2001	1350	.004	<.005	<.004	<.027	.069	.820
E6	Harding Drain at Carpenter Road near Patterson	06/21/2001	1120	<.003	.011	.025	<.027	<.006	.015
S2	San Joaquin River at Patterson Bridge near Patterson	06/20/2001	0910	<.003	<.005	<.004	<.027	<.006	.104
E7	Westport Drain near Modesto	06/21/2001	0940	<.003	<.005	<.004	<.027	<.006	E.004
W4	Olive Avenue Drain near Patterson	06/21/2001	0950	<.003	<.005	.007	<.027	<.006	.097
W5	Del Puerto Creek at Vineyard Road near Patterson	06/20/2001	1440	<.003	<.005	<.004	E.017	<.006	.705
S3	San Joaquin River below WSID pump above Tuolumne River near Westley	06/21/2001	1120	<.003	<.005	.005	<.027	<.006	.133
E9	Tuolumne River at Shiloh Road Bridge near Grayson	06/21/2001	1230	<.003	<.005	<.004	<.027	<.006	.018
W6	Hospital Creek at River Road near Patterson	06/21/2001	1400	<.003	<.005	<.004	<.027	<.006	.088
W7	Ingram Creek at River Road near Patterson	06/21/2001	1310	E.001	<.005	E.002	<.027	<.006	1.080
E11	Stanislaus River at Caswell State Park near Ripon	06/21/2001	1300	<.003	<.005	<.004	<.027	<.006	E.004
S4	San Joaquin River near Vernalis	06/21/2001	1220	<.003	<.005	<.004	<.027	<.006	.048

**28 Occurrence, Distribution, Instantaneous Loads, and Yields of Dissolved Pesticides, San Joaquin River Basin, Calif.**
**Table 10.** Streamflow and dissolved pesticide concentrations for sites sampled during June 2001 in the San Joaquin River Basin—Continued.

 [E, estimated concentration; ft<sup>3</sup>/s, cubic feet per second; M, deleted due to interferences; µg/L, microgram per liter; <, less than; ND, no data]

Site code	Station name	Date	Time	Metrobuzin concentration (µg/L)	Molinate concentration (µg/L)	Napro-pamide concentration (µg/L)	Prometron concentration (µg/L)	Pronamide concentration (µg/L)	Propachlor concentration (µg/L)
E1	Bear Creek at Bert Crane Road near Merced	06/20/2001	0830	<0.006	<0.002	<0.007	<0.015	<0.004	<0.010
S1	San Joaquin River near Stevinson	06/20/2001	1110	<.006	<.002	E.005	<.015	<.004	<.010
G1	Salt Slough at Highway 165 near Stevinson	06/20/2001	1040	<.006	.013	<.007	<.015	.005	<.010
G2	Los Banos Creek at Highway 140	06/20/2001	0910	<.006	<.005	<.007	E.002	<.004	<.010
G3	Mud Slough near Gustine	06/20/2001	0950	<.006	.170	<.007	E.002	<.004	<.010
E2	Livingston Canal at Livingston Treatment Plant near Livingston	06/20/2001	1010	<.006	<.002	<.007	<.015	<.004	<.010
E3	Highline Canal Spill near Hilmar	06/20/2001	1110	<.006	<.005	<.007	<.015	<.004	<.010
E5	Merced River at River Road Bridge near Newman	06/20/2001	1340	<.006	E.001	<.007	<.015	<.004	<.010
W1	Newman Wasteway at Highway 33 near Gustine	06/20/2001	1200	<.006	E.001	<.007	E.003	<.004	<.010
W2	Orestimba Creek at River Road near Crows Landing	06/20/2001	1150	<.006	.006	<.007	<.015	<.004	<.010
W3	Spanish Grant Combined Drain near Patterson	06/20/2001	1350	<.112	<.002	.090	<.015	<.004	<.010
E6	Harding Drain at Carpenter Road near Patterson	06/21/2001	1120	<.006	<.002	<.007	<.015	<.004	<.010
S2	San Joaquin River at Patterson Bridge near Patterson	06/20/2001	0910	<.006	.008	<.007	<.015	<.004	<.010
E7	Westport Drain near Modesto	06/21/2001	0940	<.006	<.002	.007	<.015	<.004	<.010
W4	Olive Avenue Drain near Patterson	06/21/2001	0950	<.006	.011	<.007	<.015	<.004	<.010
W5	Del Puerto Creek at Vineyard Road near Patterson	06/20/2001	1440	<.006	.016	.072	<.015	<.004	<.010
S3	San Joaquin River below WSID pump above Tuolumne River near Westley	06/21/2001	1120	<.006	.004	<.007	E.002	<.004	<.010
E9	Tuolumne River at Shiloh Road Bridge near Grayson	06/21/2001	1230	<.006	<.002	<.007	<.015	<.004	E.010
W6	Hospital Creek at River Road near Patterson	06/21/2001	1400	.009	.021	.868	<.015	<.004	<.010
W7	Ingram Creek at River Road near Patterson	06/21/2001	1310	.049	.023	.025	E.004	<.004	<.010
E11	Stanislaus River at Caswell State Park near Ripon	06/21/2001	1300	<.006	<.002	<.007	<.015	<.004	<.010
S4	San Joaquin River near Vernalis	06/21/2001	1220	<.006	.002	<.007	<.015	<.004	<.010

**Table 10.** Streamflow and dissolved pesticide concentrations for sites sampled during June 2001 in the San Joaquin River Basin—Continued.[E, estimated concentration; ft<sup>3</sup>/s, cubic feet per second; M, deleted due to interferences; µg/L, microgram per liter; <, less than; ND, no data]

Site code	Station name	Date	Time	Propargite concentration (µg/L)	Simazine concentration (µg/L)	Terbutiuron concentration (µg/L)	Thio-bencarb concentration (µg/L)	Tri-fluralin concentration (µg/L)
E1	Bear Creek at Bert Crane Road near Merced	06/20/2001	0830	0.055	<0.011	<0.016	<0.005	<0.009
S1	San Joaquin River near Stevinson	06/20/2001	1110	<.023	E.011	<.016	<.005	.016
G1	Salt Slough at Highway 165 near Stevinson	06/20/2001	1040	<.023	.013	<.016	<.005	.055
G2	Los Banos Creek at Highway 140	06/20/2001	0910	<.023	.013	E.007	<.005	<.009
G3	Mud Slough near Gustine	06/20/2001	0950	<.023	E.009	<.016	.110	<.009
E2	Livingston Canal at Livingston Treatment Plant near Livingston	06/20/2001	1010	<.023	<.011	<.016	<.005	<.009
E3	Highline Canal Spill near Hilmar	06/20/2001	1110	.045	E.004	<.016	E.002	<.009
E5	Merced River at River Road Bridge near Newman	06/20/2001	1340	.100	E.004	<.016	<.005	E.003
W1	Newman Wasteway at Highway 33 near Gustine	06/20/2001	1200	<.023	.049	<.016	<.005	E.007
W2	Orestimba Creek at River Road near Crows Landing	06/20/2001	1150	.036	.013	<.016	<.005	.123
W3	Spanish Grant Combined Drain near Patterson	06/20/2001	1350	<.500	.026	<.016	<.005	.220
E6	Harding Drain at Carpenter Road near Patterson	06/21/2001	1120	<.023	E.008	<.016	<.005	E.009
S2	San Joaquin River at Patterson Bridge near Patterson	06/20/2001	0910	<.066	.011	<.016	<.005	.011
E7	Westport Drain near Modesto	06/21/2001	0940	<.069	E.006	<.016	<.005	.011
W4	Olive Avenue Drain near Patterson	06/21/2001	0950	<.023	.014	<.016	E.003	.237
W5	Del Puerto Creek at Vineyard Road near Patterson	06/20/2001	1440	<.023	.022	<.016	<.005	.134
S3	San Joaquin River below WSID pump above Tuolumne River near Westley	06/21/2001	1120	<.023	E.009	<.016	<.005	.010
E9	Tuolumne River at Shiloh Road Bridge near Grayson	06/21/2001	1230	<.023	E.008	<.016	<.005	<.009
W6	Hospital Creek at River Road near Patterson	06/21/2001	1400	<.023	.013	<.016	<.005	1.120
W7	Ingram Creek at River Road near Patterson	06/21/2001	1310	.062	.013	<.016	<.005	.405
E11	Stanislaus River at Caswell State Park near Ripon	06/21/2001	1300	<.023	<.011	<.016	<.005	<.009
S4	San Joaquin River near Vernalis	06/21/2001	1220	<.023	E.007	<.016	<.005	E.006

**30 Occurrence, Distribution, Instantaneous Loads, and Yields of Dissolved Pesticides, San Joaquin River Basin, Calif.**

**Table 11.** Streamflow and dissolved pesticide concentrations for sites sampled during August 2001 in the San Joaquin River Basin.

[E, estimated concentration; ft<sup>3</sup>/s, cubic feet per second; µg/L, microgram per liter; <, less than; ND, no data]

Site code	Station name	Date	Time	Stream-flow (ft <sup>3</sup> /s)	Alachlor concentration (µg/L)	Atrazine concentration (µg/L)	Atrazine, deethyl concentration (µg/L)	Carbaryl concentration (µg/L)	Chlorpyrifox concentration (µg/L)
E1	Bear Creek at Bert Crane Road near Merced	08/01/2001	0850	—	<0.002	<0.007	<0.006	<0.041	<0.005
S1	San Joaquin River near Stevinson	08/02/2001	1310	1.0	<.002	.012	<.006	<.041	E.005
G1	Salt Slough at Highway 165 near Stevinson	08/01/2001	1240	177	<.002	.009	<.006	E.009	.009
G2	Los Banos Creek at Highway 140	08/01/2001	0940	9.2	<.002	.008	<.006	<.041	<.005
G3	Mud Slough near Gustine	08/01/2001	1030	68.2	<.002	.011	E.006	<.041	.008
E2	Livingston Canal at Livingston Treatment Plant near Livingston	08/01/2001	1000	0	<.002	<.007	<.006	<.041	.005
E3	Highline Canal Spill near Hilmar	08/01/2001	1020	.2	<.002	<.007	<.006	<.041	<.005
E5	Merced River at River Road Bridge near Newman	08/01/2001	0840	132	<.002	<.007	<.006	<.041	<.005
W1	Newman Wasteway at Highway 33 near Gustine	08/01/2001	1120	14	<.002	.008	<.006	E.008	.013
W2	Orestimba Creek at River Road near Crows Landing	08/01/2001	1110	9.6	<.002	.010	<.006	E.009	.009
W3	Spanish Grant Combined Drain near Patterson	08/01/2001	1320	29.0	<.002	.008	<.006	E.064	.007
E6	Harding Drain at Carpenter Road near Patterson	08/02/2001	1020	139	<.002	E.003	<.006	<.041	.008
S2	San Joaquin River at Patterson Bridge near Patterson	08/02/2001	0900	400	<.002	E.005	<.006	E.008	.006
E7	Westport Drain near Modesto	08/02/2001	0930	29.4	<.002	E.002	<.006	E.006	.015
W4	Olive Avenue Drain near Patterson	08/02/2001	0920	17.3	<.002	E.006	<.006	E.010	.006
W5	Del Puerto Creek at Vineyard Road near Patterson	08/01/2001	1420	4.6	<.002	.007	E.005	E.005	.007
S3	San Joaquin River below WSID pump above Tuolumne River near Westley	08/02/2001	1200	468	<.002	E.004	<.006	E.008	.006
E9	Tuolumne River at Shiloh Road Bridge near Grayson	08/02/2001	1130	213	<.002	E.003	E.005	E.006	.012
W6	Hospital Creek at River Road near Patterson	08/02/2001	1500	.6	.037	E.003	<.006	<.041	<.005
W7	Ingram Creek at River Road near Patterson	08/02/2001	1410	21.2	<.002	E.003	<.006	E.012	<.005
E11	Stanislaus River at Caswell State Park near Ripon	08/02/2001	1010	367	<.002	<.007	<.006	<.041	.005
S4	San Joaquin River near Vernalis	08/02/2001	1040	1,220	<.002	E.003	E.005	<.041	.008

**Table 11.** Streamflow and dissolved pesticide concentrations for sites sampled during August 2001 in the San Joaquin River Basin—Continued.[E, estimated concentration; ft<sup>3</sup>/s, cubic feet per second; µg/L, microgram per liter; <, less than; ND, no data]

Site code	Station name	Date	Time	Cyanazine concentration (µg/L)	DCPA concentration (µg/L)	DDE, <i>p,p'</i> -concentration (µg/L)	Diazinon concentration (µg/L)	Dieldrin concentration (µg/L)	EPTC concentration (µg/L)
E1	Bear Creek at Bert Crane Road near Merced	08/01/2001	0850	<0.018	<0.003	<0.003	<0.005	<0.005	<0.002
S1	San Joaquin River near Stevinson	08/02/2001	1310	4.340	<.003	<.004	<.005	<.005	.029
G1	Salt Slough at Highway 165 near Stevinson	08/01/2001	1240	.063	<.003	<.003	.042	<.005	.014
G2	Los Banos Creek at Highway 140	08/01/2001	0940	E.011	<.003	<.003	.007	<.005	.257
G3	Mud Slough near Gustine	08/01/2001	1030	E.010	<.003	<.003	.007	<.005	.050
E2	Livingston Canal at Livingston Treatment Plant near Livingston	08/01/2001	1000	<.018	<.003	<.003	<.005	<.005	<.002
E3	Highline Canal Spill near Hilmar	08/01/2001	1020	<.018	<.003	<.003	E.004	<.005	<.002
E5	Merced River at River Road Bridge near Newman	08/01/2001	0840	<.018	<.003	<.003	<.005	<.005	<.002
W1	Newman Wasteway at Highway 33 near Gustine	08/01/2001	1120	<.018	<.003	E.005	.036	.007	.072
W2	Orestimba Creek at River Road near Crows Landing	08/01/2001	1110	<.018	.005	E.016	.022	.010	.078
W3	Spanish Grant Combined Drain near Patterson	08/01/2001	1320	<.018	<.003	E.009	.034	.009	.047
E6	Harding Drain at Carpenter Road near Patterson	08/02/2001	1020	<.018	<.003	<.003	.013	<.005	<.002
S2	San Joaquin River at Patterson Bridge near Patterson	08/02/2001	0900	.056	<.003	<.003	.030	<.005	.014
E7	Westport Drain near Modesto	08/02/2001	0930	<.018	<.003	<.003	E.004	<.005	.002
W4	Olive Avenue Drain near Patterson	08/02/2001	0920	.069	<.003	<.003	.038	<.005	.022
W5	Del Puerto Creek at Vineyard Road near Patterson	08/01/2001	1420	.024	<.003	.004	.010	<.005	.049
S3	San Joaquin River below WSID pump above Tuolumne River near Westley	08/02/2001	1200	.051	<.003	<.003	.020	<.005	.014
E9	Tuolumne River at Shiloh Road Bridge near Grayson	08/02/2001	1130	<.018	<.003	<.003	.009	<.005	.005
W6	Hospital Creek at River Road near Patterson	08/02/2001	1500	.035	<.003	.004	.022	.013	.010
W7	Ingram Creek at River Road near Patterson	08/02/2001	1410	.019	<.003	.011	.011	<.005	.008
E11	Stanislaus River at Caswell State Park near Ripon	08/02/2001	1010	<.018	<.003	<.003	<.005	<.005	<.002
S4	San Joaquin River near Vernalis	08/02/2001	1040	.020	<.003	<.003	.012	<.005	.007

**32 Occurrence, Distribution, Instantaneous Loads, and Yields of Dissolved Pesticides, San Joaquin River Basin, Calif.**

**Table 11.** Streamflow and dissolved pesticide concentrations for sites sampled during August 2001 in the San Joaquin River Basin—Continued.

[E, estimated concentration; ft<sup>3</sup>/s, cubic feet per second; µg/L, microgram per liter; <, less than; ND, no data]

Site code	Station name	Date	Time	Ethal-fluralin concentration (µg/L)	Etho-prophos concentration (µg/L)	HCH, alpha-concentration (µg/L)	HCH, gamma-concentration (µg/L)	Mala-thion concentration (µg/L)	Metolachlor concentration (µg/L)
E1	Bear Creek at Bert Crane Road near Merced	08/01/2001	0850	<0.009	<0.005	<0.005	<0.004	<0.027	0.031
S1	San Joaquin River near Stevinson	08/02/2001	1310	<.009	<.005	<.005	<.004	<.027	1.380
G1	Salt Slough at Highway 165 near Stevinson	08/01/2001	1240	<.009	<.005	<.005	<.004	E.016	.146
G2	Los Banos Creek at Highway 140	08/01/2001	0940	<.009	<.005	<.005	<.004	<.027	.039
G3	Mud Slough near Gustine	08/01/2001	1030	<.009	<.005	<.005	<.004	<.027	.173
E2	Livingston Canal at Livingston Treatment Plant near Livingston	08/01/2001	1000	<.009	<.005	<.005	<.004	<.027	<.013
E3	Highline Canal Spill near Hilmar	08/01/2001	1020	<.009	<.005	<.005	<.004	<.027	<.013
E5	Merced River at River Road Bridge near Newman	08/01/2001	0840	<.009	<.005	<.005	<.004	<.027	E.010
W1	Newman Wasteway at Highway 33 near Gustine	08/01/2001	1120	<.009	<.005	<.005	<.004	E.010	.198
W2	Orestimba Creek at River Road near Crows Landing	08/01/2001	1110	<.009	.007	<.005	<.004	E.009	.235
W3	Spanish Grant Combined Drain near Patterson	08/01/2001	1320	<.009	<.005	<.005	<.004	E.006	.844
E6	Harding Drain at Carpenter Road near Patterson	08/02/2001	1020	<.009	<.005	.019	.029	<.027	E.004
S2	San Joaquin River at Patterson Bridge near Patterson	08/02/2001	0900	<.009	<.005	<.005	.006	E.004	.145
E7	Westport Drain near Modesto	08/02/2001	0930	<.009	<.005	<.005	<.004	E.005	.031
W4	Olive Avenue Drain near Patterson	08/02/2001	0920	<.009	<.005	<.005	E.004	<.027	.204
W5	Del Puerto Creek at Vineyard Road near Patterson	08/01/2001	1420	<.009	<.005	<.005	<.004	E.010	.210
S3	San Joaquin River below WSID pump above Tuolumne River near Westley	0802/2001	1200	<.009	<.005	<.005	E.003	<.027	.108
E9	Tuolumne River at Shiloh Road Bridge near Grayson	08/02/2001	1130	<.009	<.005	<.005	<.004	E.005	E.009
W6	Hospital Creek at River Road near Patterson	08/02/2001	1500	<.009	<.005	<.005	<.004	E.004	.217
W7	Ingram Creek at River Road near Patterson	08/02/2001	1410	.063	<.005	<.005	<.004	E.021	.746
E11	Stanislaus River at Caswell State Park near Ripon	0802/2001	1010	<.009	<.005	<.005	<.004	E.012	E.009
S4	San Joaquin River near Vernalis	08/02/2001	1040	<.009	<.005	<.005	<.004	E.020	.052



**Table 11.** Streamflow and dissolved pesticide concentrations for sites sampled during August 2001 in the San Joaquin River Basin—Continued.[E, estimated concentration; ft<sup>3</sup>/s, cubic feet per second; µg/L, microgram per liter; <, less than; ND, no data]

Site code	Station name	Date	Time	Metribuzin concentration (µg/L)	Molinate concentration (µg/L)	Napropamide concentration (µg/L)	Pendimethalin concentration (µg/L)	Propachlor concentration (µg/L)	Propargite concentration (µg/L)
E1	Bear Creek at Bert Crane Road near Merced	08/01/2001	0850	<0.006	<0.002	<0.007	<0.010	<0.010	0.026
S1	San Joaquin River near Stevinson	8/02/2001	1310	<.006	<.002	<.007	<.010	<.010	<.023
G1	Salt Slough at Highway 165 near Stevinson	8/01/2001	1240	<.006	<.004	<.007	<.010	<.010	E.021
G2	Los Banos Creek at Highway 140	8/01/2001	0940	<.006	<.002	<.007	<.010	<.010	<.023
G3	Mud Slough near Gustine	8/01/2001	1030	<.006	.024	<.007	<.010	<.010	<.023
E2	Livingston Canal at Livingston Treatment Plant near Livingston	8/01/2001	1000	<.006	<.002	<.007	<.010	<.010	<.023
E3	Highline Canal Spill near Hilmar	8/01/2001	1020	<.006	<.002	<.007	<.010	<.010	<.023
E5	Merced River at River Road Bridge near Newman	8/01/2001	0840	<.006	<.002	<.007	<.010	<.010	.025
W1	Newman Wasteway at Highway 33 near Gustine	8/01/2001	1120	<.006	.007	<.007	<.010	<.010	.051
W2	Orestimba Creek at River Road near Crows Landing	8/01/2001	1110	<.006	.006	E.006	.118	<.010	.538
W3	Spanish Grant Combined Drain near Patterson	8/01/2001	1320	.016	<.006	.020	.087	<.010	.234
E6	Harding Drain at Carpenter Road near Patterson	8/02/2001	1020	<.006	<.002	<.007	<.010	<.010	2.400
S2	San Joaquin River at Patterson Bridge near Patterson	8/02/2001	0900	<.006	<.002	<.007	.014	<.010	.054
E7	Westport Drain near Modesto	8/02/2001	0930	<.006	<.002	<.007	<.010	<.010	.398
W4	Olive Avenue Drain near Patterson	08/02/2001	0920	<.006	<.002	<.007	<.010	<.010	.040
W5	Del Puerto Creek at Vineyard Road near Patterson	08/01/2001	1420	<.010	<.005	<.007	<.010	<.010	.073
S3	San Joaquin River below WSID pump above Tuolumne River near Westley	08/02/2001	1200	<.006	<.002	<.007	<.010	<.010	<.023
E9	Tuolumne River at Shiloh Road Bridge near Grayson	08/02/2001	1130	<.006	<.002	<.007	<.010	E.010	.470
W6	Hospital Creek at River Road near Patterson	08/02/2001	1500	<.006	<.002	<.007	<.010	<.010	.173
W7	Ingram Creek at River Road near Patterson	08/02/2001	1410	<.006	<.002	<.007	<.010	<.010	.353
E11	Stanislaus River at Caswell State Park near Ripon	08/02/2001	1010	<.006	<.002	<.007	<.010	<.010	E.020
S4	San Joaquin River near Vernalis	08/02/2001	1040	<.006	<.002	<.007	<.010	<.010	<.023

**34 Occurrence, Distribution, Instantaneous Loads, and Yields of Dissolved Pesticides, San Joaquin River Basin, Calif.**
**Table 11.** Streamflow and dissolved pesticide concentrations for sites sampled during August 2001 in the San Joaquin River Basin—Continued.

[E, estimated concentration; ft<sup>3</sup>/s, cubic feet per second; µg/L, microgram per liter; <, less than; ND, no data]

Site code	Station name	Date	Time	Simazine concentration (µg/L)	Terbuthiuron concentration (µg/L)	Thiobencarb concentration (µg/L)	Trifluralin concentration (µg/L)
E1	Bear Creek at Bert Crane Road near Merced	08/01/2001	0850	<0.011	<0.016	<0.005	<0.009
S1	San Joaquin River near Stevinson	08/02/2001	1310	.015	<.016	<.005	<.009
G1	Salt Slough at Highway 165 near Stevinson	08/01/2001	1240	E.008	<.016	<.005	.026
G2	Los Banos Creek at Highway 140	08/01/2001	0940	.011	E.007	<.005	E.007
G3	Mud Slough near Gustine	08/01/2001	1030	E.010	<.016	.014	<.009
E2	Livingston Canal at Livingston Treatment Plant near Livingston	08/01/2001	1000	<.011	<.016	<.005	<.009
E3	Highline Canal Spill near Hilmar	08/01/2001	1020	<.011	<.016	<.005	<.009
E5	Merced River at River Road Bridge near Newman	08/01/2001	0840	<.011	<.016	<.005	<.009
W1	Newman Wasteway at Highway 33 near Gustine	08/01/2001	1120	.020	<.016	<.005	.163
W2	Orestimba Creek at River Road near Crows Landing	08/01/2001	1110	.015	<.016	<.005	.031
W3	Spanish Grant Combined Drain near Patterson	08/01/2001	1320	.016	<.016	<.005	.180
E6	Harding Drain at Carpenter Road near Patterson	08/02/2001	1020	<.011	<.016	<.005	<.009
S2	San Joaquin River at Patterson Bridge near Patterson	08/02/2001	0900	E.007	<.016	<.005	.014
E7	Westport Drain near Modesto	08/02/2001	0930	E.009	<.016	<.005	<.009
W4	Olive Avenue Drain near Patterson	08/02/2001	0920	E.010	<.016	<.005	.067
W5	Del Puerto Creek at Vineyard Road near Patterson	08/01/2001	1420	E.011	<.016	<.005	.070
S3	San Joaquin River below WSID pump above Tuolumne River near Westley	0802/2001	1200	E.009	<.016	<.005	.013
E9	Tuolumne River at Shiloh Road Bridge near Grayson	08/02/2001	1130	.014	<.016	<.005	<.009
W6	Hospital Creek at River Road near Patterson	08/02/2001	1500	E.007	<.016	<.005	.051
W7	Ingram Creek at River Road near Patterson	08/02/2001	1410	E.006	<.016	<.005	.087
E11	Stanislaus River at Caswell State Park near Ripon	0802/2001	1010	<.011	<.016	<.005	<.009
S4	San Joaquin River near Vernalis	08/02/2001	1040	E.009	<.016	<.005	E.008

The relation between the number of basins where a pesticide was applied and the number of basins where the dissolved pesticide was detected in water was variable. A number of pesticides were detected in water that had not been applied in the San Joaquin River Basin during the 28 days before sampling (*table 7*). Atrazine and deethylatrazine were two of the most commonly detected pesticides in water, but there were no recorded applications of atrazine within 28 days of any of the sampling periods. Dacthal, dieldrin, *p,p'*-DDE, and tebuthiuron were detected during all sampling periods despite no application, except dacthal, which was not detected in June 2001. In June and August 2001, alpha-HCH (alpha-BHC), ethoprophos, and propachlor were detected despite no application. In June 2001, prometon was detected. In August 2001, alachlor, ethalfluralin, gamma-HCH, and thiobencarb were detected although there was no application in the 28-day presample period; however, these pesticides were applied preceding the June 2001 sampling and were also detected in the June samples. Domagalski and Munday (2003) also noted detections of pesticides with no agricultural applications during regular periodic sampling at 12 sites in the San Joaquin River Basin during April to August 2001. Domagalski and Munday (2003) attributed these detections to winter-time applications, nonagricultural use, or interbasin transfers of irrigation water that included irrigation return flows containing dissolved pesticides.

The chemical and physical properties of the pesticides (*table 12*) also are important.  $K_{oc}$  is the organic carbon normalized adsorption coefficient, and pesticides having high  $\log K_{oc}$  values will sorb to the soil, making it less likely that they will be immediately transported to the surface water. Pesticides with a short hydrolysis half-life will degrade quickly if they do reach the water. Runoff potential is a categorical aggregate of the influence of water solubility, soil half-life, and  $K_{oc}$  on the likelihood of pesticide transport to surface water (Goss, 1992). Most of the pesticides detected, even though not applied in the previous 28 days, have half-lives of greater than 28 days with medium to large runoff potentials (*table 12*). Several also have high  $\log K_{oc}$  values ( $>3$ ), including dacthal, *p,p'*-DDE, dieldrin, ethalfluralin, and both forms of HCH (*table 12*). These characteristics make it likely that these pesticides will persist in the environment well after application and eventually reach surface waters at a later time.

Several pesticides that were applied in the 28 days previous to sampling were not detected in water during at least one sampling period (*table 7*). In 17 of 28 cases the applications were less than 1,000 lb of active ingredient for the entire

San Joaquin River Basin (alachlor, butylate, carbofuran, disulfoton, lindane, linuron, malathion, methyl parathion, parathion, pebulate, phorate, pronamide, and propanil). In the remaining cases, the applications were greater than 1,000 lb of active ingredient (azinphos-methyl, butylate, methyl parathion, pendimethalin, *cis*-permethrin, phorate, and propanil). The large applications of azinphos-methyl, permethrin, and propanil are particularly notable (*table 7*).

Although it is expected that applications and detections do not correspond exactly, the lack of detections of pesticides applied in large amounts is somewhat surprising. The chemical and physical properties of azinphos-methyl and permethrin can explain why these pesticides were not detected in surface water despite their high application. Azinphos-methyl has a high value for  $\log K_{oc}$  (3.00, *table 12*) relative to the other pesticides, and a short hydrolysis half-life (23 hours, *table 12*). In the case of azinphos-methyl, the short hydrolysis half-life is probably the more important factor. Permethrin has a small runoff potential, and thus is unlikely to be transported offsite. The lack of detections of propanil can be better explained by the location of its application rather than its chemical and physical properties. Propanil was used only in east-side subbasins. As mentioned earlier, the physiography of the east side, as well as the irrigation methods used there, likely lead to less transport of pesticides to surface water than on the west side.

The number of dissolved pesticides detected at any concentration varied considerably among basins (total detections in *table 13*). The larger difference between quantifiable and total detections in 2001 compared with 1994 was due to the use of the laboratory reporting level (LRL) in 2001 rather than the method detection limit (MDL) to define quantifiable detections. The LRL is more conservative, but reduces the likelihood of reporting false negatives. There was no clear pattern in frequencies of detections across years and seasons in a particular basin. Unlike pesticide applications, there was not a strong relation between the detection of dissolved pesticides in tributary basins (quantifiable detections) and basin size. In 1994 there was a significant negative correlation between basin size and quantifiable detections (Spearman's  $r = -0.53$ ,  $p < 0.05$ ). The same trend was evident in 2001, but the correlations were not statistically significant (Spearman's  $r = -0.36$  and  $-0.43$ ,  $p > 0.05$ ).

**Table 12.** Chemical and physical properties of detected pesticides and pesticides applied in the basin, but not detected in water samples.[All runoff potentials are from Goss (1992);  $K_{oc}$ , organic carbon normalized adsorption coefficient; mg/L, milligram per liter; >, greater than; ND, no data]

Analyte	Solubility (mg/L)	Log $K_{oc}$	Hydrolysis half-life at pH 7	Runoff potential
Alachlor	<sup>1</sup> 1.30E+2	<sup>2</sup> 2.23	<sup>3</sup> None at 30 days	Medium
Atrazine	<sup>1</sup> 3.00E+1	<sup>2</sup> 2.00	<sup>4</sup> 1,771 years	Large
Azinphos-methyl	<sup>1</sup> 3.00E+1	<sup>2</sup> 3.00	<sup>3</sup> 23 hours	Medium
Butylate	<sup>1</sup> 4.00E+1	<sup>2</sup> 2.60	<sup>3</sup> Stable	ND
Carbaryl	<sup>1</sup> 3.20E+1	<sup>2</sup> 2.48	<sup>4</sup> 15 days	Medium
Carbofuran	<sup>1</sup> 6.50E+2	<sup>3</sup> 1.46	<sup>4</sup> 8.2 weeks	Large
Chlorpyrifos	<sup>1</sup> 3.00E-1	<sup>2</sup> 3.78	<sup>4</sup> 35.3 days	Small
Cyanazine	<sup>2</sup> 1.70E+2	<sup>2</sup> 2.28	<sup>3</sup> Stable	Medium
Dacthal (DCPA)	<sup>2</sup> 5.00E-1	<sup>2</sup> 3.70	ND	Medium
DDE, <i>p,p'</i> -	<sup>1</sup> 4.00E-2	<sup>4</sup> 5.29	<sup>2</sup> Stable	ND
Diazinon	<sup>1</sup> 3.80E+1	<sup>5</sup> 1.60–2.63	<sup>4</sup> 184 days	Large
Dieldrin	<sup>1</sup> 1.70E-1	<sup>4</sup> 4.08–4.55	<sup>4</sup> 10.5 years	ND
Disulfoton	<sup>1</sup> 2.50E+1	<sup>2</sup> 2.78	<sup>4</sup> 1.2–103 days	Large
EPTC	<sup>1</sup> 3.70E+2	<sup>4</sup> 2.38	<sup>3</sup> Stable	Medium
Ethalfuralin	<sup>2</sup> 3.00E-1	<sup>2</sup> 3.60	<sup>3</sup> Stable after 31 days	Medium
Ethoprophos	<sup>2</sup> 7.50E+2	<sup>2</sup> 1.85	<sup>3</sup> Stable	Medium
Fonofos	<sup>2</sup> 1.69E+1	<sup>2</sup> 2.94	<sup>4</sup> 74–127 days	Large
HCH, alpha- (alpha-BHC)	<sup>1</sup> 1.00E0	<sup>4</sup> 3.28	<sup>6</sup> 207 days	ND
HCH, gamma- (Lindane)	<sup>1</sup> 8.00E0	<sup>2</sup> 3.04	<sup>6</sup> 207 days	ND
Linuron	<sup>1</sup> 6.50E+1	<sup>2</sup> 2.60	ND	Large
Malathion	<sup>1</sup> 1.45E+2	<sup>2</sup> 3.26	<sup>4</sup> 9 days (pH 6)	Small
Methyl parathion	<sup>1</sup> 2.50E+1	<sup>2</sup> 3.71	<sup>6</sup> 72 days	Medium
Metolachlor	<sup>2</sup> 5.30E+2	<sup>2</sup> 2.30	<sup>4</sup> >200 days	Large
Metribuzin	<sup>2</sup> 1.22E+3	<sup>2</sup> 1.78	ND	Large
Molinate	<sup>2</sup> 9.70E+2	<sup>2</sup> 2.28	ND	Medium
Napropamide	<sup>2</sup> 7.40E+1	<sup>4</sup> 2.83	ND	Large
Parathion	<sup>1</sup> 1.50E+1	<sup>2</sup> 3.70	<sup>4</sup> 3.5 weeks (pH 6.0)	ND
Pebulate	<sup>1</sup> 6.00E+1	<sup>4</sup> 2.80	ND	Medium
Pendimethalin	<sup>2</sup> 2.75E-1	<sup>2</sup> 3.70	ND	Medium
Permethrin, <i>cis</i> -	<sup>2</sup> 6.00E-3	<sup>2</sup> 5.00	ND	Small
Phorate	<sup>1</sup> 4.00E+1	<sup>2</sup> 3.00	<sup>4</sup> 96 hours	Large
Prometon	<sup>1</sup> 7.50E+2	<sup>2</sup> 2.18	ND	Large
Pronamide	<sup>2</sup> 1.50E+1	<sup>2</sup> 2.90	ND	Large
Propachlor	<sup>1</sup> 6.00E+2	<sup>2</sup> 1.90	ND	Medium
Propanil	<sup>1</sup> 3.00E+2	<sup>2</sup> 2.17	ND	Medium
Propargite	<sup>2</sup> 5.00E-1	<sup>2</sup> 3.60	ND	Medium
Simazine	<sup>1</sup> 5.00E0	<sup>4</sup> 2.14	ND	Large
Tebuthiuron	<sup>2</sup> 2.50E+3	<sup>4</sup> 2.79	<sup>4</sup> >64 days	Large
Thiobencarb	<sup>2</sup> 2.80E+1	<sup>2</sup> 2.95	ND	Medium
Trifluralin	<sup>1</sup> 5.00E-1	<sup>4</sup> 2.94–4.49	ND	Medium

<sup>1</sup>Suntio and others (1988)<sup>2</sup>Wauchope and others (1992)<sup>3</sup>U.S. Environmental Protection Agency (1997)<sup>4</sup>Montgomery (1993)<sup>5</sup>Howard (1991)<sup>6</sup>Howard and others (1991)

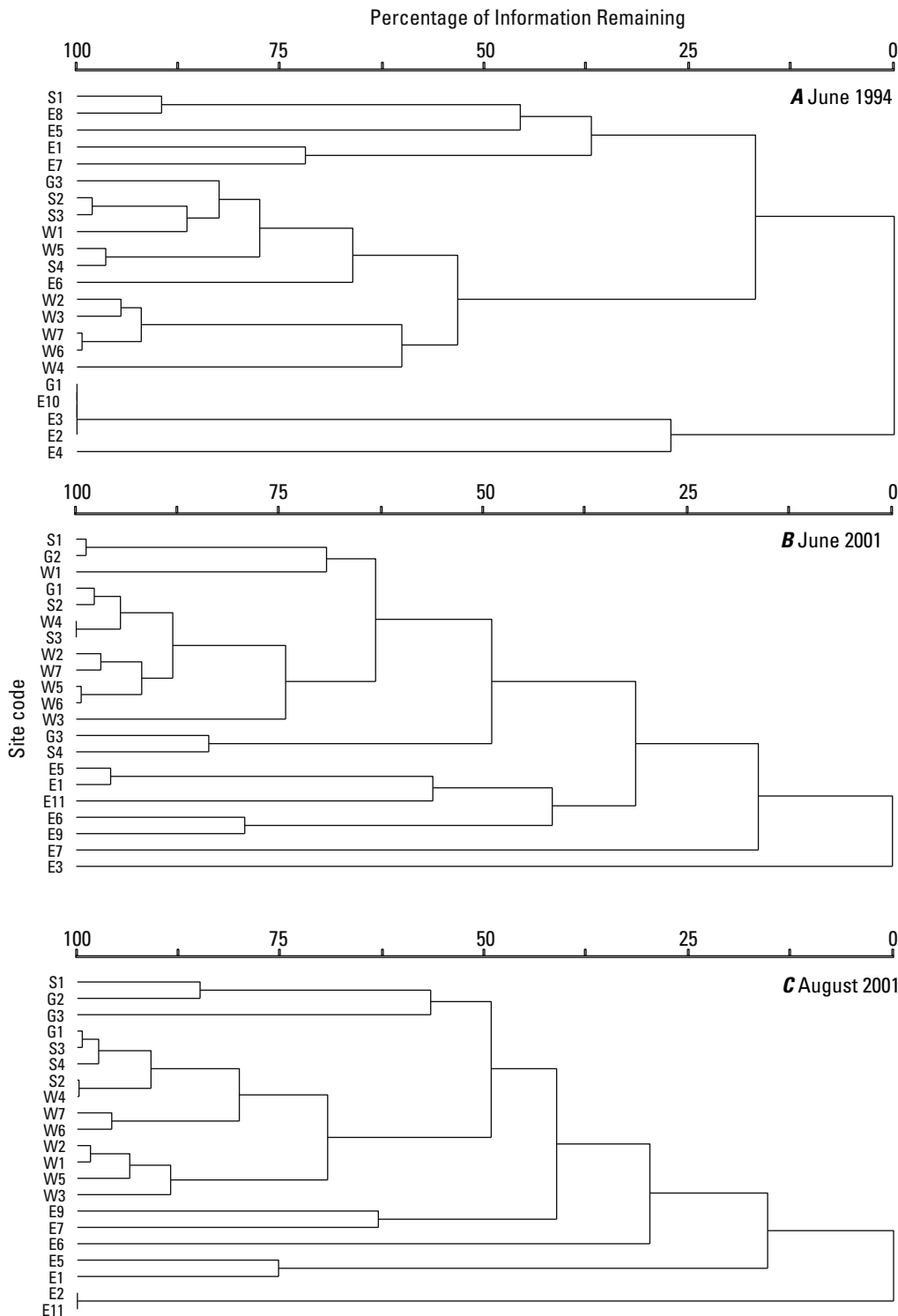
**Table 13.** Number of pesticide detections at each site.

[Quantifiable detections indicate that the pesticide concentration exceeded reporting limits used in that year. Total detections includes pesticides reported as estimated concentrations below the reporting limit. WSID, Westside Irrigation District; —, no data]

Site code	Station name	June 1994		June 2001		August 2001	
		Quantifiable detections	Total detections	Quantifiable detections	Total detections	Quantifiable detections	Total detections
E1	Bear Creek at Bert Crane Road near Merced	4	8	3	5	2	2
S1	San Joaquin River near Stevinson	6	6	5	8	6	6
G1	Salt Slough at Highway 165 near Stevinson	1	2	9	11	7	11
G2	Los Banos Creek at Highway 140	—	—	4	8	4	8
G3	Mud Slough near Gustine	10	11	5	9	7	10
E2	Livingston Canal at Livingston Treatment Plant near Livingston	0	1	0	0	1	1
E3	Highline Canal Spill near Hilmar	1	1	1	8	0	1
E4	Merced River below Merced Falls Dam near Snelling	1	4	—	—	—	—
E5	Merced River at River Road Bridge near Newman	3	3	4	8	1	2
W1	Newman Wasteway at Highway 33 near Gustine	9	11	4	11	10	13
W2	Orestimba Creek at River Road near Crows Landing	15	16	10	14	14	17
W3	Spanish Grant Combined Drain near Patterson	14	18	14	15	14	15
E6	Harding Drain at Carpenter Road near Patterson	8	9	7	11	5	7
S2	San Joaquin River at Patterson Bridge near Patterson	15	15	7	10	9	13
E7	Westport Drain near Modesto	5	5	2	8	4	9
W4	Olive Avenue Drain near Patterson	10	11	9	12	7	11
W5	Del Puerto Creek at Vineyard Road near Patterson	11	12	8	12	8	13
S3	San Joaquin River below WSID pump above Tuolumne River near Westley	11	15	8	11	6	10
E8	Tuolumne River at Modesto	8	9	—	—	—	—
E9	Tuolumne River at Shiloh Road Bridge near Grayson	—	—	5	8	5	11
W6	Hospital Creek at River Road near Patterson	16	17	11	13	8	12
W7	Ingram Creek at River Road near Patterson	17	17	13	18	8	12
E10	Stanislaus River at Ripon near Patterson	1	1	—	—	—	—
E11	Stanislaus River at Caswell State Park near Ripon	—	—	2	3	1	4
S4	San Joaquin River near Vernalis	7	8	4	8	5	10

The cluster analysis of pesticide detections (*fig. 7*) showed a very different pattern than the analysis of application (*fig. 3*). During all three sampling periods all the west-side basins clustered together at greater than 50 percent information remaining. Three or four of the San Joaquin mainstem sites also occurred in this cluster during each sampling period. The southern tributaries also tended to be associated with this cluster, but not consistently. The ranges in similarities within these clusters were similar among the sample periods. In 1994, Jaccards similarities ranged from 0.23 (W2 and G3) to 0.83 (W6 and W7). In June 2001, similarities between sites in the cluster varied from 0.29 (G2 and W3) to 0.89 (S3 and W4). In August 2001, Jaccards similarities ranged from 0.27 (W2 and S4, W3 and S4) to 0.89 (S2 and W4). The east-side tributaries showed no consistent clustering patterns. When all sites are considered, Jaccards similarities ranged from 0.06

to 1.00 in June 1994, from 0 to 0.89 in June 2001, and from 0 to 0.89 in August 2001. The values of 0 and 1.00 were due mainly to similarities between sites where only one or two pesticides were present. The first four PC axes of all three PCA of concentrations of dissolved pesticides in the tributaries had eigenvalues greater than one (*table 14*). Greater than 50 percent of the variance was explained by the first two PC axes for all three sampling periods. In all sampling periods, only one or two pesticides loaded highly on PC axes 3 and 4 (*table 11*). In 1994, molinate loaded highly on PC axis 3, and EPTC and metolachlor loaded highly on PC axis 4. In June 2001, molinate loaded highly on PC axis 3, and chlorpyrifos and simazine loaded highly on PC axis 4. In August 2001, chlorpyrifos and propargite loaded highly on PC axis 3, and cyanazine and metolachlor loaded highly on PC axis 4.



**Figure 7.** Cluster analysis of Jaccard's distances, which are based on the presence or absence of dissolved pesticides in water samples in (A) June 1994, (B) June 2001, and (C) August 2001. See *table 1* for site codes. Percentage information remaining varies from 100, starting with the individual sites, and decreases to 0 as the sites are clustered into a single group.

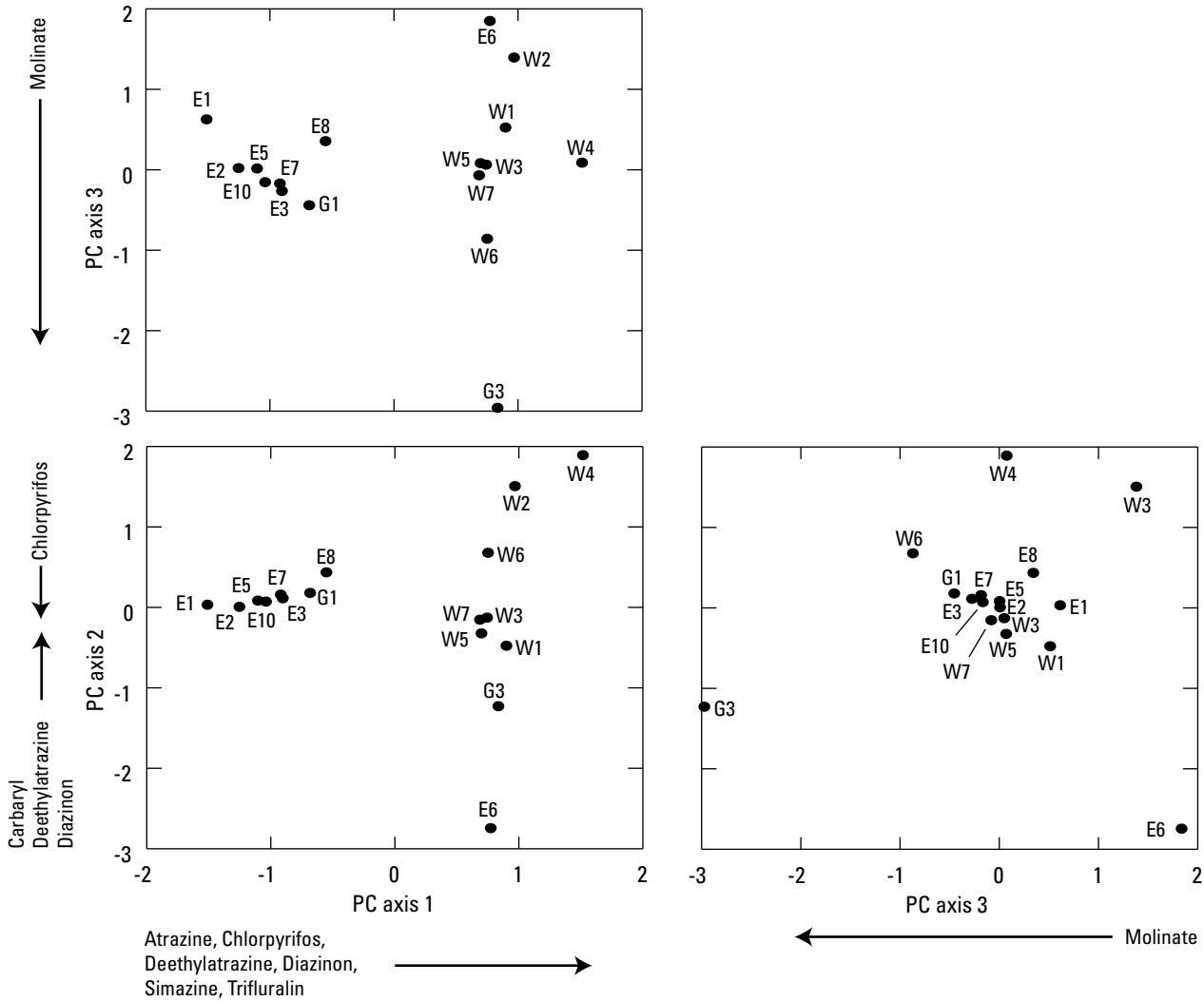
**Table 14.** Loadings of pesticides on axes from a principal component analysis (PCA) of pesticide concentrations in tributary basins for each sampling period.

[Only PCA axes with eigenvalues greater than one are shown; —, loading less than 0.50]

	PCA axis 1	PCA axis 2	PCA axis 3	PCA axis 4
<b>June 1994</b>				
Atrazine	0.83	—	—	—
Atrazine, deethyl	.61	-0.70	—	—
Carbaryl	—	-.69	—	—
Chlorpyrifos	.52	.63	—	—
Diazinon	.53	-.76	—	—
EPTC	—	—	—	0.72
Metolachlor	—	—	—	-.51
Molinate	—	—	-0.80	—
Simazine	.80	—	—	—
Trifluralin	.60	—	—	—
Percent variance explained:	3.50	25.30	12.70	11.20
<b>June 2001</b>				
Atrazine	.86	—	—	—
Chlorpyrifos	—	—	—	.80
Diazinon	—	-.87	—	—
EPTC	.97	—	—	—
Metolachlor	.76	.52	—	—
Molinate	—	—	-.89	—
Simazine	—	—	—	-.61
Trifluralin	.84	-.52	—	—
Percent variance explained:	4.60	19.00	16.00	13.30
<b>August 2001</b>				
Atrazine	.59	-.62	—	—
Chlorpyrifos	—	—	.80	—
Cyanazine	—	—	—	.53
Diazinon	.87	—	—	—
EPTC	—	-.84	—	—
Metolachlor	.75	—	—	-.57
Propargite	—	—	.69	—
Trifluralin	.84	—	—	—
Percent variance explained:	33.90	19.40	17.30	14.10

Plots of PC axis scores for the 1994 sampling period (*fig. 8*) revealed more distinct site groupings than expected on the basis of clustering results (*fig. 7A*). The large cluster of west-side tributaries, including an east-side (E6) and southern (G3) tributary, was still apparent, but the eastern tributaries also formed a tight group. The separation of the two groups was due mainly to high concentrations of atrazine, chlorpyrifos, deethylatrazine, diazinon, simazine, and trifluralin in the west-side tributaries and nondetections or low concentrations in the other tributaries. Harding Drain (E6)

differed from the west-side tributaries with respect to concentrations of carbaryl, chlorpyrifos, deethylatrazine, and diazinon (*fig. 8* and *table 9*). Harding Drain transports water from the city of Turlock's wastewater treatment plant, which might account for differences from other east-side tributaries. Mud Slough (G3) differed from all the other sites because of a large concentration of molinate (*fig. 8* and *table 9*). Molinate is used on rice, which is grown primarily in the Salt Slough and Mud Slough drainages (Domagalski and Munday, 2003).

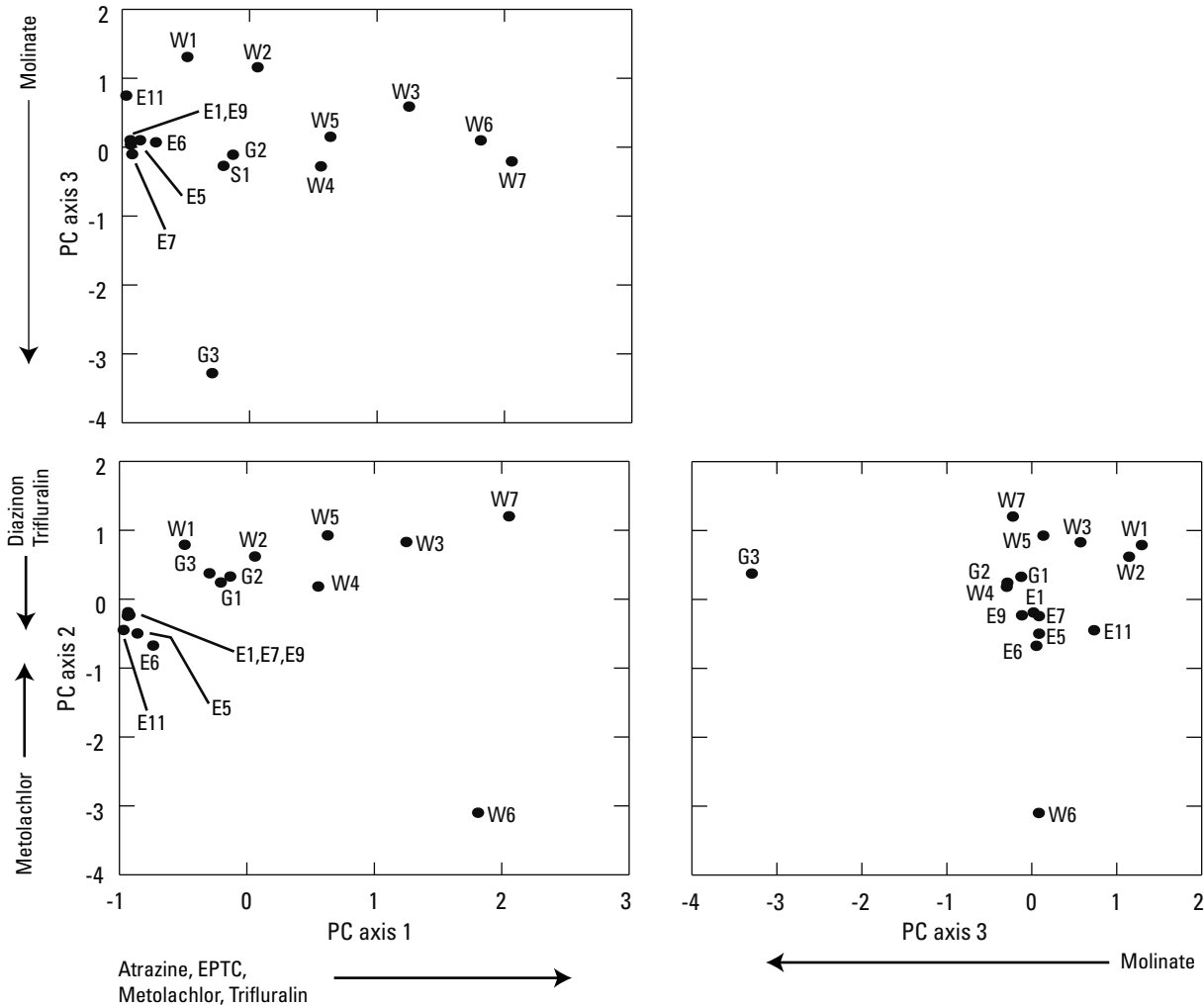


**Figure 8.** Site scores on the first three axes from a principal components analysis of dissolved pesticide concentrations in June 1994. See *table 1* for site codes. The arrows indicate the direction of increasing concentration of particular pesticides.

Similar to 1994, plots of PC axis scores for the June 2001 sampling period (*fig. 9*) revealed a different pattern than expected on the basis of clustering results (*figure 7B*). The east-side tributaries formed a very tight group on the basis of nondetections or low detections of the commonly detected pesticides (*fig. 9* and *table 10*). The west-side and southern tributaries exhibited considerable variability along PC axis 1 on the basis of concentrations of atrazine, EPTC, metolachlor, and trifluralin. PC axis 2 mainly separated Hospital Creek (W6) from the other basins (*fig. 9*) because of higher concentrations of diazinon and trifluralin and lower concentration of metolachlor, relative to the other west-side and southern tributaries (*table 10*). As in 1994, Mud Slough (G3) was different from the other basins because of a high concentration of molinate. Domagalski and Munday (2003) also documented high concentrations of molinate in the Mud Slough drainage as well as in the Salt Slough drainage.

The PC axis plots for August 2001 (*fig. 10*) were different in several ways from the plots for June 1994 and June 2001. The west-side tributaries had some variability along both PC axis 1 and PC axis 2. There was also variation among the east-site tributaries along PC axis 3. As for the other two sample periods, PC axis 1 mainly separated the east-side tributaries from the other tributaries (*fig. 10*) on the basis of nondetections or low concentrations of the commonly detected pesticides. The variation along PC axis 2 was due to differences in concentrations of atrazine and EPTC. PC axis 3 highlighted high concentrations of chlorpyrifos and propargite in three east-side tributaries—Harding Drain (E6), Westport Drain (E7), and the Tuolumne River (E9)—compared with the other east-side tributaries. The concentrations in these tributaries were similar or higher than the concentrations in the three west-side tributaries—Newman Wasteway (W1), Orestimba Creek (W2), and Spanish Grant Drain (W3)—with the highest concentrations of these pesticides (*table 11*).

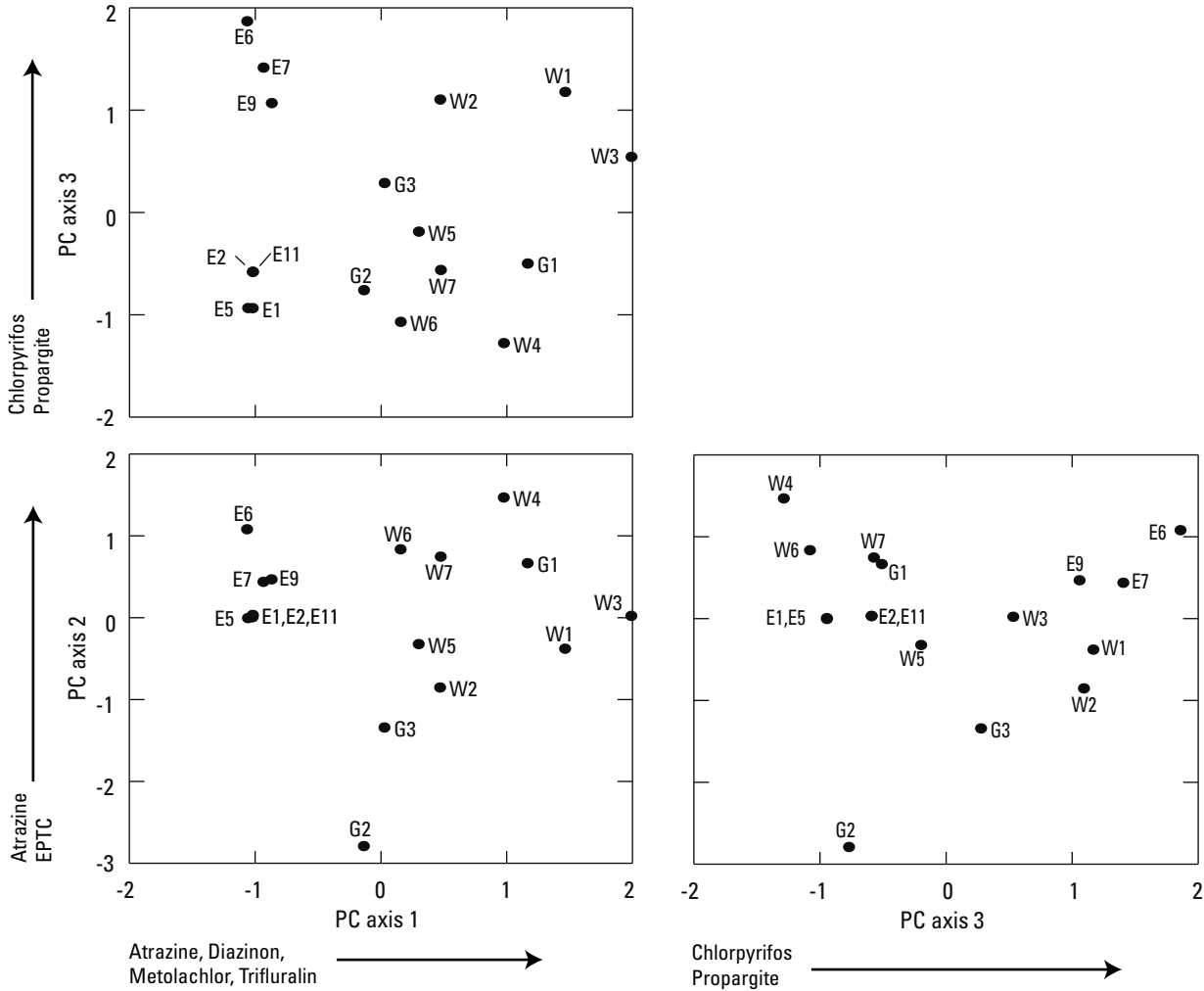




**Figure 9.** Site scores on the first three axes from a principal components analysis of dissolved pesticide concentrations in June 2001. See *table 1* for site codes. The arrows indicate the direction of increasing concentration of particular pesticides.

The differences between application and detection clusters suggest that different factors are driving the two processes. Application appears to be driven primarily by basin size, which is likely a surrogate for diversity of land use. All else being equal, detected pesticides should mirror the application pattern. This is clearly not occurring because the relation between basin size and pesticides applied is much weaker in the detection data in addition to the differences in clustering. The tight clustering of west-side basins (*fig. 7*) suggests that there is some similarity in land use or post-application practices that determine transport processes. The PCA results

also suggest differences in transport processes. The analyses of application intensity (*figs. 4–6*) show differences between east-side and west-side basins in terms of which pesticides are applied in the greatest amounts. In contrast, the PCAs of concentrations mainly reflect pesticides detected in high concentrations in west-side tributaries. These pesticides are either not detected in east-side tributaries or are only detected at low concentration. Similarly, Domagalski and Munday (2003) found that overall frequency of detection of pesticides was higher in west-side basins during their periodic sampling during April to August 2001.



**Figure 10.** Site scores on the first three axes from a principal components analysis of dissolved pesticide concentrations in August 2001. See *table 1* for site codes. The arrows indicate the direction of increasing concentration of particular pesticides.

The differences between east-side and west-side basins are likely related to many factors. Unfortunately, the data are inadequate to identify many of these factors quantitatively; however, some qualitative observations are possible. It seems likely that land use, irrigation practices, and stream size might all be important factors. As noted earlier, row crops are the dominant agricultural land use on the west side of the valley (48 percent). On the east side of the valley, row crops are less important (18 percent). Row crops are generally irrigated by furrow irrigation, but drip and flood irrigation are more common in orchards, pastures, and vineyards, which are important east-side land uses. Irrigation practices (drip or flood) and the coarser-grained soils on the east side of the valley, likely result in much of the applied irrigation water infiltrating into the groundwater. Therefore, there is probably relatively little agricultural return water to transport pesticides. Conversely, higher use of furrow irrigation and steeper land gradients combined with less permeable fine-grained soils on the west side of the valley likely result in greater quantities of agricultural return

water. The fine-grained, poorly drained soils of the west-side basins also appear to act as efficient reservoirs for long-lived chemicals such as dacthal, dieldrin, and DDT and its metabolites, including *p,p'*-DDE (Periera and others 1996; Brown 1997). The steeper gradients of the west-side streams result in greater sediment loads and greater transport of the soil-bound chemicals into surface waters. In addition, tile drains are more common in the west-side basins, particularly the Mud Slough Basin. Tile drains result in fairly short groundwater residence times and tile drainage might carry some of the more longer-lived, water soluble pesticides. Finally, any pesticide-laden agricultural return water that does eventually reach the larger east-side rivers will be diluted by reservoir releases, while most of the west-side basins contain primarily agricultural drainage water from April to August, although some operational spill occurs at times. Given these differences, it is not surprising that the west-side basins tend to have the highest concentrations.

The PCA of instantaneous pesticide loads (*table 15*) gave somewhat different results than the PCA of pesticide concentrations (*table 14*). The loadings of the pesticides were different and more of the variance was explained by PC axis 1 in the analysis of instantaneous loads (*tables 14 and 15*). In general, the same pesticides had high loadings on PC axis 1, but PC axis 1 included additional pesticides in the analysis of instantaneous loads. The differences between the instantaneous load and concentration analyses are most obvious in plots of site scores on the first two PC axes (*figs. 8–11*). In all cases, the clear separation of the east-side tributaries from the west-side and southern tributaries is lost when instantaneous loads are considered (*fig. 11*). The east-side tributaries tend to have lower instantaneous loads than the other sites, but not always.

A notable difference between the concentration (*fig. 8*) and instantaneous load results (*fig. 11*) in June 1994 is the change of position for the Tuolumne River (E8). This large east-side tributary had low pesticide concentrations, but a high discharge resulting in large instantaneous loads and the fifth highest score on PC axis 1 (*fig. 11*). The most interesting difference in June 2001 was that PC axis 2 summarized variation in instantaneous loads of chlorpyrifos and diazinon among east-side tributaries (*fig. 11*) rather than separating a single tributary, Hospital Creek (W6), from all the others (*fig. 9*) on the basis of pesticide concentrations. Another noticeable difference was the relative change in positions on PC axis 1 of Salt Slough (G1) and Hospital Creek (W6) in the analysis of instantaneous loads (*fig. 11*) compared with the analysis of concentrations (*fig. 9*). Similar differences occurred in August 2001 with Salt Slough having the highest score on PC axis 1 on the basis of loads (*fig. 11*) compared with a score similar to several west-side sites when only concentrations were considered (*fig. 10*). As in June 2001, in August 2001, PC axis 2 of the load analysis described differences among east-side tributaries (*fig. 11*), whereas PC axis 2 of the concentration analysis emphasized differences among west-side and southern tributaries (*fig. 10*).

A further contrast is provided by considering the analysis of instantaneous yields. Greater than 50 percent of the variance was explained by PC axis 1 for each of the three sampling periods (*table 16*). The pesticides loading highly on PC axis 1 were very similar to those found to load heavily on PC axis 1 of the instantaneous load analysis for each sampling period, but there were some minor differences (*tables 15 and 16*). In all cases, the separation of west-side tributaries from

the east-side tributaries noted in the analyses of concentrations (*figs. 8–10*) was reestablished (*fig. 12*). In all cases, the west-side tributaries had the highest instantaneous yields. There were a few minor exceptions with Newman Wasteway (W1) grouping with the other sites in June 2001 and Del Puerto Creek (W5) and Hospital Creek (W6) grouping with the other sites in August 2001. The major difference between the concentration and instantaneous yield analyses was that the southern tributaries grouped with the west-side tributaries in the analysis of concentrations and with the east-side tributaries in the analysis of instantaneous yields.

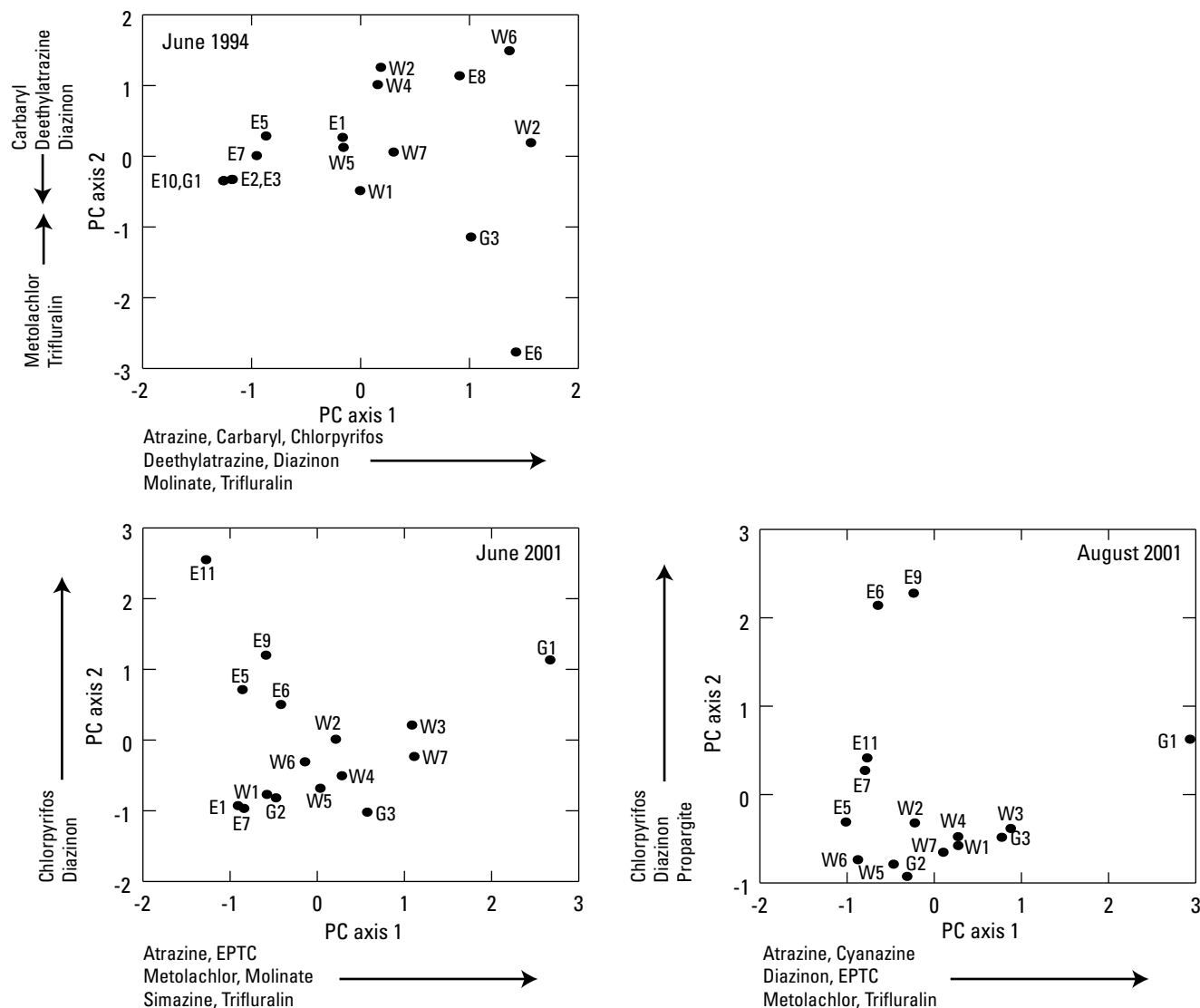
The contrasting patterns found when using concentration, instantaneous load, or instantaneous yield data are important to water quality management in several ways. First, when considering the biological effects of dissolved pesticides, concentration is the measure that is most important. Organisms experience concentrations, not instantaneous loads. Therefore, the high concentrations found in west-side basins suggest that these basins are the most stressful for aquatic life as has been found by other researchers (Foe and Connor, 1991; Foe, 1995). Conversely, when managing for a TMDL at some downstream location, a small instantaneous load represented by a toxic, but low discharge, water body, might be insignificant to the TMDL compared with the instantaneous load represented by a large volume tributary having lower concentrations of the regulated pesticide. However, the cumulative load from such small discharges cannot be ignored. This is especially true of the San Joaquin River Basin where agricultural drainage water can constitute a substantial part of the flow at the San Joaquin River near Vernalis (S4). Finally, in understanding the processes, it is important to consider instantaneous yields. By standardizing instantaneous loads by unit area, instantaneous yields give an indication of the importance of transport processes. In general, the PCA analysis did not show any strong geographic patterns in application intensity (*figs. 4–6*) that would affect instantaneous yields. The strong pattern in instantaneous yields suggests that pesticides are much more likely to enter surface waters on the west side of the valley compared with the east side of the valley. These results might be important in identifying areas where source control might be of the most benefit. Clearly, concentration, instantaneous loads, and instantaneous yields might each be important to consider, depending on the regulatory or management context.

#### 44 Occurrence, Distribution, Instantaneous Loads, and Yields of Dissolved Pesticides, San Joaquin River Basin, Calif.

**Table 15.** Loadings of pesticides on axes from a principal component analysis (PCA) of pesticide instantaneous loads in tributary basins for each sampling period.

[Only PCA axes with eigenvalues greater than one are shown. —, loading less than 0.50]

	PCA axis 1	PCA axis 2	PCA axis 3	PCA axis 4
<b>June 1994</b>				
Atrazine	0.87	—	—	—
Atrazine, deethyl	.64	-0.71	—	—
Carbaryl	.60	-.61	—	—
Chlorpyrifos	.55	—	—	-0.54
Diazinon	.73	-.52	—	—
EPTC	—	—	-0.57	—
Metolachlor	—	.53	—	—
Molinate	.58	—	—	.60
Simazine	—	—	.81	—
Trifluralin	.56	.50	—	—
Percent variance explained:	33.20	21.40	13.90	11.70
<b>June 2001</b>				
Atrazine	.92	—	—	—
Chlorpyrifos	—	.93	—	—
Diazinon	—	.93	—	—
EPTC	.89	—	—	—
Metolachlor	.89	—	—	—
Molinate	.59	—	-.78	—
Simazine	.85	—	—	—
Trifluralin	.81	—	—	—
Percent variance explained:	52.90	22.90	13.50	—
<b>August 2001</b>				
Atrazine	.90	—	—	—
Chlorpyrifos	—	.84	—	—
Cyanazine	.80	—	—	—
Diazinon	.77	.59	—	—
EPTC	.72	—	—	—
Metolachlor	.82	—	—	—
Propargite	—	.73	.50	—
Trifluralin	.75	—	.55	—
Percent variance explained:	49.10	21.10	12.60	—



**Figure 11.** Site scores on the first two axes from principal components analysis of instantaneous pesticide loads in June 1994, June 2001, and August 2001. See *table 1* for site codes. The arrows indicate the direction of increasing instantaneous loads of particular pesticides.

### Instantaneous Loads

Alachlor, EPTC, metolachlor, molinate, and trifluralin met the criteria for detailed analysis in 1994 (*table 17*). Samples in 1994 were collected in a Lagrangian manner; therefore, the same parcel of water was being sampled all the way downstream. However, water in the San Joaquin River Basin is used extensively for irrigation in June, and much of the water and pesticides from the upstream tributaries do not reach Vernalis because of diversions. Therefore, the loads of pesticides from the different tributaries were weighted in the following equation according to a loading factor (*table 17*) that took into account the diversions from the San Joaquin River downstream from each tributary:

$$\text{Percent of Vernalis load} = \left[ \frac{(\text{tributary load} \times \text{loading factor})}{\text{Vernalis load}} \right] \times 100$$

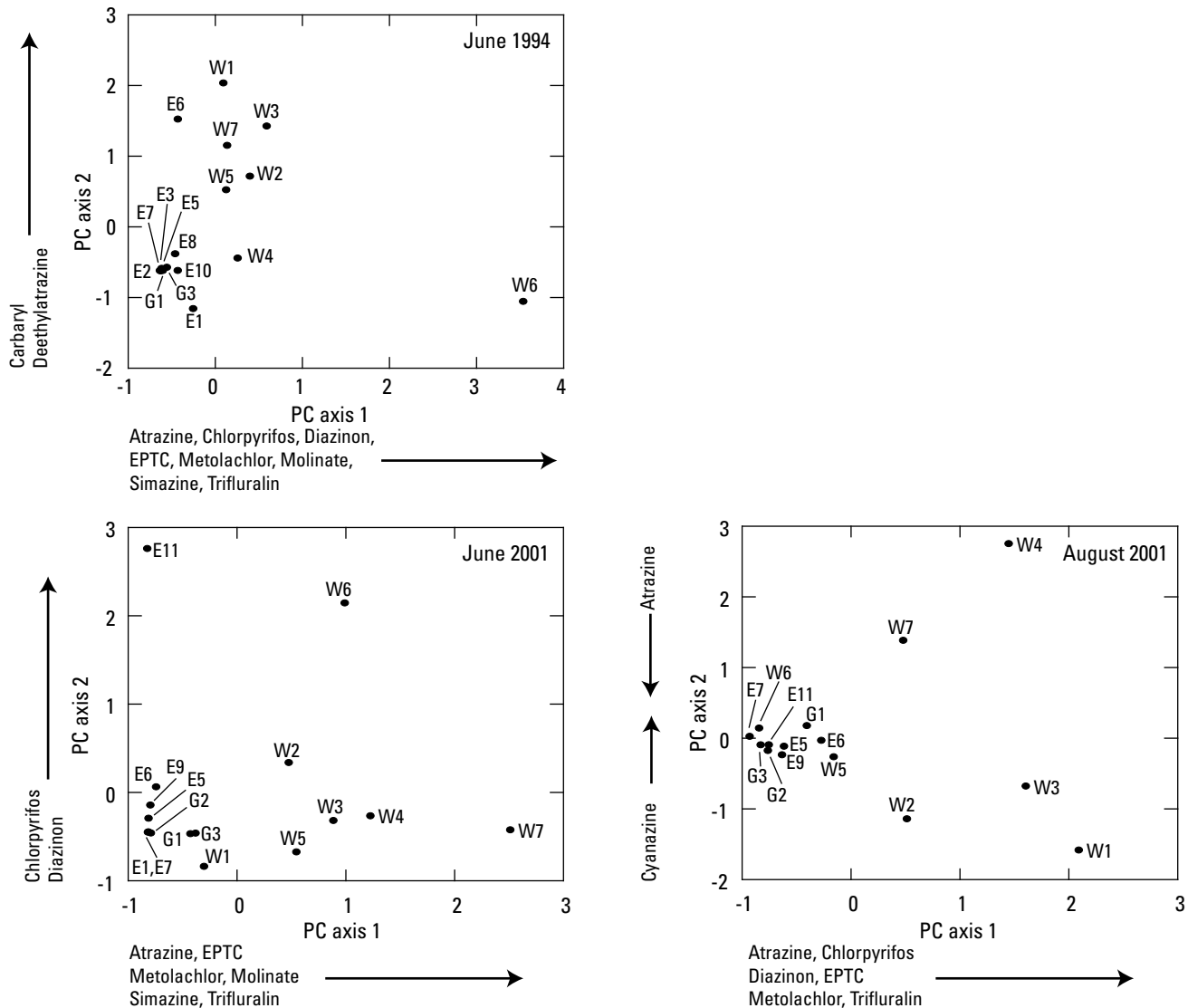
Sites upstream of the two largest diversions (Patterson Irrigation District and West Stanislaus Irrigation District) had much lower loading factors (that is, less of the load makes it to Vernalis) than sites downstream of these diversions. The Merced River below Merced Falls (E4) and the Bear Creek (E1) sites also had large diversions before reaching the mainstem of the San Joaquin River.

**46 Occurrence, Distribution, Instantaneous Loads, and Yields of Dissolved Pesticides, San Joaquin River Basin, Calif.**

**Table 16.** Loadings of pesticides on axes from a principal component analysis (PCA) of pesticide instantaneous yields in tributary basins for each sampling period.

[Only PCA axes with eigenvalues greater than one are shown; —, loading less than 0.50]

	PCA axis 1	PCA axis 2	PCA axis 3
<b>June 1994</b>			
Atrazine	0.97	—	—
Atrazine, deethyl	—	0.91	—
Carbaryl	—	.79	—
Chlorpyrifos	.55	—	-0.76
Diazinon	.90	—	—
EPTC	.60	—	—
Metolachlor	.69	—	—
Molinate	.92	—	—
Simazine	.94	—	—
Trifluralin	.93	—	—
Percent variance explained:	55.29	17.93	11.13
<b>June 2001</b>			
Atrazine	.95	—	—
Chlorpyrifos	—	.69	—
Diazinon	—	.92	—
EPTC	.98	—	—
Metolachlor	.85	—	—
Molinate	.78	—	—
Simazine	.66	—	—
Trifluralin	.86	—	—
Percent variance explained:	55.02	18.77	—
<b>August 2001</b>			
Atrazine	.73	-.63	—
Chlorpyrifos	.67	—	—
Cyanazine	—	.86	—
Diazinon	.91	—	—
EPTC	.90	—	—
Metolachlor	.74	—	—
Propargite	—	—	-.92
Trifluralin	.93	—	—
Percent variance explained:	52.67	17.99	14.37



**Figure 12.** Site scores on the first two axes from principal components analysis of instantaneous pesticide yields in June 1994, June 2001, and August 2001. See *table 1* for site codes. The arrows indicate the direction of increasing instantaneous yields of particular pesticides.

The sum of these adjusted loads from the contributing tributaries accounted for most of the loads measured at the San Joaquin River near Vernalis. Sums of loads from the tributaries range from 50 percent (molinate) to 105 percent (trifluralin) of measured loads at the San Joaquin River near Vernalis. The sums of the measured loads in this study are not expected to equal 100 percent because of unmeasured diversions and discharges in the system. As of the late 1980s, there were at least 86 agricultural diversions and 104 agricultural discharges to the San Joaquin River (Kratzer and Shelton, 1998). West-side sites accounted for most of the alachlor (79 percent), EPTC (84 percent), molinate (35 percent), and trifluralin (100 percent). East-side sites contribute most (51 percent) of the metolachlor load.

In 1994, Hospital Creek (49 percent), Del Puerto Creek (19 percent), and Ingram Creek (9 percent) were the

largest sources of alachlor. The Del Puerto Creek Basin received applications totaling 569 lb of alachlor (71.1 lb/mi<sup>2</sup>) in the 28 days preceding sampling. However, the Hospital Creek and Ingram Creek Basins had no alachlor applied in the 6 months preceding sampling. The alachlor detected may have resulted from an even earlier application or unreported application. In March 1994, 448 lb of alachlor were applied just outside the boundary of the Ingram Creek Basin, near the sampling site. Hospital Creek and Ingram Creek are unique among west-side tributaries. They have a much higher suspended sediment load and more irrigation tailwater than other sites. These factors could cause higher concentrations and loads of pesticides if pesticides stored in the soil are later transported to these tributaries with sediment and dissolve into the water.

**48 Occurrence, Distribution, Instantaneous Loads, and Yields of Dissolved Pesticides, San Joaquin River Basin, Calif.**

**Table 17.** Adjusted instantaneous loads for sites contributing to instantaneous pesticide loads at the San Joaquin River near Vernalis in June 1994.

[g/d, grams per day]

Site code	Station name	Date	Sample loading factor	Alachlor		EPTC		Metolachlor	
				Load (g/d)	Percentage of Vernalis load	Load (g/d)	Percentage of Vernalis load	Load (g/d)	Percentage of Vernalis load
S4	San Joaquin River near Vernalis	06/24/1994	1	38.0264	100.0000	92.3498	10.0000	173.8349	100.0000
S1	San Joaquin River near Stevinson	06/20/1994	.38	.0161	.0423	2.0913	2.2645	1.7695	1.0179
<b>West-side sites</b>									
G1	Salt Slough at Highway 165 near Stevinson	06/21/1994	.40	.1830	.4813	.1830	.1982	.1830	.1053
G3	Mud Slough near Gustine	06/21/1994	.41	.0281	.0739	.3371	.3650	.0281	.0162
W1	Newman Wasteway at Highway 33 near Gustine	06/22/1994	.45	.0991	.2606	1.9821	2.1463	1.9821	1.1402
W2	Orestimba Creek at River Road near Crows Landing	06/22/1994	.51	.0120	.0315	4.0734	4.4108	6.7091	3.8595
W3	Spanish Grant Combined Drain near Patterson	06/22/1994	.52	.0445	.1171	6.2350	6.7515	7.5710	4.3553
W4	Olive Avenue Drain near Patterson	06/23/1994	.73	.3527	.9275	5.6210	6.0866	.5952	.3424
W5	Del Puerto Creek at Vineyard Road near Patterson	06/23/1994	.73	7.2453	19.0533	4.4586	4.8280	1.5327	.8817
W6	Hospital Creek at River Road near Patterson	06/23/1994	.99	18.6632	49.0795	51.3237	55.5754	4.1215	2.3709
W7	Ingram Creek at River Road near Patterson	06/24/1994	.99	3.4957	9.1929	3.7646	4.0765	2.0436	1.1756
Total of west-side sites				3.1236	79.2176	77.9785	84.4382	24.7662	14.2470
<b>East-side sites</b>									
E5	Merced River at River Road Bridge near Newman	06/22/1994	.45	.1553	.4083	2.0184	2.1856	5.2789	3.0367
E6	Harding Drain at Carpenter Road near Patterson	06/22/1994	.56	.0480	.1261	1.0551	1.1426	.2398	.1380
E7	Westport Drain near Modesto	06/23/1994	.73	.0272	.0714	1.3847	1.4995	.0272	.0156
E8	Tuolumne River at Modesto	06/23/1994	.99	.2931	.7708	5.8625	6.3482	82.0753	47.2145
E10	Stanislaus River at Ripon near Patterson	06/23/1994	.99	1.2088	3.1790	1.2088	1.3090	1.2088	.6954
Total of east-side sites				1.7323	4.5556	11.5297	12.4848	88.8300	51.1002
Sum of Stevinson and west-side and east-side sites.				31.8720	83.8156	91.5994	99.1875	115.3658	66.3651



**Table 17.** Adjusted instantaneous loads for sites contributing to instantaneous pesticide loads at the San Joaquin River near Vernalis in June 1994—Continued.

[g/d, grams per day]

Site code	Station name	Date	Sample loading factor	Molinate		Trifluralin	
				Load (g/d)	Percentage of Vernalis load	Load (g/d)	Percentage of Vernalis load
S4	San Joaquin River near Vernalis	06/24/1994	1	81.4851	10.0000	51.6072	10.0000
S1	San Joaquin River near Stevinson	06/20/1994	.38	1.6087	1.9742	.0161	.0312
<b>West-side sites</b>							
G1	Salt Slough at Highway 165 near Stevinson	06/21/1994	.40	.3661	.4492	.1830	.3547
G3	Mud Slough near Gustine	06/21/1994	.41	19.3832	23.7874	.5056	.9798
W1	Newman Wasteway at Highway 33 near Gustine	06/22/1994	.45	.0220	.0270	.1101	.2134
W2	Orestimba Creek at River Road near Crows Landing	06/22/1994	.51	.0240	.0294	1.6773	3.2501
W3	Spanish Grant Combined Drain near Patterson	06/22/1994	.52	.6680	.8198	4.4535	8.6297
W4	Olive Avenue Drain near Patterson	06/23/1994	.73	.0220	.0271	5.6210	1.8918
W5	Del Puerto Creek at Vineyard Road near Patterson	06/23/1994	.73	.1115	.1368	.4877	.9450
W6	Hospital Creek at River Road near Patterson	06/23/1994	.99	6.9987	8.5889	27.2171	52.7390
W7	Ingram Creek at River Road near Patterson	06/24/1994	.99	1.1025	1.3530	11.5627	22.4053
Total of west-side sites				28.6980	35.2187	51.8181	10.4086
<b>East-side sites</b>							
E5	Merced River at River Road Bridge near Newman	06/22/1994	.45	.3105	.3811	.1553	.3009
E6	Harding Drain at Carpenter Road near Patterson	06/22/1994	.56	.0959	.1177	.0480	.0929
E7	Westport Drain near Modesto	06/23/1994	.73	.0543	.0666	.4344	.8418
E8	Tuolumne River at Modesto	06/23/1994	.99	7.9144	9.7127	.2931	.5680
E10	Stanislaus River at Ripon near Patterson	06/23/1994	.99	2.4177	2.9670	1.2088	2.3424
Total of east-side sites				1.7928	13.2452	2.1396	4.1460
Sum of Stevinson and west-side and east-side sites.				41.0995	5.4380	53.9738	104.5858

Hospital Creek (56 percent) and Spanish Grant Drain (7 percent) were the largest sources of EPTC. Neither of these basins reported agricultural application of EPTC during the 6 months preceding sampling. As for alachlor, earlier applications of EPTC, unreported application, or inter-basin transport might account for these loads.

Mud Slough (24 percent) was the largest source of the molinate load. As noted earlier, applications of pesticides to Mud and Salt Sloughs were combined because the basins are interconnected by water management infrastructure. In the 28 days preceding sampling, 3,439 lb (7.0 lb/mi<sup>2</sup>) of molinate were applied to the combined basin. Molinate is used primarily on rice. Within the study area, this crop is only grown in significant amounts in the Mud and Salt Slough Basins (Domagalski and Munday, 2003).

Tributaries contributing large portions of the trifluralin load included Hospital Creek (53 percent), Ingram Creek (22 percent), Spanish Grant Drain (9 percent), and Olive Avenue Drain (11 percent). All of these basins had applications of trifluralin in the 28 days preceding sampling. Hospital Creek had 53 lb applied (10.7 lb/mi<sup>2</sup>). Ingram Creek had 384 lb applied (34.9 lb/mi<sup>2</sup>). Spanish Grant Drain had 274 lb applied (12.5 lb/mi<sup>2</sup>). Olive Avenue Drain had 29 lb applied (3.7 lb/mi<sup>2</sup>).

The Tuolumne River at Modesto (47 percent) was the major source of metolachlor. During the 28 days before sampling, 746 lb of metolachlor were applied in the basin (2.9 lb/mi<sup>2</sup>). The agreement between the tributary loads and measured loads at the San Joaquin River near Vernalis (S4) was very good in 1994, as would be expected with the Lagrangian sampling design.

## Summary and Conclusion

Of the 48 pesticides analyzed in this study, 31 were reported applied in the 28 days preceding the June 1994 sampling, 25 in the 28 days preceding the June 2001 sampling, and 24 in the 28 days preceding the August 2001 sampling. The number of pesticides applied in tributary basins was highly correlated with basin area, resulting in the larger basins forming a distinct cluster of sites with similar applications of a variety of pesticides. Smaller basins had fewer pesticides applied and often not the same pesticides as neighboring basins. The PCA analysis of application intensity indicated that the west-side tributary basins generally were different from all the other basins in June 1994 and 2001; however, this geographic pattern was not apparent in August 2001.

The number of dissolved pesticides detected was similar among sampling periods with 26 detected in June 1994, 28 in June 2001, and 27 in August 2001 (table 7). Concentrations of chlorpyrifos equaled or exceeded the California CMC at six sites in June 1994 and five sites in June 2001. There was a single exceedance of the California CMC for diazinon in June 2001. A number of pesticides that were not applied in

the 28 days preceding sampling were detected during each sampling period. These detections were likely due to earlier applications. There also were pesticides that were applied in the 28 days preceding sampling that were not detected during sampling. These nondetections likely were due to a combination of the chemical and physical characteristics of the particular pesticide and to a variety of other land use and water use factors.

Unlike pesticide applications, there was not a strong relationship between basin area and the number of pesticides detected. Cluster analysis revealed high similarity among west-side basins (fig. 7). The PCA results generally showed east-side and west-side basins forming distinct groups owing to high concentrations of pesticides in west-side basins and low concentrations or nondetections of pesticides in east-side basins. These differences in concentrations may be due to differences in land use, soil characteristics, and irrigation practices that result in greater irrigation return flows in the west-side basins. The distinction between west-side and east-side basins became less clear when instantaneous loads were considered owing to the higher discharges in some east-side basins. High discharge can cause even a low concentration to result in a significant load. Consideration of instantaneous yields indicated that more pesticide is transported out of west-side basins per unit area than out of east-side basins. These contrasts between results for concentrations, instantaneous loads, and instantaneous yields are important to managers and regulators depending on their focus. High concentrations are important when considering toxicity to biota. Instantaneous loads may be just as important in the regulatory context of TMDLs. Instantaneous yields may indicate where management practices may be most effective.

The analysis of June 1994 loads that were based on Lagrangian sampling generally showed good concordance between tributary loads and the integrated load at the San Joaquin River near Vernalis. Tributary loads were often associated with large applications of particular pesticides within the basin. In general, west-side basins accounted for the largest percentages of loads at the San Joaquin near Vernalis, but this was not always the case.

In conclusion, there were geographic differences in pesticide concentrations, instantaneous loads, and instantaneous yields within the valley portion of the San Joaquin River Basin. In general, west-side basins were different from east-side basins; however, there were exceptions in each of the analyses. The factors generating these differences between basins could not be rigorously quantified, but likely include basin size, land use, soil characteristics, irrigation practices, and differences in stream discharge.

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