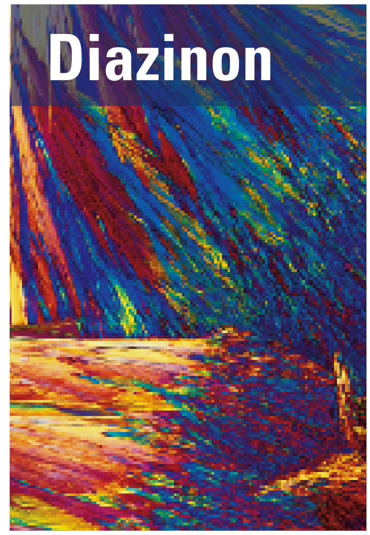
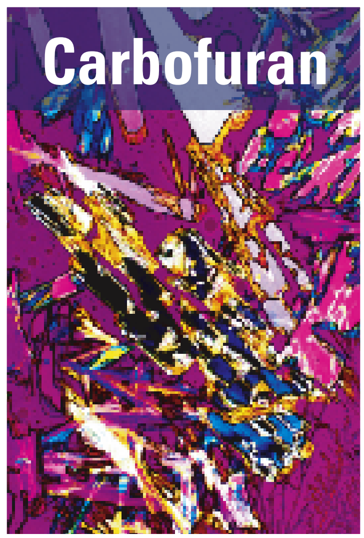
Evaluation of Diazinon and Chlorpyrifos Concentrations and Loads, and Other Pesticide Concentrations, at Selected Sites in the San Joaquin Valley, California, April to August, 2001

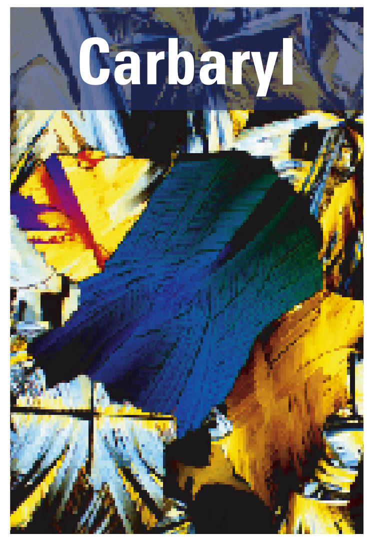
Water-Resources Investigations Report 03-4088

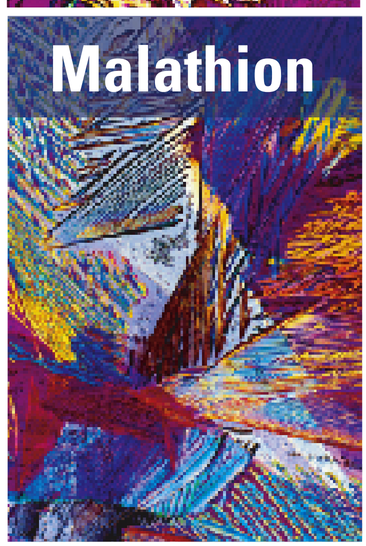
Prepared in cooperation with the

CALIFORNIA DEPARTMENT OF PESTICIDE REGULATION









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

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U.S. DEPARTMENT OF THE INTERIOR

GALE A. NORTON, *Secretary*

U.S. GEOLOGICAL SURVEY

Charles G. Groat, *Director*

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For additional information write to:

U.S. Geological Survey
Water Resources
Placer Hall, Suite 2012
6000 J Street
Sacramento, California 95819-6129
http://ca.water.usgs.gov

Copies of this report can be purchased from:

U.S. Geological Survey
Information Services
Building 810
Box 25286, Federal Center
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FRONT COVER:

Some common pesticides recrystallized and photographed under microscopes using a variety of polarized and fluorescent lighting.
Images courtesy of: *Michael W. Davidson at Florida State University*

FIGURES

TABLES

CONVERSION FACTORS , ABBREVIATIONS, AND ACRONYMS

Multiply	By	To obtain
kilogram (kg)	2.205	pound, avoirdupois
kilogram per square kilometer (kg/km^2)	5.710	pounds per square mile
kilogram per square kilometer (km^2)	0.008922	pounds per acre
square kilometer (km^2)	0.3861	square mile
square kilometer (km^2)	247.1	acre

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

$$°F=(1.8\ °C)+32.$$

ABBREVIATIONS

µg/L, microgram per liter

L, liter

EPA, U.S. Environmental Protection Agency

NAWQA, National Water-Quality Assement (Program)

NWQL, National Water Quality Laboratory

USGS, U.S. Geological Survey

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ABSTRACT

Twelve sites in the San Joaquin Valley of California were monitored weekly during the growing and irrigation season of 2001 for a total of 51 pesticides and pesticide degradation products, with primary interest on the concentration, load, and basin yield of organophosphorus insecticides, especially diazinon and chlorpyrifos. Diazinon was detected frequently, up to 100 percent of the time, at many of the sampling sites, but with generally low concentrations. For all sites, 75 percent of all measured diazinon concentrations were less than 0.02 μg/L, and 90 percent of all measured diazinon concentrations were less than 0.06 μg/L. The highest diazinon concentrations were measured in samples from two west-side tributaries to the San Joaquin River, Orestimba Creek, and Del Puerto Creek. The median concentration of chlorpyrifos was at or less than the laboratory reporting limit (0.005 μg/L) for most sites with the exceptions of two tributaries to the San Joaquin River: Orestimba Creek and the Tuolumne River. For all sites, 75 percent of all measured chlorpyrifos concentrations were less than 0.03 μg/L and 90 percent of all measured chlorpyrifos concentrations were less than 0.07 μg/L. The total load of diazinon out of the basin was just over 7 kilograms, which accounted for about 0.17 percent of the total agricultural applications. The diazinon load from the monitored upstream tributaries accounted for about 50 percent of the load at the mouth of the San Joaquin River. The streamflow from the selected monitored tributaries accounted for about 83 percent of the streamflow at the mouth of the San Joaquin River. The total load of chlorpyrifos out of the basin was 3.75 kilograms, and this accounted for approximately 0.007 percent of the total amount applied. Other pesticides that were frequently detected during this study included herbicides such as metolachlor, simazine, and trifluralin, and insecticides such as carbaryl, carbofuran, and propargite. At Orestimba Creek, DDE, a degradation product of DDT, was detected at a frequency of 95 percent.

INTRODUCTION

Residues of pesticides in surface waters of the San Joaquin Valley have been discussed in many previous studies (Kuivila and Foe, 1995; Domagalski, 1997a,b; Domagalski and others, 1997; Panshin and others, 1998; Kratzer, 1998; Kratzer, 1999). In most of those studies the emphasis was on storm-water runoff because of both the higher concentrations and mass loadings of pesticides during storms and the co-occurrence of pesticides and incidents of toxicity to aquatic life (Kuivila and Foe, 1995; de Vlaming and others, 2000; Werner and others, 2000). Because of this history of pesticide detections, the associated toxicity to aquatic life, and the linkage of the toxicity to pesticide concentrations, several waterways of the San Joaquin Valley (fig. 1*A*) are listed as water-quality impaired (U.S. Environmental Protection Agency, accessed March 21, 2002). Also shown (fig. 1) is land use and land cover. This 303(d) list of water-quality impaired streams identifies the specific streams that are not meeting water quality goals, the nature of the impairment, and the priority for development of a management plan. The management plan, which is designed to improve water quality, or to bring the streams up to water quality standards, is referred to as a total maximum daily load (TMDL) plan. The 303(d) list shows that several streams in the San Joaquin Valley, including the San Joaquin River, are impaired because of pesticides (U.S. Environmental Protection Agency, accessed March 21, 2002). The most frequent impairments are attributed to organophosphorus insecticides such as diazinon and chlorpyrifos.

Although it is assumed that most of the unintentional transport of pesticides from fields to streams occurs in winter in response to rainfall-induced runoff, relatively few studies have investigated the occurrence of pesticides in streams during the spring through summer growing season. During this season, there is usually very little or no rainfall in the San Joaquin Valley, and successful agriculture is dependent on the availability of irrigation water (Dubrovsky and others, 1998). A significant amount of pesticides may be used during the growing season. (See the Results and Discussion section later in the report, which includes information on seasonal application of pesticides and compares them with loads in the Sacramento River at Vernalis). Domagalski (1997b) completed a study at three sites within the San Joaquin Valley and demonstrated the high temporal variability of pesticide concentrations that can occur during the irrigation season. Panshin and others (1998) completed a one-year study in 1993 of pesticide concentrations at a site on the San Joaquin River and three of its tributaries. They noted that pesticide occurrence in stream water was highly related to temporal patterns of use and to the extent that irrigation return flows or storm water runoff could contribute to the water budget of the streams where pesticide samples were collected.

On the basis of the listing of streams within the San Joaquin Basin as water quality impaired because of pesticides and agricultural runoff, a TMDL plan will be developed to allocate the loads of diazinon to streams from various sources. Successful implementation of the TMDL plan requires a knowledge of sources and loadings of pesticides to streams throughout the year so that management plans can be implemented to bring the streams into compliance with water quality objectives. This study addresses the variation in pesticide concentration and loads, with emphasis on organophosphorus insecticides, during the irrigation season (April through August) at 12 sites within the San Joaquin Valley (fig. 2). Drainage basins also are shown in figure 2. Sites for this study were chosen on the main stem of the San Joaquin River and at major tributaries on both sides of the river. Although the emphasis of the study is on organophosphorus insecticides, other insecticides and herbicides and several degradation products were also analyzed in samples collected during this study, and their co-occurrence with the organophosphorus insecticides is addressed. Another study was conducted during the same period at additional sites in order to understand the effects of these pesticides on aquatic communities. That study had fewer sampling events and will be reported separately.

DESCRIPTION OF STUDY AREA

The perennial San Joaquin River drains 19,023 km^2, of which 11,134 km^2, are in the Sierra Nevada, 5,887 km^2 are in the San Joaquin Valley, and 2,002 km^2 are in the Coast Ranges (figs. 1 and 2). According to U.S. Geological Survey (USGS) streamflow data for 1951–1995, 66 percent of the average streamflow in the San Joaquin River comes from three major Sierran tributaries: the Merced River (15 percent), the Tuolumne River (30 percent), and the Stanislaus River (21 percent) (U.S. Geological Survey, accessed January 12, 2002). The remaining streamflow comes from the Bear Creek Basin, Mud and Salt Sloughs, and the ephemeral creeks that drain from the west, including Orestimba and Del Puerto Creeks, drainage canals that flow directly into the San Joaquin River, and occasionally the upper San Joaquin River above Bear Creek during especially high flows (Kratzer and others, 2002).

The San Joaquin Valley, a flat structural basin, has hot summers and mild winters characteristic of its arid-to-semiarid Mediterranean climate. Average temperatures, in degrees Celsius, range from about 5 to 10 during the winter to about 29 during the summer. The eastern slope of the Coast Ranges and the valley are in the rain shadow of the Coast Ranges. The major

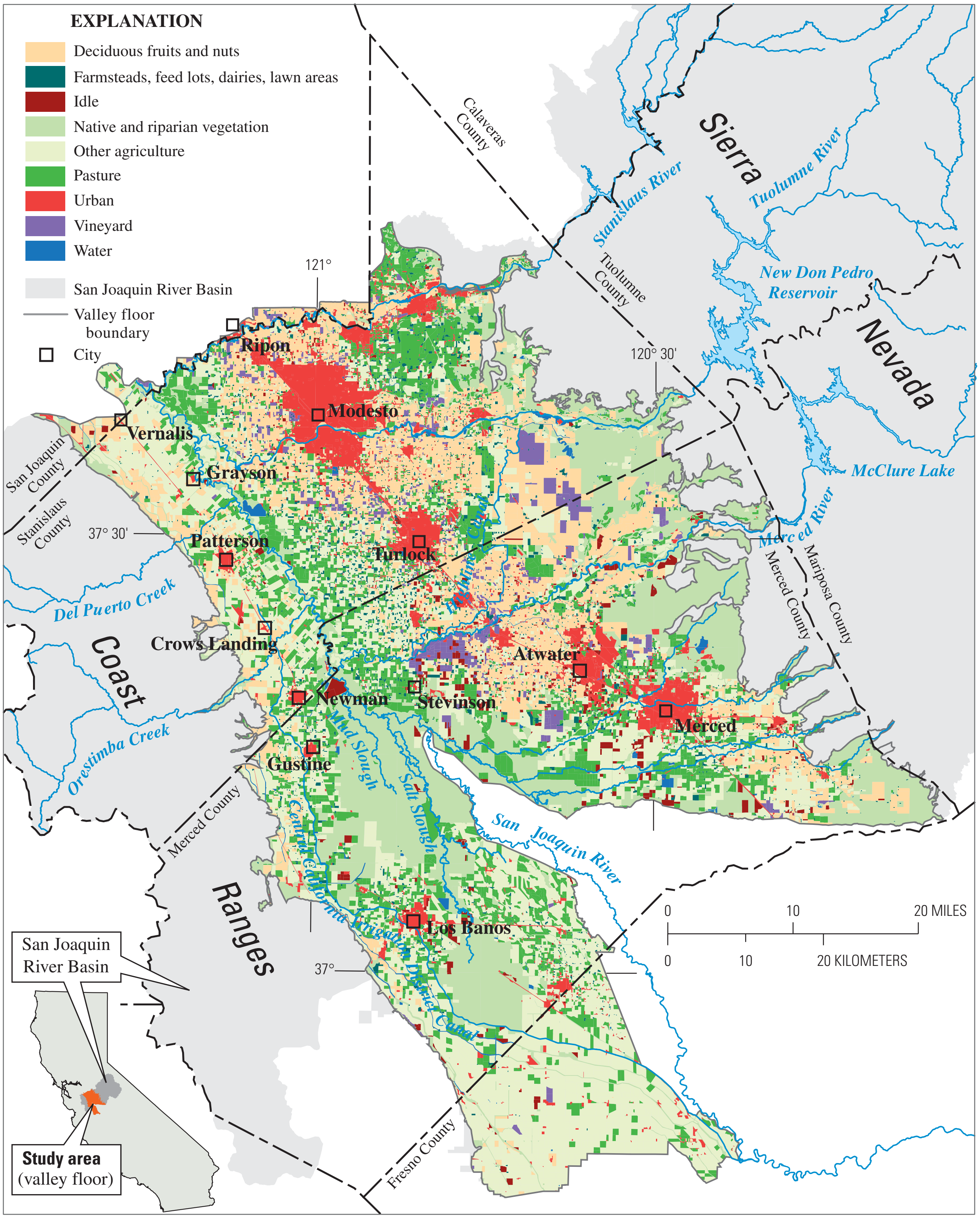
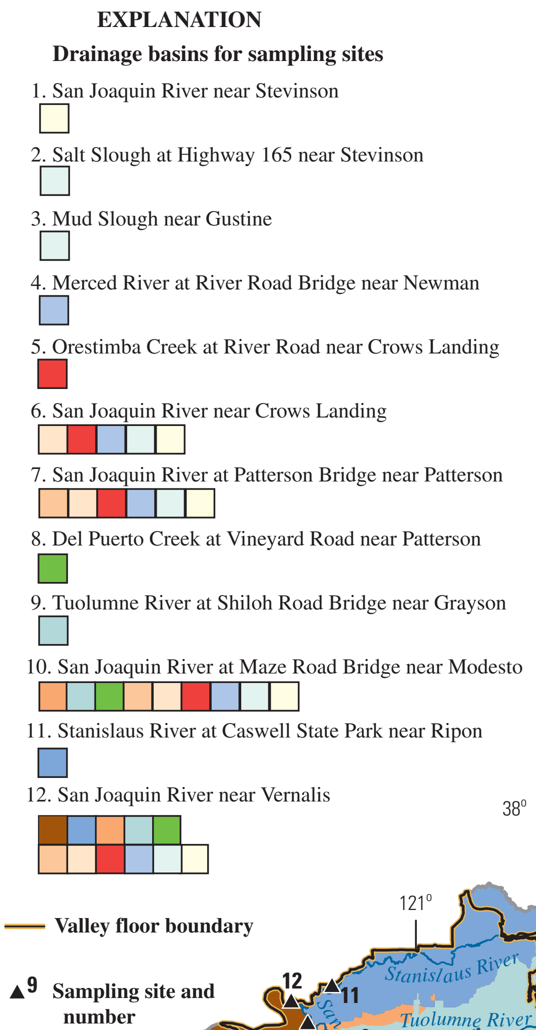


Figure 1. The San Joaquin Valley study area showing land use and land cover.

Site name	Number of pesticides with detection frequency greater than or equal to 50%
1. San Joaquin River near Stevinson	5
2. Salt Slough at Highway 165 near Stevinson	11
3. Mud Slough near Gustine	9
4. Merced River at River Road Bridge near Newman	5
5. Orestimba Creek at River Road near Crows Landing	15
6. San Joaquin River near Crows Landing	9
7. San Joaquin River at Patterson Bridge near Patterson	11
8. Del Puerto Creek at Vineyard Road near Patterson	11
9. Tuolumne River at Shiloh Road Bridge near Grayson	7
10. San Joaquin River at Maze Road Bridge near Modesto	9
11. Stanislaus River at Caswell State Park near Ripon	5
12. San Joaquin River near Vernalis	9



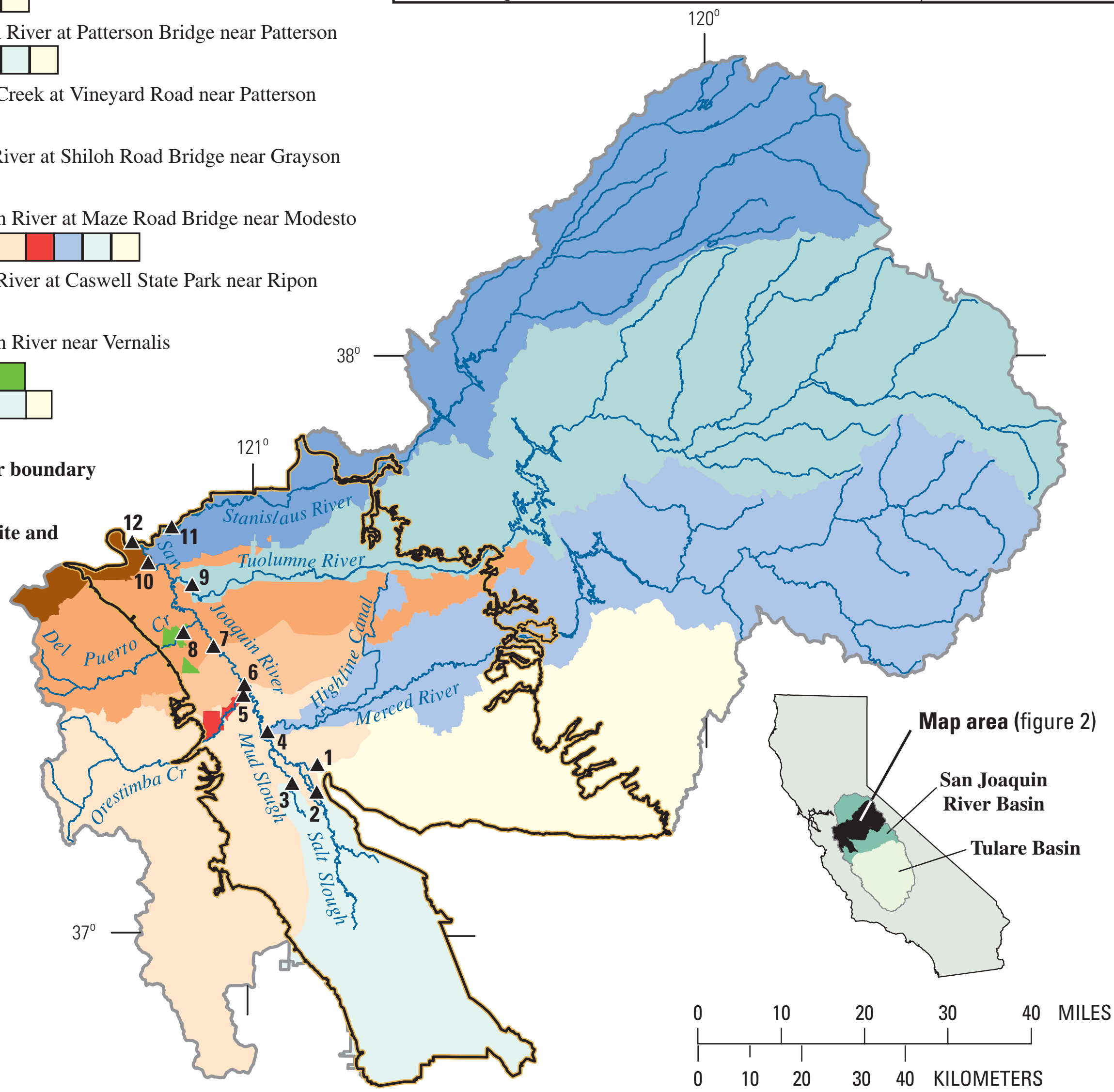


Figure 2. Drainage basin boundaries and site locations.

source of water entering the basin is the heavy precipitation, occurring both as rain and snow, that falls on the western slope of the Sierra Nevada. The average annual precipitation ranges from 13 to 41 cm in the valley and increases with altitude in the Sierra Nevada to amounts ranging from 101.6 to more than 228.6 cm. Although monthly and annual precipitation in the study area is highly variable, most of the precipitation (more than 80 percent) falls during November through April with peak precipitation usually occurring during January. (Gronberg and others, 1998; Panshin and others, 1998; and Bertoldi and others, 1991).

The predominant land uses in the study area and adjacent areas include forests in the Sierra Nevada, rangeland in the Coast Ranges and the Sierra Nevada foothills, and urban and agricultural land on the valley floor—with most of valley floor land devoted to agriculture (fig. 1). The agricultural land-use is extremely diversified with row crops, orchards, vineyards, and pasture throughout. The combination of a long growing season and a supply of water for irrigation results in an exceptionally productive agricultural economy in the San Joaquin Valley (Gronberg and others, 1998).

Sediments, soils, and water quality in the valley are profoundly influenced by the sharp contrast between the bedrock geology of the Coast Ranges and that of the Sierra Nevada. The Coast Ranges, on the west side of the valley, have a core of Franciscan-complex rocks of Late Jurassic to Late Cretaceous or Paleocene age and ultramafic rocks of Mesozoic age, overlain by marine and continental sediments. The Sierra Nevada on the east side of the valley is composed of primarily pre-Tertiary granitic rocks and is separated from the valley by a foothill belt of Mesozoic and Paleozoic marine rocks and Mesozoic metavolcanic rocks (California Division of Mines and Geology, 1958; 1959; 1964; 1965a,b; 1966; 1967; 1969). Soils and sediments in the western part of the valley, derived from the Coast Ranges alluvium, tend to be of finer texture and have higher clay content and lower permeability than those of the eastern part of the valley. By contrast, the sediments in the eastern part of the valley are highly permeable, medium- to coarse-grained sands with low total organic carbon. Deposits on the east side are finest near the valley trough and coarsest near the upper parts of the alluvial fans (Gronberg and others, 1998 and Panshin and others, 1998).

During this study, 12 San Joaquin River and tributary sites in the lower San Joaquin Basin were sampled (table 1) for dissolved organophosphorus pesticides and other pesticide compounds, from 20 to 24 times each, beginning April 11, 2001, and ending August 21, 2001 (fig. 2). The study was timed to coincide with the growing and irrigation season to determine if there were significant sources of pesticide runoff to the San Joaquin River during that timeframe. Sampling locations included five sites along the mainstem of the San Joaquin River: the San Joaquin River near Stevinson, near Crows Landing, at Patterson Bridge near Patterson, at Maze Road Bridge near Modesto, and near Vernalis. The San Joaquin River near Vernalis is the basin outlet. This site receives streamflow from upstream portions of the basin and, therefore, characterizes the water quality in the basin in general. The San Joaquin River near Stevinson is the upstream boundary of the perennial San Joaquin River.

Three major east side tributary sites were sampled including the Stanislaus River at Caswell State Park near Ripon, the Tuolumne River at Shiloh Road Bridge near Grayson, and the Merced River at River Road Bridge near Newman. During the growing season, streamflow in these three tributaries consists of managed releases from upstream reservoirs and irrigation return flow. The four small tributaries sampled on the west side of the San Joaquin River exclusively drain agricultural areas during the growing season and include Orestimba Creek at River Road near Crows Landing, Del Puerto Creek at Vineyard Road near Patterson, Mud Slough near Gustine, and Salt Slough at Highway 165 near Stevinson.

Basin boundaries for the 12 sampled sites are shown in figure 2. The three large eastside tributaries—the Merced, Tuolumne, and Stanislaus Rivers—have basins that extend beyond the valley floor into the Sierra Nevada. The two small westside tributaries, Orestimba Creek and Del Puerto Creek, have smaller defined basins that do not correspond to their respective stream channels and extend into the Coast Ranges. Smaller basins were defined for Orestimba and Del Puerto Creeks on the basis of known drainage patterns for the San Joaquin Valley floor. In both cases, the basins shown correspond to the areas that potentially discharge irrigation drainage waters to the San Joaquin River.

Table 1. Site names, U.S. Geological Survey (USGS) identification numbers, and drainage basin areas, San Joaquin Valley, California

[km^2, square kilometer]

	Site Name	USGS Identification Number	Drainage Basin Area - Valley Floor (km^2)
1.	San Joaquin River near Stevinson	11260815	1,142
2.	Salt Slough at Highway 165 near Stevinson	11261100	[1]1,254
3.	Mud Slough near Gustine	11262900	[1]Mud/Salt combined area
4.	Merced River at River Road Bridge near Newman	11273500	634
5.	Orestimba Creek at River Road near Crows Landing	11274538	28
6.	San Joaquin River near Crows Landing	11274550	3,881
7.	San Joaquin River at Patterson Bridge near Patterson	11274570	4,220
8.	Del Puerto Creek at Vineyard Road near Patterson	11274653	21
9.	Tuolumne River at Shiloh Road Bridge near Grayson	11290200	437
10.	San Joaquin River at Maze Road Bridge near Modesto	11290500	5,378
11.	Stanislaus River at Caswell State Park near Ripon	374209121103800	447
12.	San Joaquin River near Vernalis	11303500	5,887

[1]Combined area = site 2 area plus site 3 area

METHODS AND QUALITY CONTROL

Sample Collection Methods

Sample collection methods used during this study were developed on the basis of site location, stream channel characteristics, and hydrologic conditions. For example, during the sampling period, April through August 2001, stream flows were generally decreasing, at least at the large river or stream sites. In some of the smaller tributaries, such as Orestimba Creek, stream flow was mainly limited to irrigation runoff. The low flows coupled with the characteristics of some of the channels necessitated the development of study-specific sampling techniques that were not previously outlined in established sampling protocols. Sampling methods included integrated grab samples collected from wide channels spanned by bridges, midpoint grab samples collected from narrow channels either by wading or by reaching the midpoint from the bank, and dip samples collected from a dock extending into the channel or from the bank at a point where the greatest amount of flow was channeled. In all cases, a method was used that would provide representative samples for a given stream under a given flow situation. In that way, water samples could be collected that adequately represented the average concentration of pesticides present in the water at the time of sample collection.

Integrated Grab Samples

Integrated grab samples were collected from the bridge at three equally spaced locations using a grab sampler holding a 3-L Teflon bottle at the following sites: San Joaquin River near Stevinson, Salt Slough at Highway 165 near Stevinson, Mud Slough near Gustine, Merced River at River Road Bridge near Newman, San Joaquin River at Patterson Bridge near Patterson, and Tuolumne River at Shiloh Road Bridge near Grayson. To obtain a representative sample at locations where streams are wider, integrated grab samples were collected from the bridge at five equally spaced locations using a grab sampler holding a 3-L Teflon bottle. Sites where five sampling points were necessary include the San Joaquin River at Maze Road Bridge near Modesto and the San Joaquin River near Vernalis.

Midpoint Grab Samples

The Del Puerto Creek at Vineyard Road near Patterson site could be waded, and midpoint grab samples were collected using a 3-L Teflon bottle. The system at this site was too shallow to accommodate any other type of sampling method or sampling equipment.

With the exception of the initial sample, midpoint grab samples were collected at a narrowing of the channel, using a 3-L Teflon bottle, at Orestimba Creek at River Road near Crows Landing. Because of the high runoff, the initial sample was an integrated grab collected from the bridge using a grab sampler holding a 3-L Teflon bottle.

Dip Samples

Samples were routinely collected by dipping a 3-L Teflon bottle into the stream channel from a floating dock located on the right bank of the San Joaquin River near Crows Landing. There were also three mid-channel integrated replicate samples collected by boat at this site using a grab sampler holding a 3-L Teflon bottle. Data from these three samples were used to assess the variability, if any, that would result when comparing integrated samples collected midstream with dip samples collected from the dock. To collect samples at the Stanislaus River at Caswell State Park near Ripon, a 3-L bottle was dipped into the stream from the bank at a point where the greatest amount of flow was channeled.

Calculation of Loads and Yields

Mass loadings of pesticides for the period of this study (April 1 through August 31, 2001) were calculated by multiplying the instantaneous streamflow measurements, collected every 15 minutes, by the measured pesticide concentrations in micrograms per liter. The amount of mass loading for each 15 minute interval was thereby calculated by integrating the amount of discharge and pesticide mass over the 15 minute interval. These calculations were then repeated for the entire period of the study and the amount of pesticide mass was summed. Continuous measurements of streamflow were available for all but two sites (Del Puerto Creek at Vineyard Road near Patterson and the San Joaquin River at Maze Road Bridge near Modesto). Pesticide concentrations before, between, and after, sampling events were interpolated, and the calculation of interpolated concentrations multiplied by the instantaneous measurement was completed for each reported value of streamflow (at each 15 minute interval). For sampling times, when a given pesticide concentration was below reporting limits, a concentration of one half the reporting limit was used as the concentration. The calculated masses were summed over the time interval of this study. Although Del Puerto Creek and the San Joaquin River at Maze Road Bridge near Modesto did not have instantaneous streamflow measurements, an estimate of continuous discharge was made using the instantaneous values of discharge measured at the time of collection, and then interpolating the discharge between sampling events. Therefore, the calculation of pesticide load for the Del Puerto Creek and San Joaquin River at Maze Road Bridge near Modesto sites are estimates. The calculation of yield, for each basin, is simply the load for the period of this study divided by the area of the basin. Only that part of the drainage basins that are in the floor of the San Joaquin Valley (figs. 1 and 2) were used for the yield calculation.

Quality Control Data and Sample Types

Data obtained from field quality control samples are used to estimate the bias and variability from sample collection, processing, and analysis. Bias refers to a systematic error manifested as a consistent positive or negative deviation from the known or true value. Variability is defined as random error in independent measurements that may result with repeated application of the process under specified conditions.

The three types of field quality control samples routinely collected during this study were field blanks, field matrix spikes, and field replicates. Blanks and field matrix spikes estimate bias, and field replicates estimate variability. The number, type, and sites for quality control sampling were chosen in accordance with published protocols (Mueller and others, 1997).

Surrogate compounds, added to all environmental, spike, and blank samples that were analyzed for pesticides, detect sample handling problems, such as sample spillage or leakage during extraction, throughout the analytical process. Surrogate compounds are similar in chemical properties to some of the target analytes, but are not expected to be in the environmental samples. Surrogates also can be used to evaluate matrix effects on analyte recovery when compared with recovery in reagent spike samples (Fitzgerald, 1997).

Field Blank Samples

Blank samples were used to evaluate bias resulting from contamination of environmental samples by the analytes of interest during sample collection, processing, shipping, or analysis. Source solution used to process blank samples consisted of water that had undetectable concentrations of measured constituents. Pesticide-grade water from the National Water Quality Laboratory (NWQL) in Denver, Colorado, was used as source solution for the blank samples collected during this study. Field blanks were collected at a sampling site using the same equipment as that used for sampling stream water. The same sample collection and processing procedures were used. The blank samples were collected after the sampling and processing equipment had been cleaned in the field according to published procedures (Mueller and others, 1997). The field cleaning procedure was used after a river or stream sample was collected in order to ensure that none of the equipment contributed residual amounts of pesticides to subsequently collected samples.

Replicate Samples

Replicates measure the variability in water samples that could occur during sample collection, processing, and analysis. To collect the replicate sample sets for this study, two environmental samples were collected in sequence and processed identically according to methods described in Mueller and others, 1997. Sequential replicates also provide a measure of variability associated with short-term environmental fluctuation (Mueller and others, 1997). Replicate samples collected from two of the sites, the San Joaquin River near Stevinson (collected June 12, 2001) and the San Joaquin River at Crows Landing (collected June 19, 2001) were split replicates with the integrated grab sample serving as the same source for both the environmental sample and the replicate. These samples were intended to be an environmental and a spiked sample, but since spike solution was not added at the laboratory, the data were used for replicate analysis. Split replicates provide a measure of the variability introduced during sample processing and analysis only (Mueller and others, 1997).

In addition to the sixteen replicate sample sets collected for routine quality control analyses, two other replicate evaluations were conducted during this study. There were three replicate sample sets collected at the San Joaquin River near Crows Landing site to determine the variability between dip samples collected at the dock and integrated grab samples collected mid channel by boat. Four replicate sample sets were used to compare the variability between samples collected by the USGS with those collected by the State of California's Regional Water Quality Control Board (RWQCB). The USGS–RWQCB replicates were collected at Merced River at River Road Bridge near Newman, Orestimba Creek at River Road near Crows Landing, Del Puerto Creek at Vineyard Road near Patterson, and San Joaquin River near Vernalis.

Spiked Samples

Spiked samples measure bias caused by analyte degradation or sample matrix interference, or to test for the effects of sample matrix on the analyses of specific constituents. A spike is an environmental sample fortified with a known concentration of selected analytes. Spiked samples were obtained by collecting one sample that was split into two samples as previously described for replicate samples. One of the samples was fortified with spike solution at the NWQL and the other was designated as the environmental sample (Mueller and others, 1997).

Sample Processing and Analysis and Laboratory Quality Control

One-liter samples were filtered in the laboratory by pumping the water through a glass fiber filter. The filter support was constructed of aluminum, and an all-Teflon system was used to pump the water. At the laboratory, two surrogate compounds, diazinon *d*-10 and α-HCH-d_6 were injected and the water was passed through a C-18 solid phase extraction cartridge. The cartridges were subsequently dried and eluted using a mixture of hexane and isopropanol (3:1), concentrating the solution into to a smaller volume. Analysis was completed by capillary column gas chromatography coupled to a quadruple mass spectrometer operating in the selected ion monitoring mode. Complete details of the method are given by Zaugg and others (1995). The pesticides that were analyzed and their method reporting limits are given in table 2. The methodology used to determine method reporting limits is given by Zaugg and others (1995), with the exception of acetochlor analysis. The method described by Lindley and others (1996) was used for acetochlor. The results of laboratory quality control for the timeframe of this

Table 2. Pesticides or pesticide degradation products analyzed and associated laboratory reporting limits

[µg/L, microgram per liter]

Pesticide or Pesticide Degradation product	Laboratory Reporting Limit (µg/L)	Pesticide or Pesticide Degradation product	Laboratory Reporting Limit (µg/L)
2,6-Diethylaniline	0.006	Malathion	0.027
Acetochlor	0.006	Metolachlor	0.013
Alachlor	0.045	Metribuzin	0.006
α-HCH	0.0046	Molinate	0.0016
Atrazine	0.007	Napropamide	0.007
Azinphos-methyl	0.05	Parathion	0.01
Benfluralin	0.01	Parathion-methyl	0.006
Butylate	0.002	Pebulate	0.0041
Carbaryl	0.041	Pendimethalin	0.022
Carbofuran	0.02	*cis*-Permethrin	0.006
Chlorpyrifos	0.005	Phorate	0.011
Cyanazine	0.018	Prometon	0.015
Dacthal	0.003	Propachlor	0.01
p,p′-DDE	0.0025	Propanil	0.011
Desethylatrazine	0.006	Propargite	0.023
Diazinon	0.005	Propyzamide	0.0041
Dieldrin	0.0048	Simazine	0.005
Disulfoton	0.021	Tebuthiuron	0.016
EPTC	0.002	Terbacil	0.034
Ethalfluralin	0.009	Terbufos	0.017
Ethoprophos	0.005	Thiobencarb	0.0048
Fonofos	0.0027	Triallate	0.0023
Lindane	0.004	Trifluralin	0.009
Linuron	0.035		

study, are given in table 3. The laboratory quality control study consisted of spiking each of the measured pesticides into purified water (pesticide grade) to a concentration of 0.1 µg/L. A total of 295 samples were analyzed in this manner. Some pesticides such as diazinon and chlorpyrifos had acceptable recoveries and the standard deviations of the recoveries were also acceptable. The mean recoveries of diazinon and chlorpyrifos were 95.09 percent and 90.25 percent, respectively. The standard deviations of the recoveries were 8.36 percent and 10.64 percent respectively. Some compounds, however, had highly variable recovery. For example, the standard deviation of recovery of carbaryl was 110 percent, and that for carbofuran was almost 80 percent. This poor variability for certain compounds must be considered when evaluating both the field-level quality control data and environmental data as discussed in subsequent sections.

Pesticides can be detected at concentrations below the laboratory reporting limit. The presence of those compounds is verified from the mass spectral data, but the associated concentrations are considered estimates.

Field-Level Quality Control Data Analysis

All samples were submitted to NWQL for analysis. Variability between replicate samples is presented as the relative percentage difference (RPD) and as the absolute difference in concentration units. The RPD is calculated as the absolute difference between values of the replicate pair divided by their average value and multiplied by 100. Results were calculated for replicate pairs where analyte concentration was above the laboratory reporting limit in both samples. Estimated values were treated as detections for replicate analysis.

Table 3. Results of laboratory spiking and recovery of pesticides into purified water (pesticide grade), San Joaquin Valley, California

[Amount spiked is 0.1 microgram per liter. Results for mean, median, standard deviation, and 75th and 25th percentiles are in percent, nonrounded. µg/L, microgram per liter]

Compound	Amount spiked (µg/L)	Total number of samples	Mean	Median	Standard deviation	75th percentile	25th percentile
2,6-Diethylanaline	0.1	295	93.81	92.17	12.33	100.85	86.28
EPTC	0.1	295	90.91	90.55	13.34	98.26	85.93
Butylate	0.1	295	89.89	88.39	10.00	94.55	84.20
Pebulate	0.1	295	92.65	90.64	9.90	97.36	86.26
Tebuthiuron	0.1	295	110.23	108.47	21.55	123.66	94.78
Molinate	0.1	295	91.88	90.68	9.52	96.58	85.92
Propachlor	0.1	295	99.44	97.32	14.89	105.89	90.38
Ethoprop	0.1	295	83.02	83.07	14.11	89.79	76.07
Ethalfluralin	0.1	295	76.16	75.52	13.01	84.82	66.76
Trifluralin	0.1	295	66.05	65.79	13.50	73.76	55.50
Benfluralin	0.1	295	65.57	65.18	11.22	71.68	58.48
Phorate	0.1	295	65.82	67.17	18.32	78.45	55.59
α-HCH	0.1	295	90.38	91.07	13.03	96.49	85.88
Prometon	0.1	295	92.23	91.53	12.23	97.41	84.89
Simazine	0.1	295	87.44	88.47	14.63	97.37	75.00
Carbofuran	0.1	295	109.55	94.22	79.47	113.97	83.81
Atrazine	0.1	295	96.43	95.08	10.56	103.80	88.53
γ-HCH (Lindane)	0.1	295	97.08	97.27	12.32	103.49	89.92
Terbufos	0.1	295	70.32	72.63	15.71	80.78	61.98
Pronamide	0.1	295	90.21	90.43	14.65	96.55	83.45
Fonofos	0.1	295	87.31	90.27	15.38	95.61	80.26
Diazinon	0.1	295	95.09	94.92	8.36	100.00	90.91
Disulfoton	0.1	290	41.38	43.22	26.86	64.75	16.32
Terbacil	0.1	295	77.29	77.72	22.81	92.92	63.24
Triallate	0.1	295	88.87	89.45	7.53	93.97	84.12
Propanil	0.1	295	99.63	99.12	14.76	107.83	90.30
Metribuzin	0.1	295	83.65	83.90	12.36	91.19	76.59
Acetochlor	0.1	295	96.76	95.90	10.99	102.54	90.63
Parathion-methyl	0.1	295	86.91	83.91	19.19	98.18	73.36
Carbaryl	0.1	295	108.64	87.09	109.91	108.53	68.50
Alachlor	0.1	295	95.22	94.87	10.35	101.32	88.57
Linuron	0.1	295	103.31	100.00	27.01	120.61	83.68
Malathion	0.1	295	86.75	83.93	16.36	94.12	76.78
Thiobencarb	0.1	295	94.40	94.74	7.96	100.00	88.81
Metolachlor	0.1	295	98.52	97.32	11.52	106.70	90.00
Cyanazine	0.1	295	92.72	93.46	24.07	104.20	78.41
Chlorpyrifos	0.1	295	90.25	89.74	10.64	96.60	84.02
Parathion	0.1	295	89.08	85.26	20.91	97.84	75.33
Dacthal (DCPA)	0.1	295	99.90	99.14	10.65	105.45	93.89
Pendimethalin	0.1	295	69.15	66.27	15.47	76.60	60.60
Napropamide	0.1	295	88.16	85.53	14.76	93.10	79.23
p,p′-DDE	0.1	295	62.69	63.54	7.70	67.69	57.85
Dieldrin	0.1	295	91.02	88.91	10.75	96.52	84.37
Propargite	0.1	295	73.58	66.28	28.36	79.19	57.23
Azinphos-methyl	0.1	295	78.48	72.99	33.44	98.29	53.42
cis-Permethrin	0.1	295	41.63	42.20	8.40	46.50	36.88

Spike recovery percentages were calculated according to instructions provided by NWQL (Mueller and others, 1997). The corresponding environmental sample submitted with each spiked sample was used to determine any detectable background concentrations of the spiked analytes. If an analyte was detected in the environmental sample, the concentration was subtracted from the concentration result of the spiked sample to provide the adjusted value needed to calculate the spike recovery percentages. If results were estimated values, spike recovery percentages were not calculated.

Blank Samples

Twelve blank sample sets were submitted for analysis of 47 pesticide compounds. However, one of the blank samples was ruined during analysis and, therefore, only eleven of the sample sets could be evaluated. Detections of two compounds were limited to one sample collected at Orestimba Creek at River Road near Crows Landing on June 19, 2001, where atrazine and metolachlor were estimated at concentrations of 0.005 µg/L (method reporting limits are 0.007 and 0.013 µg/L, respectively). There were no other analytes detected in any of the blank samples. Therefore, the analysis of the blank samples shows only very minor potential bias and, as a result, there is no need to qualify any of the environmental data.

Routine Quality Control Replicate Samples

Sixteen replicate sample sets were submitted for analysis. The variability of the samples, represented as the RPD and as the absolute difference in concentration units, is given in table 4 with the numbers and types of detection results for each compound. Seventeen of the 47 compounds returned nondetection results for all environmental and replicate samples. Two other compounds, alpha BHC and pendimethalin, could not be evaluated because of nondetection results or nondetections paired with estimated values. Of the 28 remaining compounds, 10 had only one replicate pair that could be evaluated; therefore, a median value is not applicable to those analytes. Eighteen of 47 compounds had two or more replicate pairs that could be evaluated. Median RPD values range from 0 to 11 percent for the following: atrazine, desethyl with four sets evaluated, metribuzin with three sets evaluated, and trifluralin with 11 sets evaluated. Median RPD results for the other 15 constituents range from 5 percent for EPTC with 13 evaluations to 83 percent for lindane, which had 2 sample sets included in the calculations. Although none of the compounds had maximum RPD results in excess of 100 percent, atrazine and lindane both had maximum RPD values of 100 percent. The maximum differences in concentration units for these analytes is small, however, at 0.004 µg/L for atrazine and 0.003 µg/L for lindane, and both maximum differences are less than the reporting limits for the compounds with atrazine at 0.007 µg/L and lindane at 0.004 µg/L.

Replicate samples indicate that variability resulting from sample collection (sequential replicate data), processing, and analysis (sequential and split replicate data) is generally low, and is within the amount previously determined for the analytical method (Zaugg and others, 1995, Lindley and others, 1996).

Replicate Samples Comparing Collection Methods at San Joaquin River near Crows Landing

Three replicate sample sets were collected at San Joaquin River near Crows Landing to see what variability, if any, would be detected between dip samples collected from the dock and integrated grab samples collected from a boat at mid channel (table 5). Thirty-five of the 47 compounds returned nondetection results for all environmental and replicate samples. For carbaryl and malathion, there was only one pair included in the calculations for each of those compounds; therefore, determining a median value is not applicable. Of the ten remaining analytes for which either two or three replicate pairs were evaluated, median RPD values ranged from zero percent for diazinon, metolachlor, and molinate, to a high of 40 percent for atrazine. Maximum RPD percentages for those constituents for which two or three replicate pairs could be evaluated, range from 15 percent for diazinon (three sample sets included in calculations) to a high of 78 percent for cyanazine (three sample sets included in calculations). A comparison of replicate data indicates that there is little variability, overall, between samples collected from the dock and those collected mid channel at this site, and therefore, the data collected by the two methods are comparable.

Table 4. Results of replicate analyses of pesticides or pesticide degradation products, San Joaquin Valley, California

[Results were calculated for replicate pairs where analyte concentration was detected in both samples. Estimated values (E) are included in calculations as detections. Number of significant figures does not reflect analytical method reporting levels. N, number of pairs included in the calculations. n/a, not applicable. µg/L, micrograms per liter]

Analyte (number of detections)	N	Relative difference, in percentage			Difference, in concentration units µg/L		
		Minimum	Maximum	Median	Minimum	Maximum	Median
2,6-Diethylaniline (no detections)	0	n/a	n/a	n/a	n/a	n/a	n/a
Acetochlor (no detections)	0	n/a	n/a	n/a	n/a	n/a	n/a
Alachlor (no detections)	0	n/a	n/a	n/a	n/a	n/a	n/a
Alpha BHC	0	n/a	n/a	n/a	n/a	n/a	n/a
(15 nondetect sets; 1 set with a nondetect and an E value)							
Atrazine	11	0	100	11	0	0.004	0.001
(5 nondetect sets; 4 sets with detections; 7 sets with E values)							
Benfluralin (no detections)	0	n/a	n/a	n/a	n/a	n/a	n/a
Butylate (no detections)	0	n/a	n/a	n/a	n/a	n/a	n/a
Carbaryl	6	0	83	43	0	0.076	0.016
(7 nondetect sets; 6 sets with E values; 3 sets with nondetect and E values)							
Carbofuran	3	0	37	10	0	0.019	0.001
(12 nondetect sets; 3 sets with E values; 1 set with a nondetect and an E value)							
Chlorpyrifos	7	0	33	13	0	0.002	0.001
(5 nondetect sets; 7 sets with detections; 4 sets with nondetect and E values)							
Cyanazine	3	8	17	8	0.001	0.006	0.001
(11 nondetect sets; 1 set with detections; 2 sets with E values; 2 sets with nondetect and E values)							
Dacthal (DCPA)	1	0	0	n/a	0	0	n/a
(15 nondetect sets; 1 set with E values)							
Atrazine, desethyl	4	0	0	0	0	0	0
(9 nondetect sets; 4 sets with E values; 3 sets with nondetect and E values)							
Diazinon	12	0	67	19	0	0.006	0.001
(3 nondetect sets; 6 sets with detections; 4 sets with E values; 2 sets with detection and E value pairs; 1 set with a nondetect and an E value)							
Dieldrin (no detections)	0	n/a	n/a	n/a	n/a	n/a	n/a
Disulfoton (no detections)	0	n/a	n/a	n/a	n/a	n/a	n/a
EPTC	13	0	20	5	0	0.015	0.002
(2 nondetect sets; 12 sets with detections; 1 set with E values; 1 set with a detect and a nondetect)							
Ethalfluralin	1	24	24	n/a	0.006	0.006	n/a
(15 nondetect sets; 1 set with detections)							
Ethoprop (no detections)	0	n/a	n/a	n/a	n/a	n/a	n/a
Fonofos	1	0	0	n/a	0	0	n/a
(15 nondetect sets; 1 set with E values)							
Lindane	2	67	100	83	0.002	0.003	0.0025
(14 nondetect sets; 1 set with E values; 1 set with a detect and an E value)							
Linuron (no detections)	0	n/a	n/a	n/a	n/a	n/a	n/a
Malathion	2	0	25	12.5	0	0.002	0.001
(13 nondetect sets; 2 sets with E values; 1 set with a nondetect and an E value)							
Azinphos-methyl	1	62	62	n/a	0.009	0.009	n/a
(15 nondetect sets; 1 set with E values)							
Parathion, methyl	1	5	5	n/a	0.003	0.003	n/a
(15 nondetect sets; 1 set with detections)							
Metolachlor	15	0	29	6	0	0.054	0.003

Table 4. Results of replicate analyses of pesticides or pesticide degradation products, San Joaquin Valley, California—*Continued*

Analyte (number of detections)	N	Relative difference, in percentage			Difference, in concentration units µg/L		
		Minimum	Maximum	Median	Minimum	Maximum	Median
(14 sets with detections; 1 set with E values; 1 set with a nondetect and an E value)							
Metribuzin	3	0	18	0	0	0.002	0
(12 nondetect sets; 1 set with detections; 1 set with E values; 1 set with a detect and an E value pair; 1 set with a nondetect and an E value)							
Molinate	9	0	24	8	0	0.006	0.001
(7 nondetect sets; 8 sets with detections; 1 set with E values)							
Napropamide	3	0	56	18	0	0.022	0.001
(12 nondetect sets; 2 sets with detections; 1 set with E values; 1 set with a nondetect and an E value)							
p,p'-DDE	1	0	0	n/a	0	0	n/a
(13 nondetect sets; 1 set with E values; 2 sets with nondetects and E values)							
Parathion (no detections)	0	n/a	n/a	n/a	n/a	n/a	n/a
Pebulate	1	22	22	n/a	0.018	0.018	n/a
(14 nondetect sets; 1 set with detections; 1 set with a detect and a nondect)							
Pendimethalin	0	n/a	n/a	n/a	n/a	n/a	n/a
(15 nondetect sets; 1 set with a nondetect and an E value)							
Permethrin (no detections)	0	n/a	n/a	n/a	n/a	n/a	n/a
Phorate (no detections)	0	n/a	n/a	n/a	n/a	n/a	n/a
Prometon	2	0	67	33	0	0.001	0.0005
(12 nondetect sets; 2 sets with E values; 2 sets with nondetect and E values)							
Pronamide	1	0	0	n/a	0	0	n/a
(15 nondetect sets; 1 set with E values)							
	0	n/a	n/a	n/a	n/a	n/a	n/a
Propachlor (no detections)							
Propanil (no detections)	0	n/a	n/a	n/a	n/a	n/a	n/a
Propargite	1	15	15	n/a	0.01	0.01	n/a
(12 nondetect sets; 1 set with detections; 2 sets with detect and nondetect pairs; 1 set with a nondetect and an E value)							
Simazine	14	0	29	9	0	0.007	0.001
(9 sets with detections; 5 sets with E values; 2 sets with nondetect and E values)							
Tebuthiuron	1	0	0	n/a	0	0	n/a
(13 nondetect sets; 1 set with E values; 2 sets with nondetect and E values)							
Terbacil (no detections)	0	n/a	n/a	n/a	n/a	n/a	n/a
Terbufos (no detections)	0	n/a	n/a	n/a	n/a	n/a	n/a
Thiobencarb	4	0	15	7	0	0.001	0.0005
(11 nondetect sets; 4 sets with detections; 1 set with a nondetect and an E value)							
Triallate (no detections)	0	n/a	n/a	n/a	n/a	n/a	n/a
Trifluralin	11	0	50	0	0	0.004	0
(4 sets with detections; 7 sets with E values; 1 nondetect set; 4 sets with nondetect and E values)							

Table 5. Variability of three sample sets from the San Joaquin River near Crows Landing, California, comparing data from grab samples collected at a dock to data from integrated samples collected at mid-channel

[Results were reported for replicate pairs where analyte concentration was detected in both samples. Estimated values (E) are included in calculations as detections. Number of significant figures does not reflect analytical method reporting levels. N, number of pairs included in the calculations. n/a, not applicable. µg/L, micrograms per liter]

Analyte (number of detections)	N	Relative difference (percent)			Difference, in concentration units (µg/L)		
		Minimum	Maximum	Median	Minimum	Maximum	Median
2,6-Diethylaniline (no detections)	0	n/a	n/a	n/a	n/a	n/a	n/a
Acetochlor (no detections)	0	n/a	n/a	n/a	n/a	n/a	n/a
Alachlor (no detections)	0	n/a	n/a	n/a	n/a	n/a	n/a
α-BHC (no detections)	0	n/a	n/a	n/a	n/a	n/a	n/a
Atrazine	3	10	46	40	0.001	0.003	0.003
(1 set with detections; 2 sets with detection and E value pairs)							
Atrazine, desethyl (no detections)	0	n/a	n/a	n/a	n/a	n/a	n/a
Benfluralin (no detections)	0	n/a	n/a	n/a	n/a	n/a	n/a
Butylate (no detections)	0	n/a	n/a	n/a	n/a	n/a	n/a
Carbaryl	1	0	0	n/a	0	0	n/a
(1 nondetect set; 1 set with a nondetect and an E value; 1set with E values)							
Carbofuran (no detections)	0	n/a	n/a	n/a	n/a	n/a	n/a
Chlorpyrifos	3	0	67	12	0	0.003	0.001
(2 sets with detections; 1 set with a detection and E value pair)							
Cyanazine (3 sets with detections)	3	6	78	30	0.005	0.036	0.018
Dacthal (DCPA) (no detections)	0	n/a	n/a	n/a	n/a	n/a	n/a
Diazinon	3	0	15	0	0	0.001	0
(1 set with detections; 1 set with E values; 1 set with a detection an E value)							
Dieldrin (no detections)	0	n/a	n/a	n/a	n/a	n/a	n/a
Disulfoton (no detections)	0	n/a	n/a	n/a	n/a	n/a	n/a
EPTC (3 sets with detections)	3	0	29	7	0	0.043	0.001
Ethalfluralin (no detections)	0	n/a	n/a	n/a	n/a	n/a	n/a
Ethoprop (no detections)	0	n/a	n/a	n/a	n/a	n/a	n/a
Fonofos (no detections)	0	n/a	n/a	n/a	n/a	n/a	n/a
Lindane (no detections)	0	n/a	n/a	n/a	n/a	n/a	n/a
Linuron (no detections)	0	n/a	n/a	n/a	n/a	n/a	n/a
Malathion (2 nondetect sets; 1 set with E values)	1	40	40	n/a	0.002	0.002	n/a
Azinphos-methyl (no detections)	0	n/a	n/a	n/a	n/a	n/a	n/a
Parathion, methyl (no detections)	0	n/a	n/a	n/a	n/a	n/a	n/a
Metolachlor (3 sets with detections)	3	0	16	0	0	0.038	0
Metribuzin (no detections)	0	n/a	n/a	n/a	n/a	n/a	n/a
Molinate (1 nondetect set; 2 sets with detections)	2	0	29	0	0	0.001	0
Napropamide (no detections)	0	n/a	n/a	n/a	n/a	n/a	n/a
p,p′-DDE (no detections)	0	n/a	n/a	n/a	n/a	n/a	n/a
Parathion (no detections)	0	n/a	n/a	n/a	n/a	n/a	n/a
Pebulate (no detections)	0	n/a	n/a	n/a	n/a	n/a	n/a
Pendimethalin	2	5	46	26	0.001	0.006	0.0035
(2 sets with detections; 1 set with a detect and nondetect pair)							
Permethrin (no detections)	0	n/a	n/a	n/a	n/a	n/a	n/a
Phorate (no detections)	0	n/a	n/a	n/a	n/a	n/a	n/a
Prometon (no detections)	0	n/a	n/a	n/a	n/a	n/a	n/a

Table 5. Variability of three sample sets from the San Joaquin River near Crows Landing, California, comparing data from grab samples collected at a dock to data from integrated samples collected at mid-channel—*Continued*

Analyte (number of detections)	N	Relative difference (percent)			Difference, in concentration units (µg/L)		
		Minimum	Maximum	Median	Minimum	Maximum	Median
Pronamide (no detections)	0	n/a	n/a	n/a	n/a	n/a	n/a
Propachlor (no detections)	0	n/a	n/a	n/a	n/a	n/a	n/a
Propanil (no detections)	0	n/a	n/a	n/a	n/a	n/a	n/a
Propargite (no detections)	0	n/a	n/a	n/a	n/a	n/a	n/a
Simazine (3 sets with E values)	3	0	18	12	0	0.001	0.001
Tebuthiuron (no detections)	0	n/a	n/a	n/a	n/a	n/a	n/a
Terbacil (no detections)	0	n/a	n/a	n/a	n/a	n/a	n/a
Terbufos (no detections)	0	n/a	n/a	n/a	n/a	n/a	n/a
Thiobencarb (no detections)	0	n/a	n/a	n/a	n/a	n/a	n/a
Triallate (no detections)	0	n/a	n/a	n/a	n/a	n/a	n/a
Trifluralin (3 sets with detections)	3	8	21	13	0.001	0.003	0.002

Comparison of Sample-Collection Methods

Four sample sets were collected and submitted to NWQL for analysis to determine potential variability between samples collected according to USGS protocol and those collected according to the California RWQCB sampling methodology (table 6). The sites used for the comparisons were Merced River at River Road Bridge near Newman, Orestimba Creek at River Road near Crows Landing, Del Puerto Creek at Vineyard Road near Patterson, and San Joaquin River near Vernalis.

The RWQCB personnel collected grab samples from the banks of each of the four sites at the same time that samples were being collected by USGS personnel. RWQCB protocol calls for sample collection by submerging a clean, amber colored, 1-liter glass bottle into the stream channel from the bank. The sample bottle was filled, capped immediately, iced, and shipped overnight to the NWQL. Research conducted by the RWQCB at these locations prior to sampling included reconnaissance of the sites, determination of upstream characteristics, and comparison of water quality data collected by various methods. The RWQCB research concluded that waters at these sites were well mixed and that a homogeneous sample, representative of the channel, could be collected for pesticide analysis from the bank at each of these sites.

Twenty-eight of the 47 compounds analyzed were not detected in any of the samples. Two compounds, lindane and propanil, were not evaluated owing to nondetection results or nondetections paired with a detected or estimated value. Of the remaining 17 analytes, only one replicate pair could be evaluated for chlorpyrifos, cyanazine, atrazine desethyl, malathion, azinphos-methyl, parathion methyl, molinate, napropamide, and *p,p*-DDE and, therefore, determination of a median value for those compounds is not applicable. Eight of the 47 compounds had two to four replicate pairs that were evaluated. Of those, the median RPD values range from zero to 38 percent and maximum RPD results range from 9 to 53 percent.

Variability between samples collected by the two agencies was low overall, which suggests that the data collected by the two methods are comparable.

Spiked Samples

Six samples, collected at select sites, were spiked with 47 pesticide compounds and submitted to the NWQL for analysis. Median and mean spike recovery data are included as percentages in table 7 for compounds with detection results. Recoveries were not calculated for those compounds for which detection values were reported as estimates (E code). Mean recoveries were included so that recovery data from this study could be compared with the mean recoveries obtained during the methods of analysis study (Zaugg and others, 1995, Lindley and others, 1996). Table 7 shows median recoveries ranging from 47 percent for permethrin to 120 percent for metolachlor, and mean recoveries ranging from 47 percent for permethrin to 115 percent for linuron. The methods of analysis study shows similar recovery results from seven determinations

Table 6. Variability of four sample sets comparing USGS sample collection methods with those of the State of California Regional Water Quality Control Board

[Results were calculated for replicate pairs where analyte concentration was detected in both samples. Estimated values "E" were included in calculations as detections. Number of significant figures does not reflect analytical method reporting levels. N, number of pairs included in the calculations. n/a, not applicable. All samples were analyzed by the USGS National Water Quality Laboratory, Denver, Colorado.The sites included in this comparison are: Merced River at River Road Bridge near Newman, Orestimba Creek at River Road near Crows Landing, Del Puerto Creek at Vineyard Road near Patterson, and San Joaquin River near Vernalis, California. µg/L, microgram per liter]

Analyte	N	Relative difference (percent)			Difference, in concentration units (µg/L)		
		Minimum	Maximum	Median	Minimum	Maximum	Median
2,6-Diethylaniline (no detections)	0	n/a	n/a	n/a	n/a	n/a	n/a
Acetochlor (no detections)	0	n/a	n/a	n/a	n/a	n/a	n/a
Alachlor (no detections)	0	n/a	n/a	n/a	n/a	n/a	n/a
Alpha BHC (no detections)	0	n/a	n/a	n/a	n/a	n/a	n/a
Atrazine	3	0	9	0	0	0.001	0
(1 nondetect set; 2 sets with detections; 1 set with E values)							
Atrazine, desethyl	1	0	29	0	0	0.001	0
(1 nondetect set; 1 set with E values; 2 sets with nondetect and E value pairs)							
Azinphos-methyl	1	37	37	n/a	0.024	0.024	n/a
(3 nondetect sets; 1 set with E values)							
Benfluralin (no detections)	0	n/a	n/a	n/a	n/a	n/a	n/a
Butylate (no detections)	0	n/a	n/a	n/a	n/a	n/a	n/a
Carbaryl	2	0	40	0	0	0.003	0
(2 nondetect sets; 2 sets with E values)							
Carbofuran (no detections)	0	n/a	n/a	n/a	n/a	n/a	n/a
Chlorpyrifos	1	0	30	0	0	0.009	0
(3 nondetect sets; 1 set with detections)							
Cyanazine	1	0	0	0	0	0	0
(3 nondetect sets; 1 set with detections)							
Dacthal (DCPA) (no detections)	0	n/a	n/a	n/a	n/a	n/a	n/a
p,p′-DDE	1	10	10	n/a	0.001	0.001	n/a
(2 nondetect sets; 1 set with detections; 1 set with a detect and a nondetect)							
Diazinon	3	5	22	11	0.001	0.001	0.001
(1 nondetect set; 2 sets with detections; 1 set with E values)							
Dieldrin (no detections)	0	n/a	n/a	n/a	n/a	n/a	n/a
Disulfoton (no detections)	0	n/a	n/a	n/a	n/a	n/a	n/a
EPTC	3	0	15	12	0	0.005	0.003
(3 sets with detections; 1 set with a detect and a nondetect)							
Ethalfluralin (no detections)	0	n/a	n/a	n/a	n/a	n/a	n/a
Ethoprop (no detections)	0	n/a	n/a	n/a	n/a	n/a	n/a
Fonofos (no detections)	0	n/a	n/a	n/a	n/a	n/a	n/a
Lindane	0	n/a	n/a	n/a	n/a	n/a	n/a
(3 nondetect sets; 1 set with a detect and a nondetect)							
Linuron (no detections)	0	n/a	n/a	n/a	n/a	n/a	n/a
Malathion	1	53	53	n/a	0.015	0.015	n/a
(3 nondetect sets; 1 set with a detect and an E value)							
Metolachlor	4	0	9	4	0	0.013	0.005
(3 sets with detections; 1 set with E values)							
Metribuzin (no detections)	0	n/a	n/a	n/a	n/a	n/a	n/a
Molinate	1	15	15	n/a	0.006	0.006	n/a
(2 nondetect sets; 1 set with detections; 1 set with a detect and a nondetect)							

Table 6. Variability of four sample sets comparing USGS sample collection methods with those of the State of California Regional Water Quality Control Board—*Continued*

Analyte	N	Relative difference (percent)			Difference, in concentration units (µg/L)		
		Minimum	Maximum	Median	Minimum	Maximum	Median
Napropamide	1	22	22	n/a	0.001	0.001	n/a
(3 nondetect sets; 1 set with E values)							
Parathion (no detections)	0	n/a	n/a	n/a	n/a	n/a	n/a
Parathion-methyl	1	39	39	n/a	0.011	0.011	n/a
(3 nondetect sets; 1 set with detections)							
Pebulate (no detections)	0	n/a	n/a	n/a	n/a	n/a	n/a
Pendimethalin (no detections)	0	n/a	n/a	n/a	n/a	n/a	n/a
Permethrin (no detections)	0	n/a	n/a	n/a	n/a	n/a	n/a
Phorate (no detections)	0	n/a	n/a	n/a	n/a	n/a	n/a
Prometon (no detections)	0	n/a	n/a	n/a	n/a	n/a	n/a
Pronamide (no detections)	0	n/a	n/a	n/a	n/a	n/a	n/a
Propachlor (no detections)	0	n/a	n/a	n/a	n/a	n/a	n/a
Propanil	0	n/a	n/a	n/a	n/a	n/a	n/a
(3 nondetect sets; 1 set with a nondetect and an E value)							
Propargite	2	26	49	38	0.025	0.122	0.0735
(2 nondetect sets; 2 sets with detections)							
Simazine	4	11	22	15	0.001	0.003	0.002
(2 sets with detections; 2 sets with E values)							
Tebuthiuron (no detections)	0	n/a	n/a	n/a	n/a	n/a	n/a
Terbacil (no detections)	0	n/a	n/a	n/a	n/a	n/a	n/a
Terbufos (no detections)	0	n/a	n/a	n/a	n/a	n/a	n/a
Thiobencarb (no detections)	0	n/a	n/a	n/a	n/a	n/a	n/a
Triallate (no detections)	0	n/a	n/a	n/a	n/a	n/a	n/a
Trifluralin (2 sets with detections; 2 sets with E values)	4	0	13	6	0	0.004	0.001

of the compounds at 0.1 µg/L in surface water samples and six determinations of the compounds at 0.1 µg/L in reagent water. This general similarity in the amounts of spike recovered in the samples collected in this study with those collected in the methods of analysis study (Zaugg and others, 1995) indicates that the pesticides are recovered in a similar amount, and that no effects of the sample matrix are limiting the recovery of the pesticides.

Recovery values could not be determined for five compounds in table 7: carbaryl, carbofuran, atrazine desethyl, azinphos-methyl, and terbacil because all values for spiked samples were estimated. The same compounds have previously been described as "pesticides having poor performance and reported with an E code" (Zaugg and others, 1995).

Surrogates Added to All Samples

Two surrogate compounds—diazinon-d_{10} and alpha HCH-d_6 (hexachlorocyclohexane)—were added to 83 samples submitted to the NWQL for analysis (table 8). Median recoveries were 105 and 96 percent, respectively, and the mean recoveries were 106 and 95 percent, respectively. The mean surrogate recovery results from this study compare favorably with results obtained during the methods of analysis study for which recovery values for diazinon-d_{10} were reported as 88 percent in 6 reagent water samples (at 0.1 µg/L) and 85 percent in 7 surface water samples (at 0.1 µg/L). Recovery values for alpha HCH-d_6 were reported as 90 percent in 6 reagent water samples and 84 percent in 7 surface water samples (both at 0.1 µg/L) (Zaugg and others, 1995).

In summary, the results of field level quality control sampling showed that the samples did not have any bias with respect to contamination, the analyses were precise within the guidelines previously documented (Zaugg and others, 1995, Lindley and others, 1996), and the recoveries of pesticides spiked into the water sample were within the levels expected.

Table 7. Recovery of pesticide matrix spikes

.[Recovery data are given in percentages. Spike recovery was calculated according to protocols of the National Water quality Laboratory (Mueller and others, 1997). Spike recovery calculations were not included for estimated (E) values. No. samples, number of samples where recovery values could be calculated]

Compound (explanation for fewer than 6 samples)	Number of samples	Spike recovery in percent			
		Minimum	Maximum	Median	Mean
2,6-Diethylaniline	6	66	108	89	89
Acetochlor	6	93	126	112	110
Alachlor	6	92	122	111	109
Alpha BHC	6	73	106	89	89
Atrazine (E values for 4 environmental samples)	2	91	106	99	99
Atrazine, desethyl (E values for 6 spiked samples)	0	Spike recovery could not be calculated because all concentrations were estimated			
Azinphos-methyl (E values for 6 spiked samples)	0	Spike recovery could not be calculated because all concentrations were estimated			
Benfluralin	6	45	121	66	73
Butylate	6	83	113	89	93
Carbaryl (E values for 6 spiked samples)	0	Spike recovery could not be calculated because all concentrations were estimated			
Carbofuran (E values for 6 spiked samples)	0	Spike recovery could not be calculated because all concentrations were estimated			
Chlorpyrifos (E values for 3 environmental samples)	3	79	95	89	88
Cyanazine (E values for 2 environmental samples)	4	85	118	110	106
Dacthal (DCPA)	6	89	134	98	103
p,p'-DDE	6	46	67	61	57
Diazinon (E value for 1 environmental sample)	5	88	125	107	106
Dieldrin	6	86	103	98	96
Disulfoton (E values for 2 spiked samples)	4	58	100	61	70
EPTC	6	74	100	83	86
Ethalfluralin	6	59	122	75	82
Ethoprop	6	73	122	89	91
Fonofos	6	83	120	101	101
Lindane	6	90	116	98	101
Linuron	6	89	180	107	115
Malathion	6	75	134	96	98
Parathion, methyl	6	82	164	108	114
Metolachlor	6	86	129	120	113
Metribuzin	6	76	100	87	89
Molinate	6	79	114	95	94
Napropamide	6	92	116	103	103
Parathion	6	81	180	102	109
Pebulate	6	86	114	93	95
Pendimethalin	6	60	126	81	87
Permethrin	6	38	59	47	47
Phorate	6	49	101	65	70
Prometon	6	74	136	91	95
Pronamide	6	89	126	97	101
Propachlor	6	94	143	104	111
Propanil	6	88	142	117	112
Propargite	6	71	98	91	87

Table 7. Recovery of pesticide matrix spikes—*Continued*

Compound (explanation for fewer than 6 samples)	Number of samples	Spike recovery in percent			
		Minimum	Maximum	Median	Mean
Simazine (E values for 3 environmental samples)	3	89	121	97	102
Tebuthiuron	6	96	141	107	114
Terbacil (E values for 6 spiked samples)	0	Spike recovery could not be calculated because all concentrations were estimated			
Terbufos (E value for 1 spiked sample)	5	74	102	85	87
Thiobencarb (E value for 1 environmental sample)	5	101	129	111	112
Triallate	6	83	103	97	95
Trifluralin (E value for 1 environmental sample)	5	46	111	71	75

Table 8. Recovery of surrogate compounds

[The minimum, maximum, and median values are in percentage recovered]

Surrogate compound	Samples	Minimum	Maximum	Median	Mean	Standard deviation
Diazinon-d_{10}	83	81	139	105	106	11
alpha HCH-d_6 (hexachlorocyclohexane)	83	68	119	96	95	9

RESULTS AND DISCUSSION

Discharge and Pesticide Loads

Plots of either continuous or instantaneous stream discharge, and concentrations of diazinon and chlorpyrifos for the period of record (April through August, 2001) are shown in figures 3 through 14. Records of continuous discharge were obtained when the sampling site was co-located with a gaging station, but instantaneous discharges were obtained at sites without stream flow gages. The instantaneous stream discharge, in all cases, was measured at the time of collection of water samples for pesticide analysis. The larger rivers, such as the San Joaquin, Merced, Tuolumne, and Stanislaus, show small decreases of stream discharge in the early part of the study (April and May) and relatively stable flow conditions thereafter. The higher discharges at the start of the study are attributed to the end of the snowmelt runoff season or to managed releases of water, and the stable discharges in late spring through summer are attributed to managed releases of water for irrigation and(or) to meet water quality standards for salinity in downstream bodies of water. Higher flows of the San Joaquin River during April 15 through May 15 were the result of managed releases of water from the Sierran reservoirs for fisheries management.

Results of pesticide detection frequency at specific sites are shown in tables 9 through 20. For the farthest upstream site on the San Joaquin River (San Joaquin River near Stevinson), only five pesticides were detected at a frequency of 50 percent or higher. Diazinon and chlorpyrifos were detected at a frequency of 20 percent and 30 percent, respectively. Pesticides detected at higher frequency were all herbicides (atrazine, cyanazine, EPTC, metolachlor, and simazine). These herbicides were detected at a frequency of 90 percent or greater. The maximum, minimum and median concentrations of pesticide detections also are given in the tables. Because diazinon and chlorpyrifos were detected at a frequency of less than 50 percent, the median concentrations are the respective method reporting limits. Maximum concentrations of most detected pesticides for the San Joaquin River near Stevinson (table 9) site tended to be low. The maximum concentrations of two pesticides, cyanazine and metolachlor, exceeded 1 µg/L. The highest measured concentration of any pesticide was for cyanazine, at 4.14 µg/L, although the median concentration of cyanazine was only 0.025 µg/L.

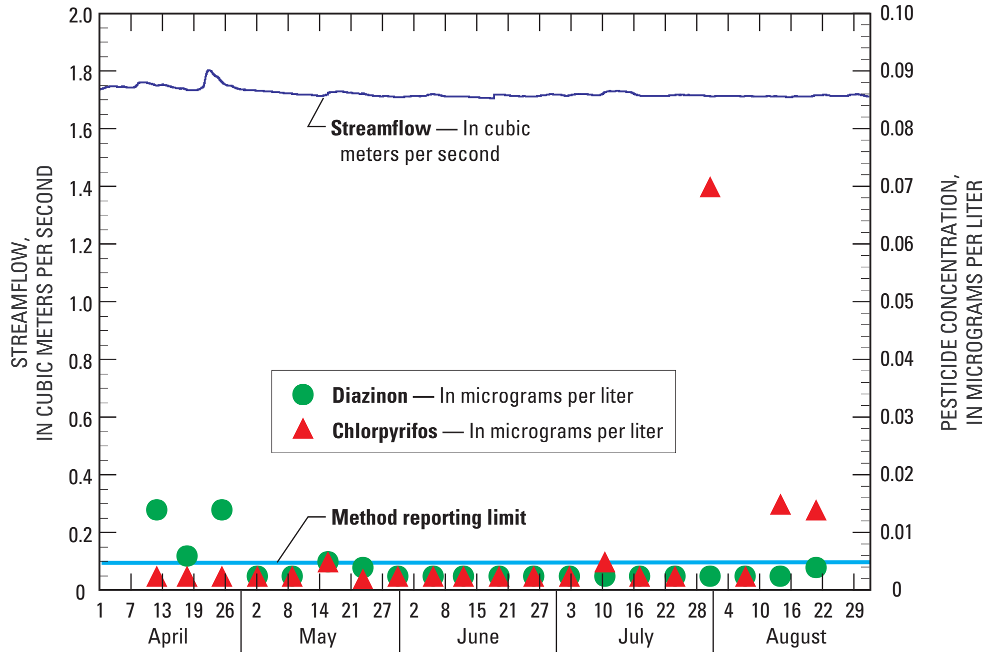


Figure 3. Streamflow, and diazinon and chlorpyrifos concentrations, for the San Joaquin River at Stevinson, California, sampling site for 2001.

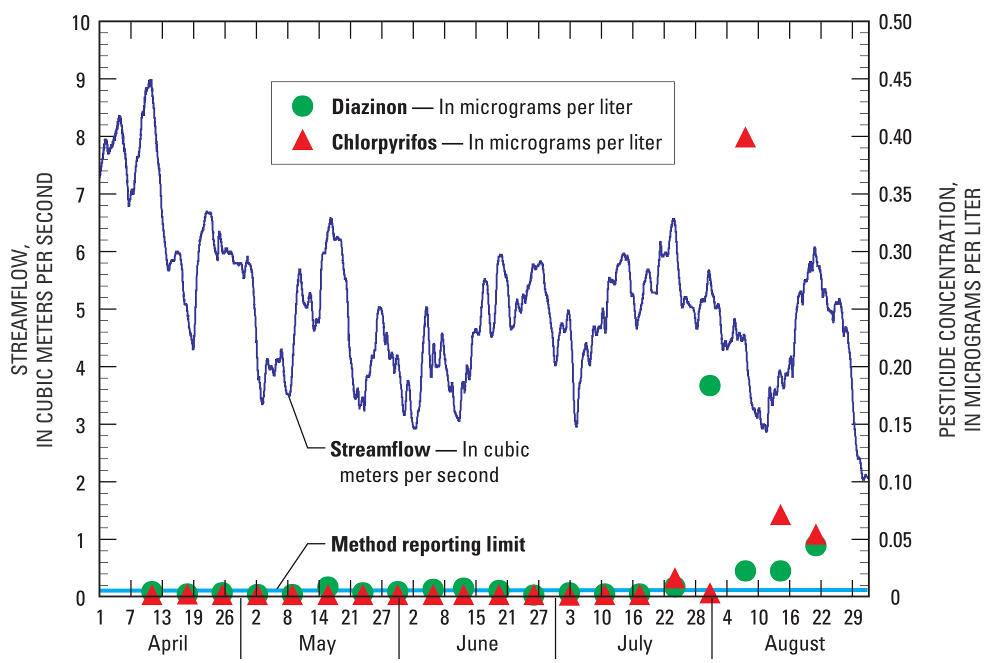


Figure 4. Streamflow, and diazinon and chlorpyrifos concentrations, for the Salt Slough at Highway 165 near Stevinson, California, sampling site for 2001.

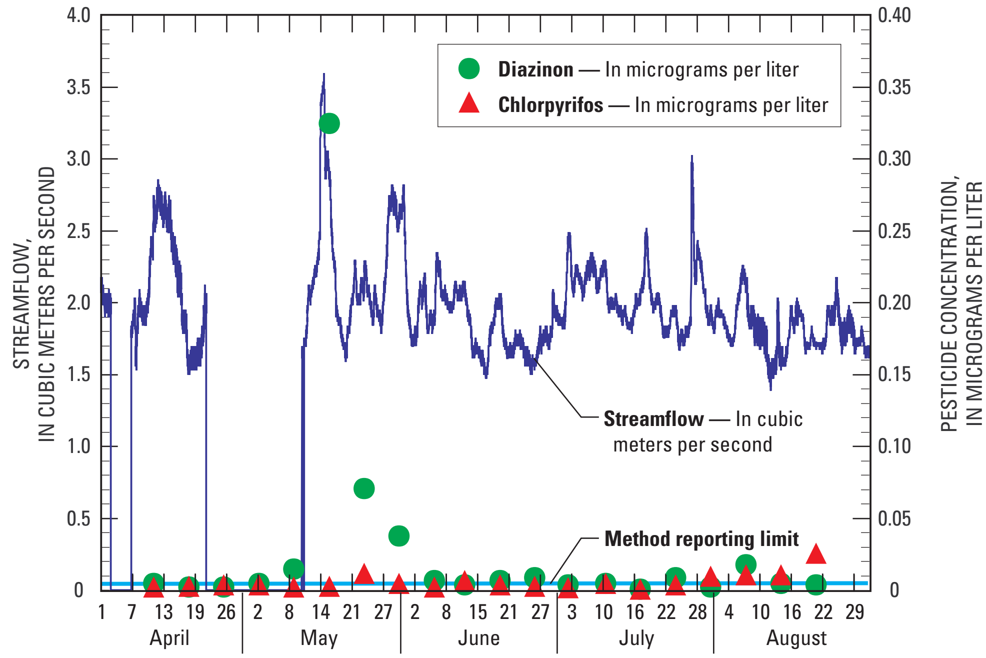


Figure 5. Streamflow, and diazinon and chlorpyrifos concentrations, for the Mud Slough near Gustine, California, sampling site for 2001.

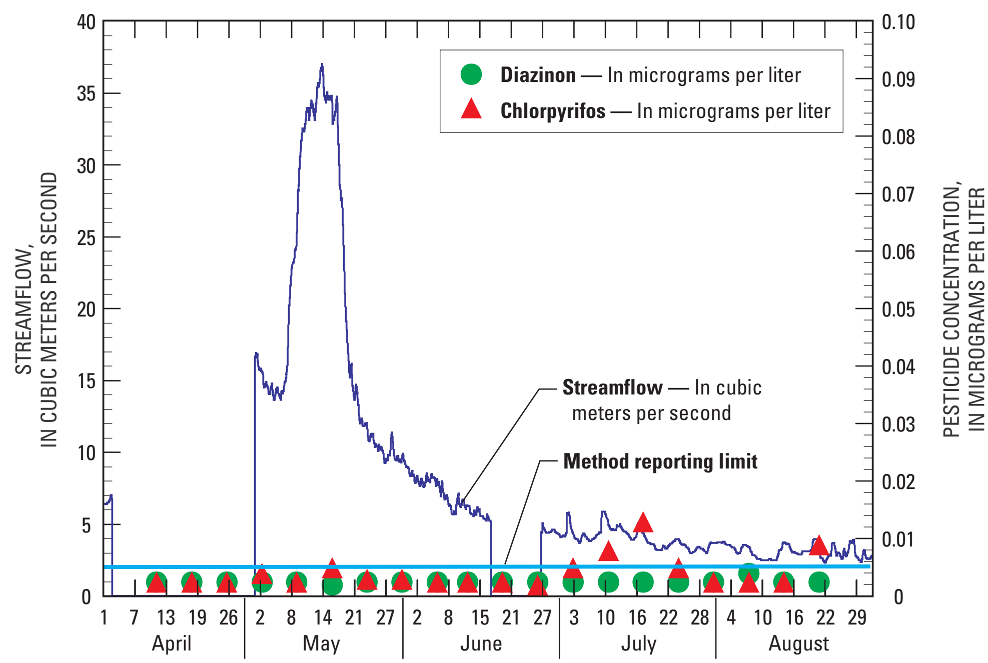


Figure 6. Streamflow, and diazinon and chlorpyrifos concentrations, for the Merced River at River Road Bridge near Newman, California, sampling site for 2001.

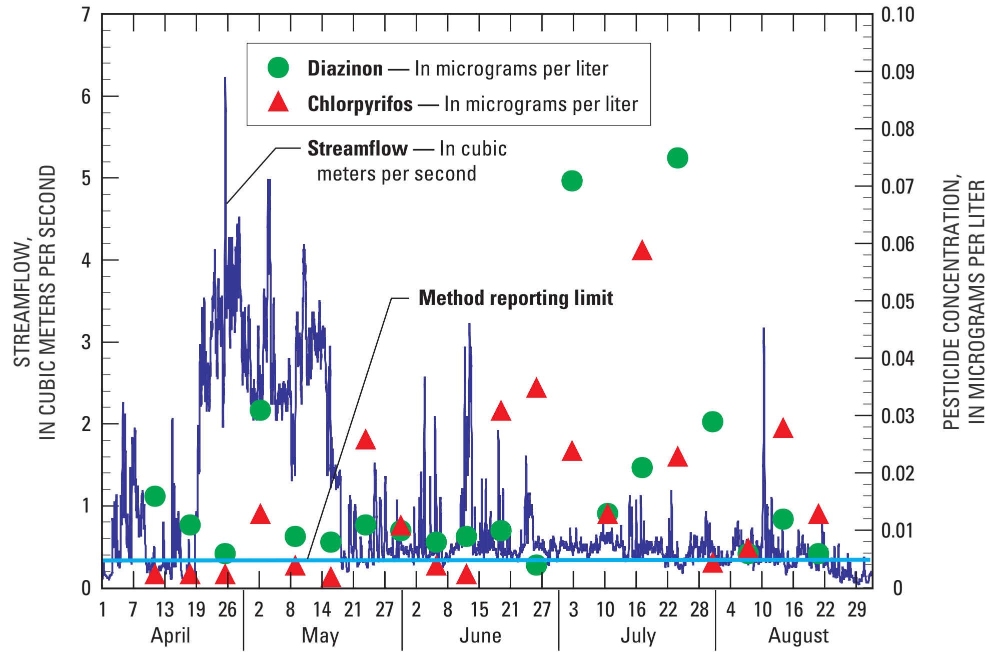


Figure 7. Streamflow, and diazinon and chlorpyrifos concentrations, for the Orestimba Creek at River Road near Crows Landing, California, sampling site for 2001.

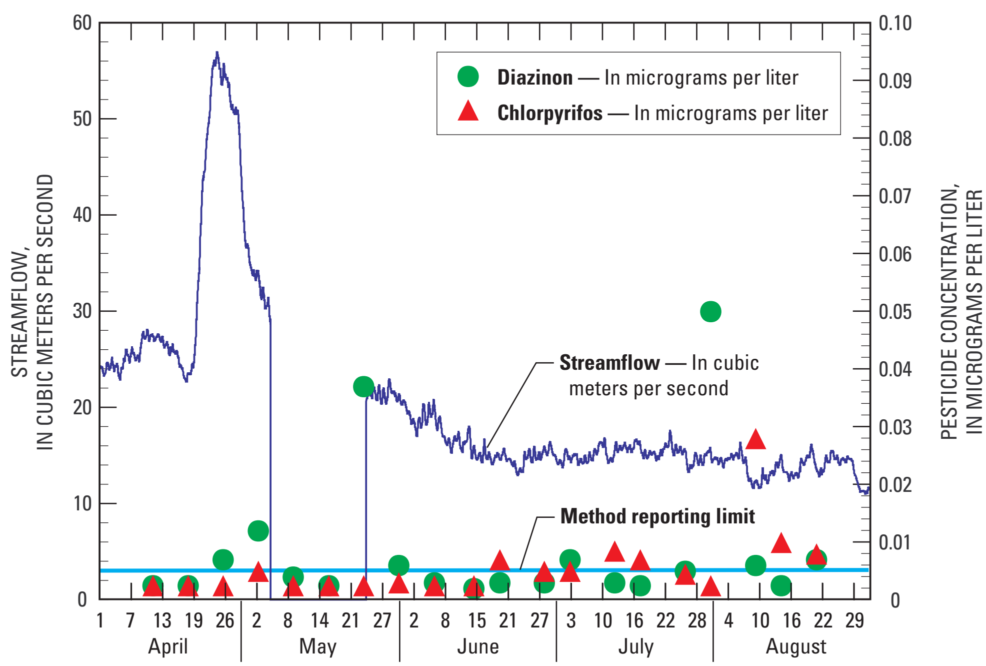


Figure 8. Streamflow, and diazinon and chlorpyrifos concentrations, for the San Joaquin River near Crows Landing, California, sampling site for 2001.

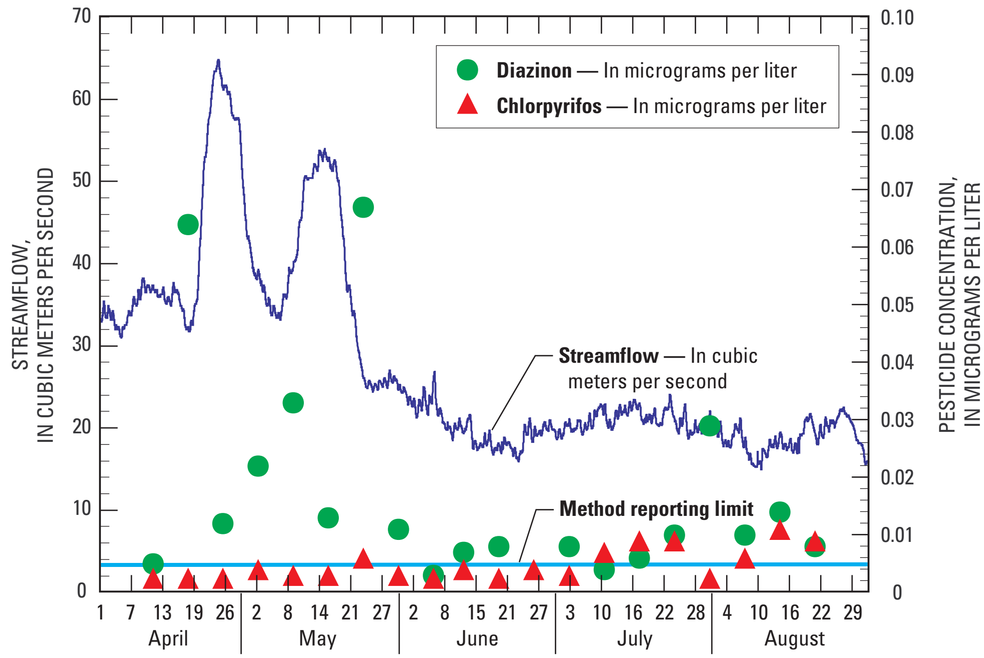


Figure 9. Streamflow, and diazinon and chlorpyrifos concentrations, for the San Joaquin River at Patterson Bridge near Patterson, California, sampling site for 2001.

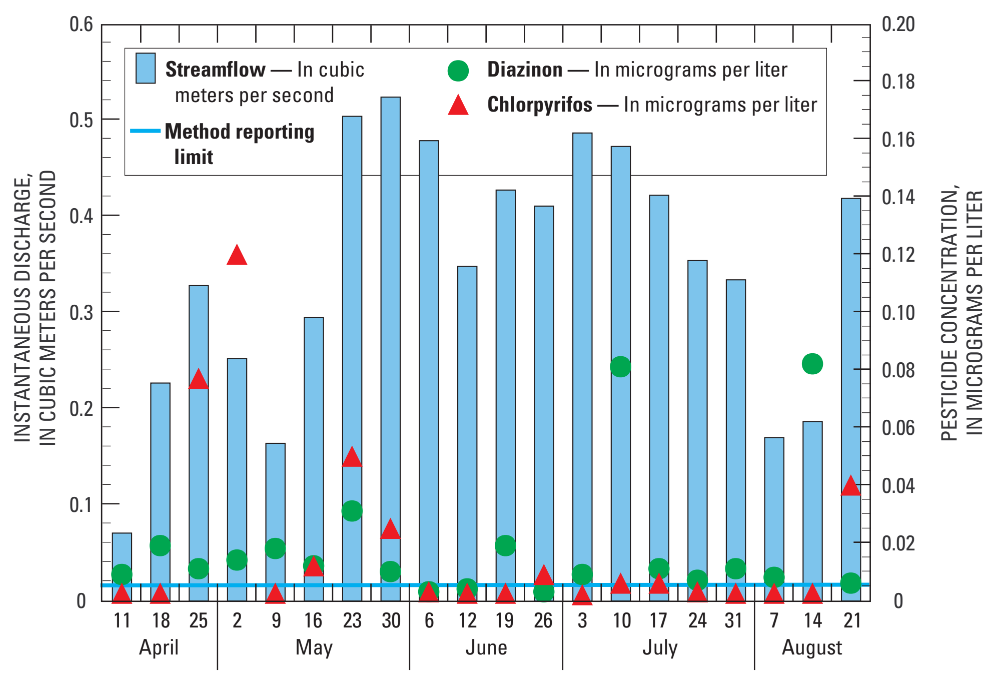


Figure 10. Streamflow, and diazinon and chlorpyrifos concentrations, for the Del Puerto Creek at Vineyard Road near Patterson, California, sampling site for 2001.

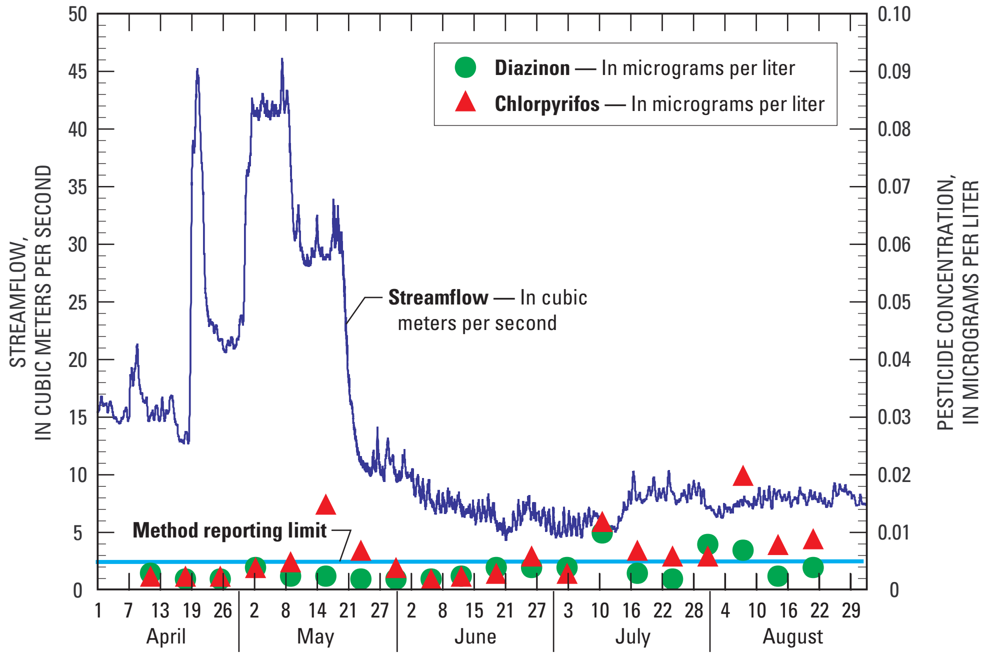


Figure 11. Streamflow, and diazinon and chlorpyrifos concentrations, for the Tuolumne River at Shiloh Road Bridge near Grayson, California, sampling site for 2001.

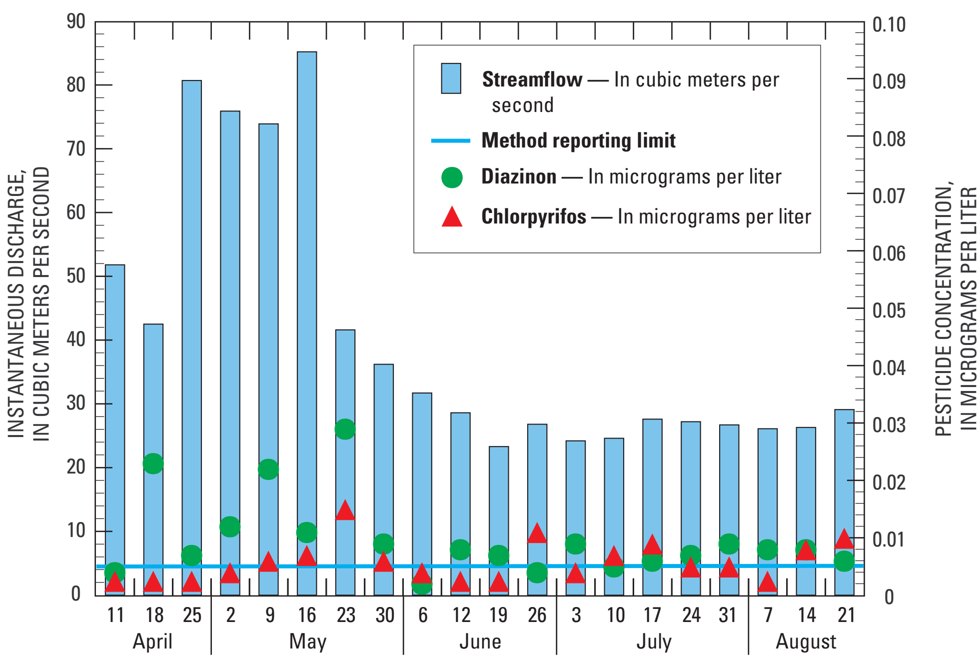


Figure 12. Streamflow, and diazinon and chlorpyrifos concentrations, for the San Joaquin River at Maze Road Bridge near Modesto, California, sampling site for 2001.

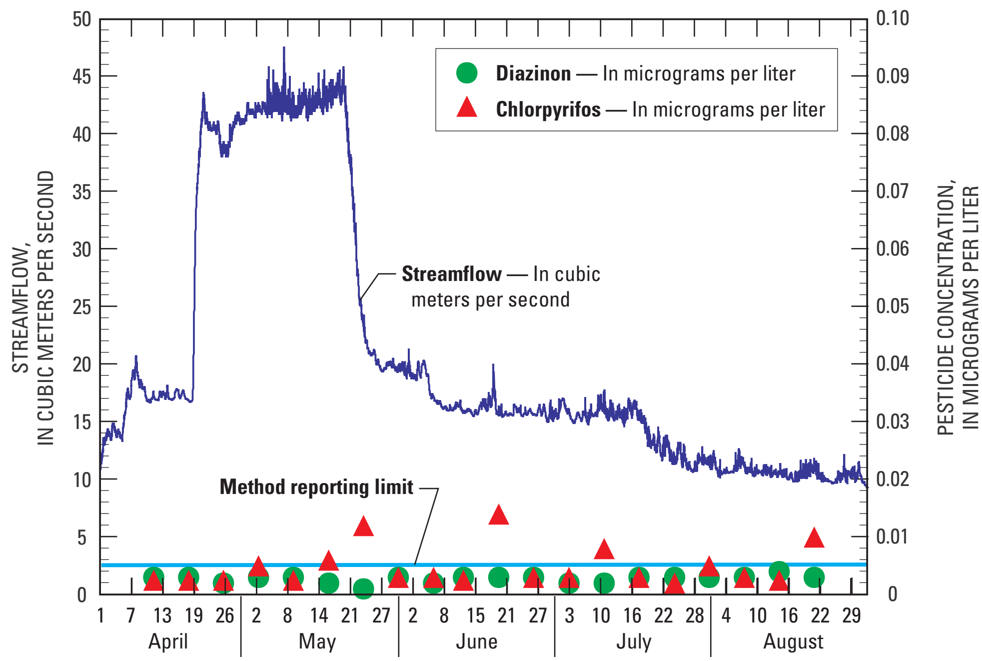


Figure 13. Streamflow, and diazinon and chlorpyrifos concentrations, for the Stanislaus River at Caswell State Park near Ripon, California, sampling site for 2001.

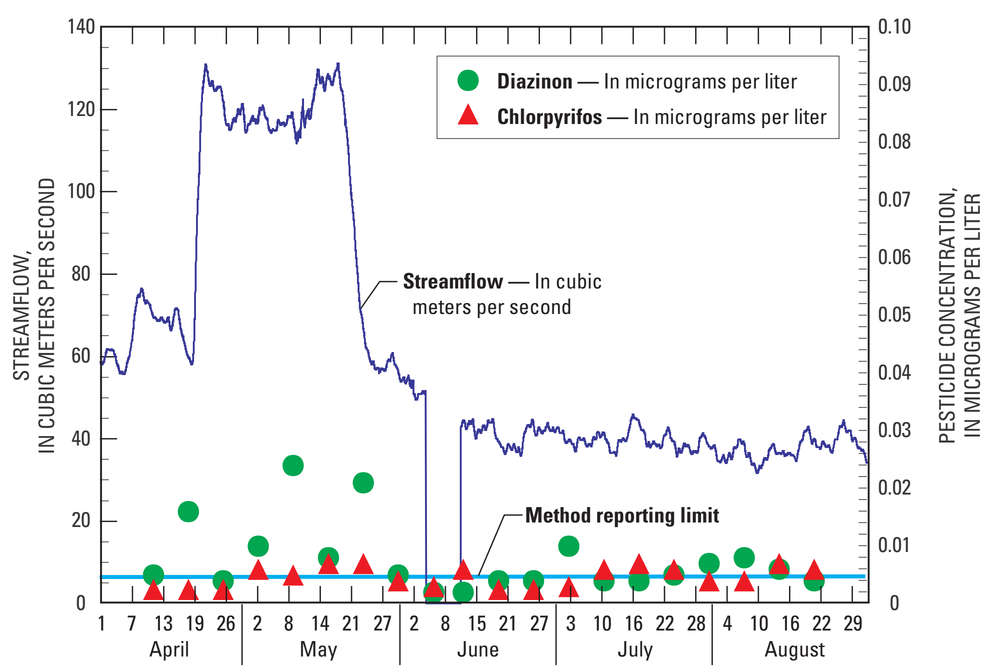


Figure 14. Streamflow, and diazinon and chlorpyrifos concentrations, for the San Joaquin River near Vernalis, California, sampling site for 2001.

Table 9. Frequency of occurrence of pesticides, San Joaquin River at Stevinson, California

[The median concentrations denoted with a less than sign (<) indicate that the detection frequency was less than 50 percent and therefore, the median concentration is the detection limit. Concentrations are in micrograms per liter. D, degradation product; H, herbicide; I, insecticide; e, estimated concentration]

Pesticide	Type of pesticide	Maximum concentration	Minimum concentration	Median concentration	Detection frequency (percent)
2,6-Diethylaniline	D	<0.002	<0.002	<0.002	0
Acetochlor	H	<0.004	<0.004	<0.004	0
Alachlor	H	<0.002	<0.002	<0.002	0
α-BHC	I	<0.005	<0.005	<0.005	0
Atrazine	H	0.016	e0.003	e0.007	95
Atrazine, desethyl	D	e0.006	e0.001	<0.006	35
Benfluralin	H	<0.01	<0.01	<0.01	0
Butylate	H	<0.002	<0.002	<0.002	0
Carbaryl	I	e0.035	e0.035	<0.041	5
Carbofuran	I	e0.011	e0.005	<0.02	15
Chlorpyrifos	I	0.014	e0.002	<0.005	20
Cyanazine	H	4.14	e0.013	0.025	90
Dacthal (DCPA)	H	e0.001	e0.001	<0.003	5
p,p′-DDE	D	0.003	0.003	<0.003	5
Diazinon	I	0.014	e0.004	<0.005	30
Dieldrin	H	<0.005	<0.005	<0.005	0
Disulfoton	I	<0.021	<0.021	<0.021	0
EPTC	H	0.156	0.005	0.012	100
Ethalfluralin	H	<0.009	<0.009	<0.009	0
Ethoprop	I	e0.004	e0.004	<0.005	5
Fonofos	I	<0.003	<0.003	<0.003	0
Lindane	I	<0.004	<0.004	<0.004	0
Linuron	H	<0.035	<0.035	<0.035	0
Malathion	I	<0.027	<0.027	<0.027	0
Azinphos-methyl	I	<0.05	<0.05	<0.05	0
Parathion, methyl	I	<0.006	<0.006	<0.006	0
Metolachlor	H	1.1	e0.009	0.172	100
Metribuzin	H	<0.006	<0.006	<0.006	0
Molinate	H	0.071	0.006	<0.002	20
Napropamide	H	<0.007	<0.007	<0.007	0
Parathion	I	<0.007	<0.007	<0.007	0
Pebulate	H	<0.002	<0.002	<0.002	0
Pendimethalin	H	<0.01	<0.01	<0.01	0
Permethrin	I	<0.006	<0.006	<0.006	0
Phorate	I	<0.011	<0.011	<0.011	0
Prometon	H	e0.006	e0.001	<0.015	20
Pronamide	H	<0.004	<0.004	<0.004	0
Propachlor	H	<0.01	<0.01	<0.01	0
Propanil	H	<0.011	<0.011	<0.011	0
Propargite	I	<0.023	<0.023	<0.023	0
Simazine	H	0.108	e0.004	0.014	100
Tebuthiuron	H	e0.005	e0.003	<0.016	10
Terbacil	H	<0.034	<0.034	<0.034	0
Terbufos	I	<0.017	<0.017	<0.017	0
Thiobencarb	H	<0.005	<0.005	<0.005	0
Triallate	H	<0.002	<0.002	<0.002	0
Trifluralin	H	e0.006	e0.003	<0.009	20

Table 10. Frequency of occurrence of pesticides at Salt Slough at Hwy 165, Stevinson, California

[The median concentrations denoted with a less than sign (<) indicate that the detection frequency was less than 50 percent and therefore, the median concentration is the detection limit. Concentrations are in micrograms per liter. D, degradation product; H, herbicide; I, insecticide; e, estimated concentration]

Pesticide	Type of pesticide	Maximum concentration	Minimum concentration	Median concentration	Detection frequency (percent)
2,6-Diethylaniline	D	<0.002	<0.002	<0.002	0
Acetochlor	H	0.004	0.004	<0.004	5
Alachlor	H	<0.002	<0.002	<0.002	0
Alpha BHC	I	<0.005	<0.005	<0.005	0
Atrazine	H	0.02	e0.002	0.007	85
Atrazine, desethyl	D	e0.005	e0.002	<0.006	20
Benfluralin	H	e0.007	e0.007	<0.01	5
Butylate	H	<0.002	<0.002	<0.002	0
Carbaryl	I	e0.236	e0.004	e0.018	90
Carbofuran	I	e0.529	e0.009	<0.02	50
Chlorpyrifos	I	0.4	e0.002	<0.005	30
Cyanazine	H	0.886	e0.006	e0.018	55
Dacthal (DCPA)	H	e0.002	e0.001	<0.003	20
p,p'-DDE	D	<0.003	<0.003	<0.003	0
Diazinon	I	0.184	e0.002	0.005	90
Dieldrin	H	<0.005	<0.005	<0.005	0
Disulfoton	I	<0.021	<0.021	<0.021	0
EPTC	H	2.24	0.006	0.03	95
Ethalfluralin	H	<0.009	<0.009	<0.009	0
Ethoprop	I	<0.005	<0.005	<0.005	0
Fonofos	I	<0.003	<0.003	<0.003	0
Lindane	I	<0.004	<0.004	<0.004	0
Linuron	H	<0.035	<0.035	<0.035	0
Malathion	I	e0.012	e0.004	<0.027	25
Azinphos-methyl	I	<0.05	<0.05	<0.05	0
Parathion, methyl	I	<0.006	<0.006	<0.006	0
Metolachlor	H	0.51	e0.01	0.165	100
Metribuzin	H	<0.01	<0.006	<0.006	0
Molinate	H	0.018	0.002	0.004	50
Napropamide	H	<0.007	<0.007	<0.007	0
Parathion	I	<0.007	<0.007	<0.007	0
Pebulate	H	0.059	0.011	<0.002	15
Pendimethalin	H	e0.004	e0.004	<0.01	5
Permethrin	I	<0.006	<0.006	<0.006	0
Phorate	I	<0.011	<0.011	<0.011	0
Prometon	H	e0.003	e0.002	<0.015	15
Pronamide	H	0.041	e0.003	<0.004	10
Propachlor	H	e0.001	e0.001	<0.01	5
Propanil	H	<0.011	<0.011	<0.011	0
Propargite	I	0.037	0.037	<0.023	5
Simazine	H	0.065	e0.004	0.016	100
Tebuthiuron	H	e0.006	e0.003	<0.016	20
Terbacil	H	<0.034	<0.034	<0.034	0
Terbufos	I	<0.017	<0.017	<0.017	0
Thiobencarb	H	0.013	0.005	<0.005	25
Triallate	H	<0.002	<0.002	<0.002	0
Trifluralin	H	0.332	0.016	0.04	100

Table 11. Frequency of occurrence of pesticides at Mud Slough near Gustine, California

[The median concentrations denoted with a less than sign (<) indicate that the detection frequency was less than 50 percent and therefore, the median concentration is the detection limit. Concentrations are in micrograms per liter. D, degradation product; H, herbicide; I, insecticide; e, estimated concentration]

Pesticide	Type of Pesticide	Maximum concentration	Minimum concentration	Median concentration	Detection frequency (percent)
2,6-Diethylaniline	D	<0.002	<0.002	<0.002	0
Acetochlor	H	<0.004	<0.004	<0.004	0
Alachlor	H	0.003	0.003	<0.002	5
α-BHC	I	<0.005	<0.005	<0.005	0
Atrazine	H	0.019	e0.006	0.01	100
Atrazine, desethyl	D	e0.008	e0.003	e0.006	65
Benfluralin	H	<0.01	<0.01	<0.01	0
Butylate	H	<0.002	<0.002	<0.002	0
Carbaryl	I	e0.015	e0.007	<0.041	15
Carbofuran	I	e0.405	e0.007	<0.02	30
Chlorpyrifos	I	0.026	0.001	0.005	85
Cyanazine	H	e0.011	e0.005	<0.018	20
Dacthal (DCPA)	H	e0.002	e0.001	<0.003	20
p,p'-DDE	D	e0.0003	e0.0003	<0.003	5
Diazinon	I	0.325	e0.001	0.005	85
Dieldrin	H	<0.005	<0.005	<0.005	0
Disulfoton	I	<0.021	<0.021	<0.021	0
EPTC	H	4.73	0.002	0.018	100
Ethalfluralin	H	<0.009	<0.009	<0.009	0
Ethoprop	I	<0.005	<0.005	<0.005	0
Fonofos	I	<0.003	<0.003	<0.003	0
Lindane	I	<0.004	<0.004	<0.004	0
Linuron	H	0.198	e0.011	<0.035	15
Malathion	I	<0.027	<0.027	<0.027	0
Azinphos-methyl	I	<0.05	<0.05	<0.05	0
Parathion, methyl	I	<0.006	<0.006	<0.006	0
Metolachlor	H	0.507	e0.011	0.086	100
Metribuzin	H	0.007	0.006	<0.006	15
Molinate	H	1.33	0.006	0.036	90
Napropamide	H	e0.005	e0.005	<0.007	5
Parathion	I	<0.007	<0.007	<0.007	0
Pebulate	H	0.025	0.004	<0.002	15
Pendimethalin	H	<0.01	<0.01	<0.01	0
Permethrin	I	<0.006	<0.006	<0.006	0
Phorate	I	<0.011	<0.011	<0.011	0
Prometon	H	e0.004	e0.001	<0.015	30
Pronamide	H	e0.004	e0.004	<0.004	5
Propachlor	H	<0.01	<0.01	<0.01	0
Propanil	H	<0.011	<0.011	<0.011	0
Propargite	I	<0.023	<0.023	<0.023	0
Simazine	H	0.061	e0.003	0.012	100
Tebuthiuron	H	e0.007	e0.003	<0.016	45
Terbacil	H	<0.034	<0.034	<0.034	0
Terbufos	I	<0.017	<0.017	<0.017	0
Thiobencarb	H	0.608	e0.004	0.024	80
Triallate	H	<0.002	<0.002	<0.002	0
Trifluralin	H	0.102	e0.0005	<0.009	40

Table 12. Frequency of occurrence of pesticides at the Merced River at River Road Bridge near Newman, California

[The median concentrations denoted with a less than sign (<) indicate that the detection frequency was less than 50 percent and therefore, the median concentration is the detection limit. Concentrations are in micrograms per liter. D, degradation product; H, herbicide; I, insecticide; e, estimated concentration]

Pesticide	Type of pesticide	Maximum concentration	Minimum concentration	Median concentration	Detection frequency (percent)
2,6-Diethylaniline	D	<0.002	<0.002	<0.002	0
Acetochlor	H	<0.004	<0.004	<0.004	0
Alachlor	H	<0.002	<0.002	<0.002	0
α-BHC	I	<0.005	<0.005	<0.005	0
Atrazine	H	e0.003	e0.001	<0.007	15
Atrazine, desethyl	D	e0.002	e0.002	<0.006	5
Benfluralin	H	<0.01	<0.01	<0.01	0
Butylate	H	e0.001	e0.001	<0.002	5
Carbaryl	I	e0.01	e0.001	<0.041	35
Carbofuran	I	<0.02	<0.02	<0.02	0
Chlorpyrifos	I	0.013	e0.002	e0.005	50
Cyanazine	H	e0.012	e0.012	<0.018	5
Dacthal (DCPA)	H	e0.002	e0.002	<0.003	5
p,p'-DDE	D	<0.003	<0.003	<0.003	0
Diazinon	I	e0.004	e0.002	<0.005	10
Dieldrin	H	<0.005	<0.005	<0.005	0
Disulfoton	I	<0.021	<0.021	<0.021	0
EPTC	H	0.014	0.002	0.002	50
Ethalfluralin	H	<0.009	<0.009	<0.009	0
Ethoprop	I	<0.005	<0.005	<0.005	0
Fonofos	I	<0.003	<0.003	<0.003	0
Lindane	I	<0.004	<0.004	<0.004	0
Linuron	H	<0.035	<0.035	<0.035	0
Malathion	I	e0.004	e0.003	<0.027	10
Azinphos-methyl	I	e0.007	e0.007	<0.05	5
Parathion, methyl	I	<0.006	<0.006	<0.006	0
Metolachlor	H	0.026	e0.002	e0.006	80
Metribuzin	H	<0.006	<0.006	<0.006	0
Molinate	H	0.005	0.003	<0.002	10
Napropamide	H	<0.007	<0.007	<0.007	0
Parathion	I	<0.007	<0.007	<0.007	0
Pebulate	H	<0.002	<0.002	<0.002	0
Pendimethalin	H	e0.045	e0.045	<0.01	5
Permethrin	I	<0.006	<0.006	<0.006	0
Phorate	I	<0.011	<0.011	<0.011	0
Prometon	H	<0.015	<0.015	<0.015	0
Pronamide	H	<0.004	<0.004	<0.004	0
Propachlor	H	<0.01	<0.01	<0.01	0
Propanil	H	<0.011	<0.011	<0.011	0
Propargite	I	0.098	e0.011	<0.023	35
Simazine	H	e0.008	e0.0003	e0.005	75
Tebuthiuron	H	<0.016	<0.016	<0.016	0
Terbacil	H	<0.034	<0.034	<0.034	0
Terbufos	I	<0.017	<0.017	<0.017	0
Thiobencarb	H	<0.005	<0.005	<0.005	0
Triallate	H	<0.002	<0.002	<0.002	0
Trifluralin	H	0.017	e0.002	0.009	50

Table 13. Frequency of occurrence of pesticides at Orestimba Creek at River Road near Crows Landing, California

[The median concentrations denoted with a less than sign (<) indicate that the detection frequency was less than 50 percent and therefore, the median concentration is the detection limit. Concentrations are in micrograms per liter. D, degradation product; H, herbicide; I, insecticide; e, estimated concentration]

Pesticide	Type of pesticide	Maximum concentration	Minimum concentration	Median concentration	Detection frequency (percent)
2,6-Diethylaniline	D	<0.002	<0.002	<0.002	0
Acetochlor	H	<0.004	<0.004	<0.004	0
Alachlor	H	0.013	0.005	<0.002	10
α–BHC	I	<0.005	<0.005	<0.005	0
Atrazine	H	0.023	e0.002	0.007	85
Atrazine, desethyl	D	e0.005	e0.003	<0.006	20
Benfluralin	H	<0.01	<0.01	<0.01	0
Butylate	H	<0.002	<0.002	<0.002	0
Carbaryl	I	e0.023	e0.004	e0.011	85
Carbofuran	I	e0.041	e0.006	<0.02	30
Chlorpyrifos	I	0.059	e0.002	0.012	75
Cyanazine	H	e0.012	e0.004	<0.018	10
Dacthal (DCPA)	H	0.004	e0.001	<0.003	30
p,p'-DDE	D	0.024	e0.002	0.01	95
Diazinon	I	0.075	e0.004	0.01	100
Dieldrin	H	0.015	0.005	0.007	65
Disulfoton	I	<0.021	<0.021	<0.021	0
EPTC	H	0.23	0.009	0.024	100
Ethalfluralin	H	<0.009	<0.009	<0.009	0
Ethoprop	I	0.116	e0.003	<0.005	30
Fonofos	I	<0.003	<0.003	<0.003	0
Lindane	I	<0.004	<0.004	<0.004	0
Linuron	H	<0.035	<0.035	<0.035	0
Malathion	I	0.081	e0.004	<0.027	25
Azinphos-methyl	I	e0.053	e0.012	<0.05	25
Parathion, methyl	I	0.016	0.009	<0.006	20
Metolachlor	H	0.736	0.034	0.219	100
Metribuzin	H	0.03	e0.004	0.006	60
Molinate	H	0.028	0.003	0.004	55
Napropamide	H	0.011	e0.004	0.007	55
Parathion	I	<0.007	<0.007	<0.007	0
Pebulate	H	0.002	0.002	<0.002	5
Pendimethalin	H	0.227	e0.011	0.01	50
Permethrin	I	<0.006	<0.006	<0.006	0
Phorate	I	<0.011	<0.011	<0.011	0
Prometon	H	e0.002	e0.001	<0.015	10
Pronamide	H	<0.004	<0.004	<0.004	0
Propachlor	H	<0.01	<0.01	<0.01	0
Propanil	H	<0.011	<0.011	<0.011	0
Propargite	I	1.12	0.026	0.024	50
Simazine	H	0.119	e0.005	0.028	100
Tebuthiuron	H	e0.005	e0.005	<0.016	35
Terbacil	H	<0.034	<0.034	<0.034	0
Terbufos	I	<0.017	<0.017	<0.017	0
Thiobencarb	H	0.017	e0.003	<0.005	25
Triallate	H	<0.002	<0.002	<0.002	0
Trifluralin	H	0.152	e0.008	0.042	100

Table 14. Frequency of occurrence of pesticides at San Joaquin River near Crows Landing, California

[The median concentrations denoted with a less than sign (<) indicate that the detection frequency was less than 50 percent and therefore, the median concentration is the detection limit. Concentrations are in micrograms per liter. D, degradation product; H, herbicide; I, insecticide; e, estimated concentration]

Pesticide	Type of pesticide	Maximum concentration	Minimum concentration	Median concentration	Detection frequency (percent)
2,6-Diethylaniline	D	<0.002	<0.002	<0.002	0
Acetochlor	H	<0.004	<0.004	<0.004	0
Alachlor	H	<0.002	<0.002	<0.002	0
α–BHC	I	<0.005	<0.005	<0.005	0
Atrazine	H	0.011	e0.001	e0.006	84
Atrazine, desethyl	D	e0.003	e0.002	<0.006	21
Benfluralin	H	<0.01	<0.01	<0.01	0
Butylate	H	e0.001	e0.001	<0.002	5
Carbaryl	I	e0.129	e0.002	e0.041	58
Carbofuran	I	e0.221	e0.01	<0.02	32
Chlorpyrifos	I	0.028	e0.003	0.005	53
Cyanazine	H	0.083	e0.006	<0.018	47
Dacthal (DCPA)	H	e0.002	e0.001	<0.003	11
p,p'-DDE	D	e0.001	e0.001	<0.003	5
Diazinon	I	0.05	e0.002	0.005	74
Dieldrin	H	<0.005	<0.005	<0.005	0
Disulfoton	I	<0.021	<0.021	<0.021	0
EPTC	H	0.128	0.005	0.013	89
Ethalfluralin	H	<0.009	<0.009	<0.009	0
Ethoprop	I	<0.005	<0.005	<0.005	0
Fonofos	I	<0.003	<0.003	<0.003	0
Lindane	I	<0.004	<0.004	<0.004	0
Linuron	H	<0.035	<0.035	<0.035	0
Malathion	I	e0.016	e0.005	<0.027	16
Azinphos-methyl	I	e0.019	e0.005	<0.05	16
Parathion, methyl	I	0.059	0.059	<0.006	5
Metolachlor	H	0.216	e0.012	0.107	95
Metribuzin	H	<0.006	<0.006	<0.006	0
Molinate	H	0.066	e0.003	e0.003	53
Napropamide	H	e0.005	e0.005	<0.007	5
Parathion	I	<0.007	<0.007	<0.007	0
Pebulate	H	e0.004	e0.004	<0.002	5
Pendimethalin	H	0.02	e0.009	<0.01	42
Permethrin	I	<0.006	<0.006	<0.006	0
Phorate	I	<0.011	<0.011	<0.011	0
Prometon	H	e0.001	e0.003	<0.015	11
Pronamide	H	0.005	0.005	<0.004	5
Propachlor	H	<0.01	<0.01	<0.01	0
Propanil	H	<0.011	<0.011	<0.011	0
Propargite	I	0.041	e0.013	<0.023	21
Simazine	H	0.034	e0.004	0.012	95
Tebuthiuron	H	e0.008	e0.002	<0.016	16
Terbacil	H	<0.034	<0.034	<0.034	0
Terbufos	I	<0.017	<0.017	<0.017	0
Thiobencarb	H	0.022	0.005	<0.005	26
Triallate	H	<0.002	<0.002	<0.002	0
Trifluralin	H	0.064	e0.005	0.013	95

Table 15. Frequency of occurrence of pesticides at San Joaquin River near Patterson, California

[The median concentrations denoted with a less than sign (<) indicate that the detection frequency was less than 50 percent and therefore, the median concentration is the detection limit. Concentrations are in micrograms per liter. D, degradation product; H, herbicide; I, insecticide; e, estimated concentration]

Pesticide	Type of pesticide	Maximum concentration	Minimum concentration	Median concentration	Detection frequency (percent)
2,6-Diethylaniline	D	<0.002	<0.002	<0.002	0
Acetochlor	H	<0.004	<0.004	<0.004	0
Alachlor	H	<0.002	<0.002	<0.002	0
α-BHC	I	e0.004	e0.002	<0.005	25
Atrazine	H	0.011	e0.001	e0.007	80
Atrazine, desethyl	D	e0.005	e0.002	<0.006	25
Benfluralin	H	<0.01	<0.01	<0.01	0
Butylate	H	0.013	0.013	<0.002	5
Carbaryl	I	0.049	0.004	0.01	90
Carbofuran	I	e0.156	e0.009	<0.02	30
Chlorpyrifos	I	0.011	0.003	0.005	70
Cyanazine	H	0.136	e0.006	<0.018	45
Dacthal (DCPA)	H	e0.002	e0.002	<0.003	5
p,p'-DDE	D	e0.001	e0.001	<0.003	5
Diazinon	I	0.067	e0.001	0.01	100
Dieldrin	H	<0.005	<0.005	<0.005	0
Disulfoton	I	<0.021	<0.021	<0.021	0
EPTC	H	0.117	0.003	0.013	100
Ethalfluralin	H	<0.009	<0.009	<0.009	0
Ethoprop	I	<0.005	<0.005	<0.005	0
Fonofos	I	0.006	0.006	<0.003	5
Lindane	I	0.01	e0.001	0.004	70
Linuron	H	e0.008	e0.008	<0.035	5
Malathion	I	0.088	e0.003	<0.027	25
Azinphos-methyl	I	e0.01	e0.005	<0.05	20
Parathion, methyl	I	<0.006	<0.006	<0.006	0
Metolachlor	H	0.236	e0.01	0.104	100
Metribuzin	H	e0.005	e0.003	<0.006	20
Molinate	H	0.051	e0.003	0.003	55
Napropamide	H	0.055	e0.002	<0.007	50
Parathion	I	<0.007	<0.007	<0.007	0
Pebulate	H	0.086	0.01	<0.002	25
Pendimethalin	H	0.018	e0.008	<0.01	45
Permethrin	I	<0.006	<0.006	<0.006	0
Phorate	I	<0.011	<0.011	<0.011	0
Prometon	H	e0.002	e0.0005	<0.015	10
Pronamide	H	<0.004	<0.004	<0.004	0
Propachlor	H	<0.01	<0.01	<0.01	0
Propanil	H	<0.011	<0.011	<0.011	0
Propargite	I	e0.05	e0.008	<0.023	35
Simazine	H	0.039	e0.005	0.012	100
Tebuthiuron	H	e0.003	e0.002	<0.016	10
Terbacil	H	<0.034	<0.034	<0.034	0
Terbufos	I	<0.017	<0.017	<0.017	0
Thiobencarb	H	0.042	e0.002	<0.005	35
Triallate	H	<0.002	<0.002	<0.002	0
Trifluralin	H	0.052	e0.005	0.013	100

Table 16. Frequency of occurrence of pesticides at Del Puerto Creek at Vineyard Road near Patterson, California

[The median concentrations denoted with a less than sign (<) indicate that the detection frequency was less than 50 percent and therefore, the median concentration is the detection limit. Concentrations are in micrograms per liter. D, degradation product; H, herbicide; I, insecticide; e, estimated concentration]

Pesticide	Type of pesticide	Maximum concentration	Minimum concentration	Median concentration	Detection frequency (percent)
2,6-Diethylaniline	D	<0.002	<0.002	<0.002	0
Acetochlor	H	<0.004	<0.004	<0.004	0
Alachlor	H	<0.002	<0.002	<0.002	0
α-BHC	I	<0.005	<0.005	<0.005	0
Atrazine	H	0.018	e0.001	0.006	85
Atrazine, desethyl	D	e0.004	e0.002	<0.006	25
Benfluralin	H	<0.01	<0.01	<0.01	0
Butylate	H	0.004	0.004	<0.002	5
Carbaryl	I	e0.23	e0.002	e0.021	75
Carbofuran	I	e0.065	e0.013	<0.02	25
Chlorpyrifos	I	0.12	e0.002	0.005	60
Cyanazine	H	0.038	e0.006	<0.018	40
Dacthal (DCPA)	H	e0.002	e0.002	<0.003	10
p,p'-DDE	D	0.007	e0.001	0.003	65
Diazinon	I	0.082	e0.003	0.011	100
Dieldrin	H	e0.003	e0.003	<0.005	5
Disulfoton	I	<0.03	<0.021	<0.021	0
EPTC	H	0.474	0.005	0.045	100
Ethalfluralin	H	0.028	e0.005	<0.009	25
Ethoprop	I	<0.005	<0.005	<0.005	0
Fonofos	I	e0.003	e0.002	<0.003	10
Lindane	I	0.007	e0.001	<0.004	25
Linuron	H	e0.019	e0.019	<0.035	10
Malathion	I	0.033	e0.002	<0.027	45
Azinphos-methyl	I	e0.022	e0.007	<0.05	15
Parathion, methyl	I	0.039	e0.005	<0.006	25
Metolachlor	H	0.47	0.019	0.1	100
Metribuzin	H	0.012	e0.005	<0.006	20
Molinate	H	0.029	0.005	0.006	55
Napropamide	H	0.025	e0.002	0.007	65
Parathion	I	<0.007	<0.007	<0.007	0
Pebulate	H	0.018	e0.004	<0.002	25
Pendimethalin	H	<0.01	<0.01	<0.01	0
Permethrin	I	<0.006	<0.006	<0.006	0
Phorate	I	<0.011	<0.011	<0.011	0
Prometon	H	e0.002	e0.001	<0.015	10
Pronamide	H	<0.004	<0.004	<0.004	0
Propachlor	H	<0.01	<0.01	<0.01	0
Propanil	H	<0.011	<0.011	<0.011	0
Propargite	I	2.33	e0.015	<0.023	45
Simazine	H	0.073	e0.007	0.018	100
Tebuthiuron	H	e0.006	e0.004	<0.016	20
Terbacil	H	<0.034	<0.034	<0.034	0
Terbufos	I	e0.004	e0.004	<0.017	5
Thiobencarb	H	0.015	e0.004	<0.005	10
Triallate	H	<0.002	<0.002	<0.002	0
Trifluralin	H	1.74	e0.005	0.094	100

Table 17. Frequency of occurrence of pesticides at Tuolumne River at Shiloh Road near Grayson, California.

[The median concentrations denoted with a less than sign (<) indicate that the detection frequency was less than 50 percent and therefore, the median concentration is the detection limit. Concentrations are in micrograms per liter. D, degradation product; H, herbicide; I, insecticide; e, estimated concentration]

Pesticide	Type of pesticide	Maximum concentration	Minimum concentration	Median concentration	Detection frequency (percent)
2,6-Diethylaniline	D	<0.002	<0.002	<0.002	0
Acetochlor	H	<0.004	<0.004	<0.004	0
Alachlor	H	<0.002	<0.002	<0.002	0
α-BHC	I	<0.005	<0.005	<0.005	0
Atrazine	H	0.007	e0.001	0.004	75
Atrazine, desethyl	D	e0.006	e0.002	<0.006	45
Benfluralin	H	<0.01	<0.01	<0.01	0
Butylate	H	0.004	0.003	<0.002	20
Carbaryl	I	e0.063	e0.002	0.034	65
Carbofuran	I	<0.02	<0.02	<0.02	0
Chlorpyrifos	I	0.02	e0.002	0.006	80
Cyanazine	H	<0.018	<0.018	<0.018	0
Dacthal (DCPA)	H	e0.002	e0.002	<0.003	5
p,p'-DDE	D	<0.003	<0.003	<0.003	0
Diazinon	I	0.01	e0.002	e0.004	80
Dieldrin	H	<0.005	<0.005	<0.005	0
Disulfoton	I	<0.021	<0.021	<0.021	0
EPTC	H	0.042	0.003	0.002	50
Ethalfluralin	H	<0.009	<0.009	<0.009	0
Ethoprop	I	<0.005	<0.005	<0.005	0
Fonofos	I	<0.003	<0.003	<0.003	0
Lindane	I	<0.004	<0.004	<0.004	0
Linuron	H	<0.035	<0.035	<0.035	0
Malathion	I	e0.004	e0.002	<0.027	10
Azinphos-methyl	I	e0.018	e0.018	<0.05	5
Parathion, methyl	I	e0.005	e0.005	<0.006	5
Metolachlor	H	0.051	e0.001	e0.01	85
Metribuzin	H	<0.006	<0.006	<0.006	0
Molinate	H	0.003	e0.003	<0.002	10
Napropamide	H	<0.007	<0.007	<0.007	0
Parathion	I	<0.007	<0.007	<0.007	0
Pebulate	H	<0.002	<0.002	<0.002	0
Pendimethalin	H	e0.005	e0.003	<0.01	10
Permethrin	I	<0.006	<0.006	<0.006	0
Phorate	I	<0.011	<0.011	<0.011	0
Prometon	H	e0.002	e0.001	<0.015	10
Pronamide	H	<0.004	<0.004	<0.004	0
Propachlor	H	<0.01	<0.01	<0.01	0
Propanil	H	e0.003	e0.002	<0.011	10
Propargite	I	0.086	e0.01	<0.023	20
Simazine	H	0.064	e0.005	e0.01	95
Tebuthiuron	H	<0.016	<0.016	<0.016	0
Terbacil	H	<0.034	<0.034	<0.034	0
Terbufos	I	<0.017	<0.017	<0.017	0
Thiobencarb	H	<0.005	<0.005	<0.005	0
Triallate	H	<0.002	<0.002	<0.002	0
Trifluralin	H	e0.009	e0.001	<0.009	10

Table 18. Frequency of occurrence of pesticides at San Joaquin River at Maze Road Bridge near Modesto, California

[The median concentrations denoted with a less than sign (<) indicate that the detection frequency was less than 50 percent and therefore, the median concentration is the detection limit. Concentrations are in micrograms per liter. D, degradation product; H, herbicide; I, insecticide; e, estimated concentration]

Pesticide	Type of pesticide	Maximum concentration	Minimum concentration	Median concentration	Detection frequency (percent)
2,6-Diethylaniline	D	<0.002	<0.002	<0.002	0
Acetochlor	H	<0.004	<0.004	<0.004	0
Alachlor	H	<0.002	<0.002	<0.002	0
α–BHC	I	<0.005	<0.005	<0.005	0
Atrazine	H	0.015	e0.001	e0.005	85
Atrazine, desethyl	D	e0.008	e0.001	<0.006	40
Benfluralin	H	<0.01	<0.01	<0.01	0
Butylate	H	0.005	0.002	<0.002	15
Carbaryl	I	e0.185	e0.002	e0.022	65
Carbofuran	I	e0.041	e0.007	<0.02	25
Chlorpyrifos	I	0.015	e0.004	0.005	70
Cyanazine	H	0.044	e0.004	<0.018	50
Dacthal (DCPA)	H	e0.002	e0.002	<0.003	5
p,p′-DDE	D	e0.001	e0.001	<0.003	5
Diazinon	I	0.029	e0.002	0.008	100
Dieldrin	H	<0.005	<0.005	<0.005	0
Disulfoton	I	<0.021	<0.021	<0.021	0
EPTC	H	0.057	0.004	0.012	100
Ethalfluralin	H	e0.006	e0.004	<0.009	10
Ethoprop	I	<0.005	<0.005	<0.005	0
Fonofos	I	e0.004	e0.003	<0.003	10
Lindane	I	e0.003	e0.001	<0.004	40
Linuron	H	<0.035	<0.035	<0.035	0
Malathion	I	e0.014	e0.002	<0.027	30
Azinphos-methyl	I	e0.042	e0.042	<0.05	5
Parathion, methyl	I	0.008	0.008	<0.006	5
Metolachlor	H	0.481	e0.012	0.062	100
Metribuzin	H	e0.006	e0.005	<0.006	10
Molinate	H	0.28	0.002	<0.002	45
Napropamide	H	0.008	e0.005	<0.007	15
Parathion	I	<0.007	<0.007	<0.007	0
Pebulate	H	0.02	0.005	<0.002	15
Pendimethalin	H	0.018	e0.006	<0.01	25
Permethrin	I	<0.006	<0.006	<0.006	0
Phorate	I	<0.011	<0.011	<0.011	0
Prometon	H	e0.001	e0.001	<0.015	5
Pronamide	H	<0.004	<0.004	<0.004	0
Propachlor	H	<0.01	<0.01	<0.01	0
Propanil	H	<0.011	<0.011	<0.011	0
Propargite	I	e0.012	e0.011	<0.023	10
Simazine	H	0.062	e0.005	0.013	100
Tebuthiuron	H	<0.016	<0.016	<0.016	0
Terbacil	H	<0.034	<0.034	<0.034	0
Terbufos	I	<0.017	<0.017	<0.017	0
Thiobencarb	H	0.697	e0.002	<0.005	15
Triallate	H	<0.002	<0.002	<0.002	0
Trifluralin	H	0.017	e0.006	0.009	100

Table 19. Frequency of occurrence of pesticides at Stanislaus River at Caswell State Park near Ripon, California

[The median concentrations denoted with a less than sign (<) indicate that the detection frequency was less than 50 percent and therefore, the median concentration is the detection limit. Concentrations are in micrograms per liter. D, degradation product; H, herbicide; I, insecticide; e, estimated concentration]

Pesticide	Type of pesticide	Maximum concentration	Minimum concentration	Median concentration	Detection frequency (percent)
2,6-Diethylaniline	D	<0.002	<0.002	<0.002	0
Acetochlor	H	<0.004	<0.004	<0.004	0
Alachlor	H	<0.002	<0.002	<0.002	0
α-BHC	I	<0.005	<0.005	<0.005	0
Atrazine	H	e0.006	e0.001	<0.007	40
Atrazine, desethyl	D	e0.002	e0.001	<0.006	10
Benfluralin	H	<0.01	<0.01	<0.01	0
Butylate	H	0.005	0.004	<0.002	10
Carbaryl	I	e0.044	e0.001	<0.041	50
Carbofuran	I	e0.013	e0.013	<0.02	5
Chlorpyrifos	I	0.014	e0.002	0.005	70
Dacthal (DCPA)	H	e0.002	e0.002	<0.003	5
p,p'-DDE	D	<0.003	<0.003	<0.003	0
Diazinon	I	e0.004	e0.001	e0.004	55
Dieldrin	H	<0.005	<0.005	<0.005	0
Disulfoton	I	<0.021	<0.021	<0.021	0
Ethalfluralin	H	<0.009	<0.009	<0.009	0
Ethoprop	I	<0.005	<0.005	<0.005	0
Fonofos	I	<0.003	<0.003	<0.003	0
Lindane	I	<0.004	<0.004	<0.004	0
Linuron	H	<0.035	<0.035	<0.035	0
Malathion	I	e0.006	e0.004	<0.027	20
Azinphos-methyl	I	<0.05	<0.05	<0.05	0
Parathion, methyl	I	e0.005	e0.005	<0.006	5
Metolachlor	H	0.015	e0.001	0.01	55
Metribuzin	H	<0.006	<0.006	<0.006	0
Molinate	H	0.004	0.002	<0.002	20
Napropamide	H	<0.007	<0.007	<0.007	0
Parathion	I	<0.007	<0.007	<0.007	0
Pebulate	H	<0.002	<0.002	<0.002	0
Pendimethalin	H	<0.01	<0.01	<0.01	0
Permethrin	I	<0.006	<0.006	<0.006	0
Phorate	I	<0.011	<0.011	<0.011	0
Prometon	H	<0.015	<0.015	<0.015	0
Pronamide	H	<0.004	<0.004	<0.004	0
Propachlor	H	<0.01	<0.01	<0.01	0
Propanil	H	e0.004	e0.004	<0.011	5
Propargite	I	e0.111	e0.016	<0.023	25
Simazine	H	0.044	e0.002	e0.004	70
Tebuthiuron	H	<0.016	<0.016	<0.016	0
Terbacil	H	<0.034	<0.034	<0.034	0
Terbufos	I	<0.017	<0.017	<0.017	0
Thiobencarb	H	<0.005	<0.005	<0.005	0
Triallate	H	<0.002	<0.002	<0.002	0
Trifluralin	H	e0.005	e0.001	<0.009	20

Table 20. Frequency of occurrence of pesticides at the San Joaquin River near Vernalis, California

[The median concentrations denoted with a less than sign (<) indicate that the detection frequency was less than 50 percent and therefore, the median concentration is the detection limit. Concentrations are in micrograms per liter. D, degradation product; H, herbicide; I, insecticide; e, estimated concentration]

Pesticide	Type of pesticide	Maximum concentration	Minimum concentration	Median concentration	Detection frequency (percent)
2,6-Diethylaniline	D	<0.002	<0.002	<0.002	0
Acetochlor	H	<0.004	<0.004	<0.004	0
Alachlor	H	<0.002	<0.002	<0.002	0
α-BHC	I	e0.0004	e0.0004	<0.005	5
Atrazine	H	0.008	e0.001	e0.004	85
Atrazine, desethyl	D	e0.004	e0.002	<0.006	35
Benfluralin	H	<0.01	<0.01	<0.01	0
Butylate	H	0.008	0.004	<0.002	20
Carbaryl	I	e0.114	e0.002	<0.041	55
Carbofuran	I	e0.037	e0.01	<0.02	15
Chlorpyrifos	I	0.007	e0.003	0.005	75
Cyanazine	H	0.034	0.004	<0.018	50
Dacthal (DCPA)	H	e0.002	e0.002	<0.003	5
p,p'-DDE	D	e0.0003	e0.0003	<0.003	5
Diazinon	I	0.024	e0.002	0.005	100
Dieldrin	H	<0.005	<0.005	<0.005	0
Disulfoton	I	<0.021	<0.021	<0.021	0
EPTC	H	0.045	e0.002	0.008	100
Ethalfluralin	H	<0.009	<0.009	<0.009	0
Ethoprop	I	<0.005	<0.005	<0.005	0
Fonofos	I	<0.003	<0.003	<0.003	0
Lindane	I	0.005	e0.002	<0.004	15
Linuron	H	<0.035	<0.035	<0.035	0
Malathion	I	e0.007	e0.004	<0.027	25
Azinphos-methyl	I	e0.009	e0.009	<0.05	5
Parathion, methyl	I	0.022	0.022	<0.006	5
Metolachlor	H	0.075	e0.01	0.042	100
Metribuzin	H	e0.005	e0.005	<0.006	10
Molinate	H	0.046	e0.002	<0.002	35
Napropamide	H	0.008	e0.003	<0.007	20
Parathion	I	<0.007	<0.007	<0.007	0
Pebulate	H	0.017	e0.003	<0.002	10
Pendimethalin	H	e0.01	e0.008	<0.01	10
Permethrin	I	<0.006	<0.006	<0.006	0
Phorate	I	<0.011	<0.011	<0.011	0
Prometon	H	e0.002	e0.0004	<0.015	10
Pronamide	H	<0.004	<0.004	<0.004	0
Propachlor	H	<0.01	<0.01	<0.01	0
Propanil	H	<0.011	<0.011	<0.011	0
Propargite	I	0.044	e0.008	<0.023	10
Simazine	H	0.213	e0.005	e0.009	100
Tebuthiuron	H	e0.002	e0.002	<0.016	5
Terbacil	H	<0.034	<0.034	<0.034	0
Terbufos	I	<0.017	<0.017	<0.017	0
Thiobencarb	H	0.008	e0.002	<0.005	10
Triallate	H	<0.002	<0.002	<0.002	0
Trifluralin	H	0.014	e0.003	e0.008	90

The Salt and Mud Sloughs are two west-side tributaries to the San Joaquin River at the upper reaches of the study area. For the Salt Slough at Highway 165 near Stevinson, 10 pesticides were detected at a frequency of 50 percent or higher (table 9) and for the Mud Slough near Gustine, 9 pesticides were detected at a frequency of 50 percent of higher. Chlorpyrifos was detected at a frequency of 30 percent at the Salt Slough site (table 10), but at a frequency of 85 percent at the Mud Slough site (table 11). The detection frequency for diazinon was similar at both sites (90 percent for Salt Slough and 85 percent for Mud Slough). Herbicides detected at a frequency of 50 percent or higher for the Salt and(or) Mud Slough sites included atrazine, cyanazine, EPTC, metolachlor, molinate, simazine, thiobencarb, and trifluralin. The two herbicides used on rice, molinate and thiobencarb, had the highest concentrations at the Salt Slough and(or) Mud Slough sites. Two additional insecticides were detected at high frequency at Salt Slough, but not at Mud Slough. These were carbaryl (90 percent detection frequency) and carbofuran (50 percent detection frequency).

The Merced River, the most upstream of the three large Sierran tributaries, had a low occurrence of pesticides and only five were detected at a frequency of 50 percent or higher (table 12). Chlorpyrifos was detected at a frequency of 50 percent, but diazinon only at a frequency of 10 percent. The other pesticides detected at a frequency of 50 percent or higher were all herbicides (EPTC, metolachlor, simazine, and trifluralin). All measured concentrations for the Merced River were relatively low with many concentrations estimated owing to detections below the measurable reportable limit.

The Orestimba Creek at River Road near Crows Landing site receives runoff from the Orestimba Creek watershed and operational spills of the Central California Irrigation District (CCID) canal (fig. 1). Spills of the CCID are probably most responsible for the variation in discharge (fig. 7) observed during this study. There was a high frequency of detection of pesticides for the Orestimba Creek (table 13) (15 compounds detected at a frequency of 50 percent or higher). Both chlorpyrifos and diazinon were detected at a high frequency (75 percent for chlorpyrifos and 100 percent for diazinon). Domagalski (1997b) also detected diazinon at a high frequency at Orestimba Creek in a 1992 study. Two other insecticides, carbaryl and propargite, also were detected at a high frequency (85 percent and 50 percent, respectively). Several herbicides were detected at a high frequency (atrazine, 85 percent; EPTC, 100 percent; metolachlor, 100 percent; molinate, 55 percent; napropramide, 55 percent; pendimethalin, 50 percent; simazine, 100 percent; and trifluralin, 100 percent). Two pesticide or pesticide degradation products from historical use, dieldrin and *p,p′*-DDE, were detected at high frequency at the Orestimba Creek site (65 and 95 percent, respectively). Domagalski (1997b) also detected *p,p′*-DDE at a high frequency in his 1992 study. Although many different pesticides were detected, the maximum concentrations tended to be low and only propargite was measured at a concentration of 1 μg/L or higher. The highest measured concentration of metolachlor was 0.736 μg/L and those for chlorpyrifos and diazinon were 0.059 and 0.075 μg/L, respectively.

The San Joaquin River near Crows Landing (table 14) receives runoff from Orestimba Creek and a number of agricultural drains, and as a result, more pesticides were detected relative to what was measured at the San Joaquin River near Stevinson site (table 9). Nine pesticides were measured at a frequency of 50 percent or higher, which included both chlorpyrifos (detection frequency of 53 percent) and diazinon (detection frequency of 74 percent). A similar group of herbicides (atrazine, EPTC, metolachlor, molinate, simazine, and trifluralin) were among the frequently detected pesticides as was one other insecticide, carbaryl (58 percent detection frequency). The highest measured concentration of any pesticide was that for metolachlor at 0.216 μg/L, although carbofuran had an estimated concentration of 0.221 μg/L.

Still more pesticides were detected at a frequency of 50 percent or higher at the next most downstream site on the San Joaquin River, the San Joaquin River near Patterson (table 15). A total of eleven pesticides were detected at a frequency of 50 percent or higher. Chlorpyrifos was detected at a frequency of 70 percent and diazinon at a frequency of 100 percent. The highest concentrations of chlorpyrifos and diazinon at this site were 0.011 and 0.067 μg/L, respectively. The median concentration of these two organophosphorus insecticides was quite low and near the method reporting limit of the analytical method. Except for carbaryl and lindane, the other frequently detected pesticides were all herbicides. The highest measured concentration of any pesticide was that for metolachlor, at 0.236 μg/L.

The Del Puerto Creek drains a portion of the western San Joaquin Valley. A total of eleven pesticides were detected at a frequency of 50 percent or greater, with chlorpyrifos detected at a frequency of 60 percent and diazinon at a frequency of 100 percent (table 16). The maximum concentrations of those two pesticides were 0.12 μg/L for chlorpyrifos and 0.082 μg/L for diazinon. The other frequently detected pesticides at the Del Puerto Creek at Vineyard Road near Patterson site were herbicides with the exceptions of carbaryl and *p,p′*-DDE. As mentioned previously, use of DDT, the parent compound of DDE, has long been banned in California, but tends to occur at a high frequency in streams draining the western San Joaquin Valley. The highest measured concentration of any pesticide was propargite at 2.33 μg/L, although its detection frequency was less than 50 percent. Of the frequently detected pesticides, trifluralin, had the highest concentration at 1.74 μg/L.

The Tuolumne River is one of the three large Sierran tributaries and more pesticides were detected at a frequency of 50 percent or greater (a total of seven) than at the Merced River site. Both chlorpyrifos and diazinon were detected at a frequency of 80 percent (table 17), but the maximum concentrations were relatively low (0.02 μg/L for chlorpyrifos and 0.01 μg/L for diazinon). Another insecticide, carbaryl, was detected at a frequency of 65 percent, but all of the other frequently detected pesticides were herbicides. The highest maximum concentration of any detected pesticide was 0.086 μg/L, for propargite (detection frequency was 20 percent). Of the frequently detected pesticides, the highest measured concentration was for metolachlor at 0.051 μg/L.

Nine pesticides were detected at a frequency of 50 percent or greater at the San Joaquin River at Maze Road Bridge near Modesto, site (table 18). Chlorpyrifos and diazinon were among the detections with a frequency of 70 percent and 100 percent, respectively. The maximum concentrations of these two organophosphorus insecticides were 0.015 μg/L for chlorpyrifos and 0.029 μg/L for diazinon. Except for carbaryl, the other frequently detected pesticides for the San Joaquin River at Maze Road Bridge near Modesto site were all herbicides. The maximum measured concentration of any pesticide for this site was 0.697 μg/L for thiobencarb, which was detected at a frequency of only 15 percent.

The Stanislaus River discharges into the San Joaquin River just upstream of the San Joaquin River near Vernalis site. A total of five pesticides were detected at a frequency of 50 percent or greater at the Stanislaus River at Caswell State Park near Ripon site (table 19). Of those five, three were insecticides: carbaryl (detection frequency 50 percent), chlorpyrifos (detection frequency 70 percent), and diazinon (detection frequency 55 percent). The maximum measured concentration of chlorpyrifos was 0.014 μg/L and that for diazinon was an estimated concentration of 0.004 μg/L. The concentration was estimated because it was just at the reporting limit for the analytical method of diazinon. The highest measured concentration of any pesticide was that for simazine at 0.044 μg/L.

Nine pesticides were also detected at a frequency of 50 percent or greater for the San Joaquin River near Vernalis site (table 20). Chlorpyrifos was detected at a frequency of 75 percent and diazinon was detected at a frequency of 100 percent. The maximum concentrations of these two pesticides were 0.007 μg/L for chlorpyrifos and 0.024 μg/L for diazinon. Except for carbaryl, the other frequently detected pesticides at the San Joaquin River near Vernalis site were all herbicides. The maximum concentration of any measured pesticide was 0.213 μg/L for simazine.

The overall frequency of detection of compounds was generally greater in western tributaries to the San Joaquin River relative to those of the eastern San Joaquin Valley. The Orestimba Creek site had 15 compounds detected at a frequency of 50 percent or greater, and the Del Puerto Creek site had 11 compounds detected at a frequency of 50 percent or greater. In contrast, the Tuolumne River, an eastern tributary to the San Joaquin River had seven compounds detected at a frequency of 50 percent or greater, while the Merced and Stanislaus rivers each had only five compounds detected at a frequency of 50 percent or greater. This can, in part, be attributed to the higher discharge on the eastern tributary streams, which would tend to dilute pesticide concentrations, resulting in concentrations below the method reporting limit.

Diazinon and chlorpyrifos concentrations are of special concern because, as previously mentioned, many streams of the San Joaquin Valley are considered impaired because of the elevated concentrations of these two insecticides in water. Boxplots of diazinon and chlorpyrifos for the sites of this study are shown in figures 15 and 16. The median concentration of diazinon is less than the method reporting limit for a few sites, such as the San Joaquin River near Stevinson,

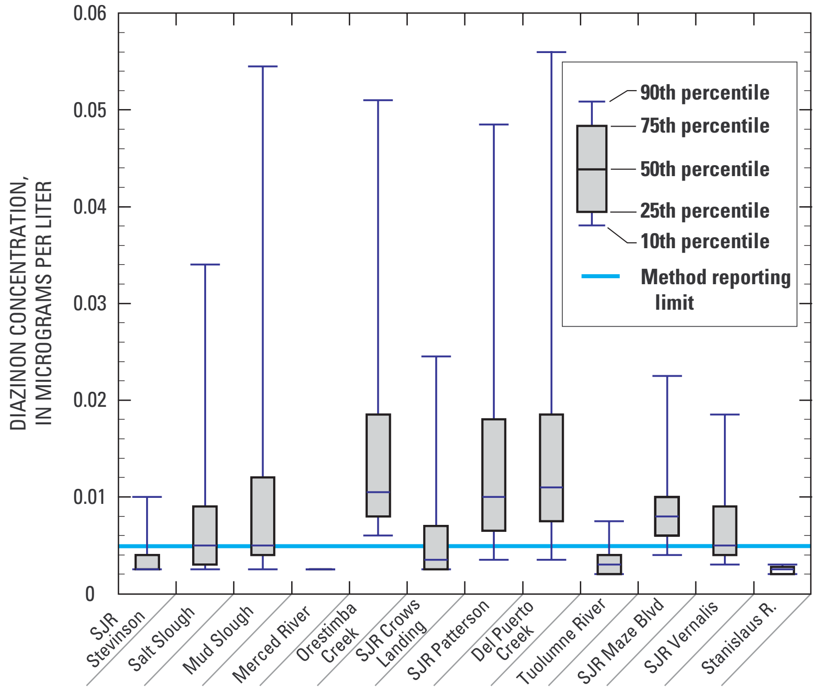


Figure 15. Boxplots of diazinon concentrations for all sampling sites, San Joaquin Valley, California. Abbreviated site names are used. R, river; SJR, San Joaquin River.

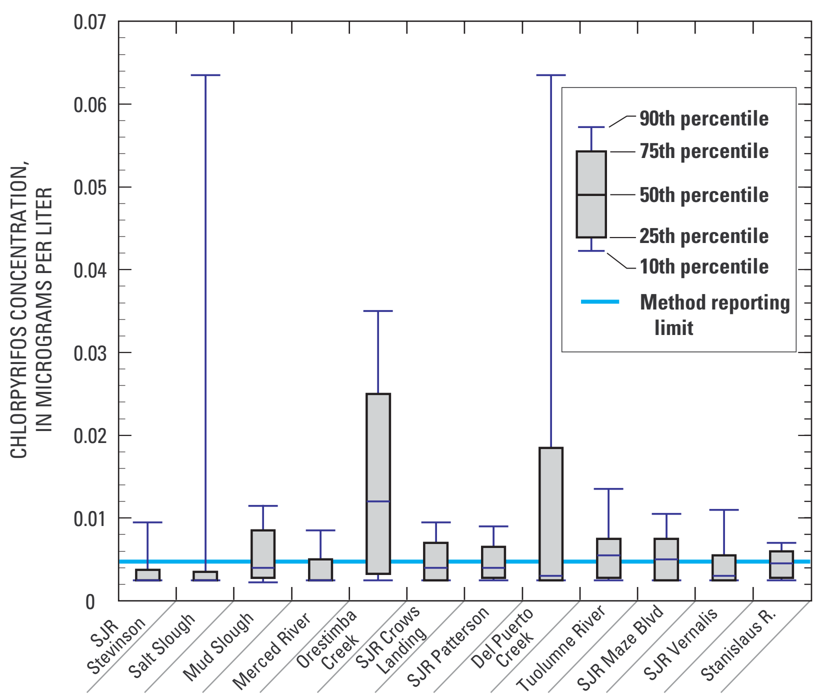


Figure 16. Boxplots of chlorpyrifos concentrations for all sampling sites, San Joaquin Valley, California. Abbreviated site names are used. R, river; SJR, San Joaquin River.

the Merced River site, the San Joaquin River at Crows Landing, the Tuolumne River site, and the Stanislaus River site. The highest diazinon concentrations were measured in samples from two of the west-side tributaries, Orestimba Creek and Del Puerto Creek. For all sites, 75 percent of all measured concentrations are less than 0.02 μg/L, and 90 percent of all measured concentrations are less than 0.06 μg/L. Those concentrations are considerably less than those measured in studies of diazinon transport during winter storm water runoff, for which concentrations at some locations exceeded 1 μg/L (Domagalski, and others, 1997, Kratzer, 1998, 1999). The median concentration of chlorpyrifos was at or less than the method reporting limit for most sites with the exceptions of Orestimba Creek and the Tuolumne River. For all sites, 75 percent of all measured concentrations are less than 0.03 μg/L and 90 percent of all measured concentrations are less than 0.07 μg/L.

The total applied amounts of frequently detected pesticides are shown in table 21 and the loads for diazinon and chlorpyrifos for all sites can be compared to the amounts applied. The total load of diazinon was calculated for all the sites of this study for which continuous records of stream discharge were available. Continuous stream discharge data were not available for the Del Puerto Creek site (fig. 10) and the San Joaquin River at Maze Road site (fig. 12). Although not all inputs to the San Joaquin River were measured during this study, the 12 selected sites accounted for nearly 83 percent of the discharge of the San Joaquin River at Vernalis. Diazinon concentrations between sampling events were estimated by linear interpolation. The loads for 11 sites are shown in table 22. The load for the San Joaquin River at Vernalis was 7,153 g or an average of 46.8 g/d. Taken together, the combined load of the Salt and Mud Sloughs accounted for about 26 percent of the diazinon load for the San Joaquin River at Vernalis. These two basins account for only 11 percent of the water that flows through the San Joaquin River at Vernalis site (table 21). The major east side tributaries accounted for almost 70 percent of the water at the San Joaquin River at Vernalis site, but only about 21 percent of the diazinon load. Of the total applications of diazinon to crops on the San Joaquin Valley floor during the period of this study, the total load of diazinon out of the San Joaquin River at Vernalis accounted for approximately 0.17 percent of the total applied.

Although the stream discharge of the sampled tributaries accounted for about 83 percent of the discharge for the San Joaquin River at Vernalis site, the load of the tributaries accounted for only about 52 percent of the diazinon load. Two possibilities for this variation are the input of diazinon from sources other than those sampled during this study, or variability in concentration at the tributary sites that was not apparent from the sampling frequency used in this study. Domagalski (1997b) demonstrated substantial variability in concentrations of pesticides as sampling frequency increases. The linear interpolation method used to estimate diazinon concentrations in between sampling events probably underestimates the actual load at the tributary sites.

The total load of chlorpyrifos was calculated for the same sites as those for diazinon. The results are shown in table 23. In contrast to the situation for diazinon, where the sum of diazinon loads from the tributaries was less than that for the San Joaquin River at Vernalis site, the total chlorpyrifos load from the tributaries exceeds that of the San Joaquin River at Vernalis site. The sum of loads for the tributary sites is about 126 percent of the load measured at the San Joaquin River at Vernalis site. Therefore, some of the tributary loads slightly overestimate the total chlorpyrifos load. The greatest load discharged from any one basin is that of Salt Slough, which accounted for 43.5 percent of the downstream load on the San Joaquin River at Vernalis site. The Salt Slough also accounted for the greatest amount of the diazinon load. The combined loads of chlorpyrifos in the Stanislaus and Tuolumne Rivers was about 60 percent of the load in the San Joaquin River at Vernalis. Of the total amount of chlorpyrifos applied to the crops of the San Joaquin Valley floor, the total load of chlorpyrifos at the San Joaquin River at Vernalis accounted for approximately 0.007 percent of the total applied.

Basin yields of pesticides are defined as the mass per unit area as measured at a sampling point, such as a stream gaging station. Basin yields for diazinon and chlorpyrifos are shown in tables 24 and 25, respectively. For each pesticide the greatest yields are for the two sampled tributaries of the western San Joaquin Valley, Orestimba Creek, and Del Puerto Creek. The basin yields on portions of the San Joaquin River also are given in tables 24 and 25. The yield of diazinon for the upper San Joaquin River site, the San Joaquin River near Stevinson, is only 0.09 g/km^2. The yield for the San Joaquin River at Crows Landing

Table 21. Pesticides applied to crops, April through August 2001, San Joaquin Valley, California

[All values are in kilograms of active ingredient. N, not applied. Preliminary data supplied by the California Department of Pesticide Regulation (California Department of Pesticide Regulation, unpub. data, 2002]

Pesticide	Almonds	Apricots	Walnuts	Peaches and nectarines	Other fruit and nut bearing Trees	Grapes	Corn (forage, fodder, human con-sumption)	Cotton	Beans (dry and succu-lent)	Field crops	Rice	Sugar beets	Tomatoes	Alfalfa	Other	Nonagri-cultural
Carbaryl	832	255	240	771	4,109	506	675	136	135	749	67	192	3,618	35	199	13
Carbofuran	N	N	N	N	N	N	N	759	N	N	N	N	N	27	N	N
Chlorpyrifos	24,826	N	13,110	10	507	17	3,222	4,597	N	2,640	N	704	N	4,229	20	N
Cyanazine	30	N	N	19	N	N	N	565	N	N	N	N	N	N	N	N
Diazinon	17	78	688	590	365	N	N	1	46	1,414	N	N	974	N	6	N
EPTC	1,211		154	N	N	N	1,049	N	N	N	N	450	700	5,110	N	N
Metolachlor	N	N	N	N	N	N	5,266	3,507	3,508	N	N	N	1,320	N	2	14
Molinate	N	N	N	N	N	N	N	N	N	N	7,733	N	N	N	N	N
Napropamide	119	N	15	N	54	78	N	N	N	64	N	N	421	N	N	N
Propargite	43,537	N	10,430	113	677	3,519	41,486	3,406	4,960	N	N	N	N	7	14	N
Simazine	3,570	N	671	14	32	23	N	N	N	N	N	N	N	N	24	N
Thiobencarb	N	N	N	N	N	N	N	N	N	N	9,245	N	14	N	N	N
Trifluralin	6,403	N	105	N	N	N	14	3,571	906	280	N	412	2,924	17,505	10	N
Total applied	80,547	333	25,412	1,516	5,746	4,143	51,711	16,540	9,555	5,145	17,045	1,757	9,970	26,913	274	27

Table 22. Diazinon loads and total stream discharge, San Joaquin Valley, California

[g, gram; g/d, gram per day; m^3, cubic meter; n/a, not applicable]

Tributary or river sites	Total diazinon load (g)	Average load (g/d)	Diazinon load at San Joaquin River at Vernalis (percent)	Total water discharge (m^3)	San Joaquin River at Vernalis discharge (percent)
Salt Slough	1,164	7.6	16.3	66,541,702	8.2
Mud Slough	730	4.8	10.2	25,926,002	3.2
Merced River	284	1.9	4.0	115,998,098	14.3
Orestimba Creek	192	1.3	2.7	12,260,201	1.5
Del Puerto Cr (estimated)	78	0.5	1.1	4,581,450	0.6
Tuolumne River	574	3.8	8.0	180,755,405	22.3
Stanislaus River	658	4.3	9.2	269,256,001	33.3
San Joaquin River Stevinson	105	0.7	1.5	22,778,256	2.8
San Joaquin River at Crows Landing	2,132	14.0	29.8	272,302,867	33.6
San Joaquin River at Patterson	6,656	43.5	93.0	366,986,085	45.3
San Joaquin River at Vernalis	7,153	46.8	n/a	809,361,920	n/a

Table 23. Chlorpyrifos loads, San Joaquin Valley, California

[g, gram; g/d, gram per day; m^3, cubic meter; n/a, not applicable]

Tributary or river sites	Total chlorpyrifos load (g)	Average load (g/d)	Chlorpyrifos load at San Joaquin River at Vernalis (percent)
Salt Slough	1,636	11	43.5
Mud Slough	173	1	4.6
Merced River	432	3	11.5
Orestimba Creek	125	1	3.3
Del Puerto Creek (estimated)	94	1	2.5
Tuolumne River	984	6	26.2
Stanislaus River	1,279	8	34.0
San Joaquin River Stevinson	241	2	6.4
San Joaquin River at Crows Landing	1,288	8	34.3
San Joaquin River at Patterson	1,605	11	42.7
San Joaquin River at Vernalis	3,758	25	n/a

Table 24. Yield of diazinon from specific portions of the San Joaquin River watershed, California

[g/km^2, gram per square kilometer]

Tributary or river sites	Yield (g/km^2)
Salt Slough/Mud Slough	1.50
Merced River	0.45
Orestimba Creek	6.90
Del Puerto Creek (estimated)	3.70
Tuolumne River	1.30
Stanislaus River	1.50
San Joaquin River Stevinson	0.09
San Joaquin River at Crows Landing	0.55
San Joaquin River at Patterson	1.58
San Joaquin River at Vernalis	1.22

Table 25. Yield of chlorpyrifos from specific portions of the San Joaquin River watershed, California

[g/km^2, gram per square kilometer]

Tributary sites	Chlorpyrifos yield (g/km^2)
Salt/Mud Slough	1.30
Merced River	0.68
Orestimba Creek	4.50
Del Puerto Creek (estimated)	4.50
Tuolumne River	2.30
Stanislaus River	2.90
San Joaquin River Stevinson	0.20
San Joaquin River at Crows Landing	0.33
San Joaquin River at Patterson	0.38
San Joaquin River at Vernalis	0.63

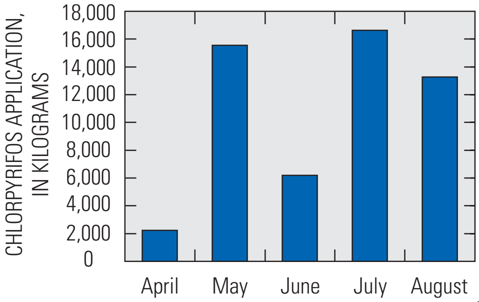
increases to 0.55 g/km^2 because of the inputs from the Merced River and Orestimba Creek. The yield for the remainder of the San Joaquin River is similar to that measured for the Tuolumne and Stanislaus Rivers. The yields for chlorpyrifos for sites along the San Joaquin River are lower than those for diazinon, except for the San Joaquin River near Stevinson site, even though the tributary yields are similar for those two organophosphorus insecticides. It is possible that chlorpyrifos is not transported conservatively after streams discharge into the San Joaquin River. Chlorpyrifos has a lower solubility and a higher partitioning constant to organic carbon relative to diazinon (Panshin and others, 1998). These properties might result in sorption to sediment particles and subsequent deposition after discharge into the San Joaquin River.

Comparison of Detected Pesticides to Applications

Pesticide-use maps of 13 pesticides are shown in figures 17 through 29. Pesticide use data were obtained from the California Department of Pesticide Regulation. All pesticide applications for agriculture in California are required to be recorded. The California Department of Pesticide Regulation maintains a computer database of those applications. The data are reviewed for accuracy and published in annual reports. The pesticide-use data analyzed for this report were preliminary in that all accuracy checks were not completed at the time of the publication. As noted earlier, a table of the crops to which these pesticides were applied is shown in table 21. Most pesticides that were detected at a frequency of 50 percent or greater were selected for these maps, unless there was no application during the period of sample collection. For example, although atrazine or its degradation product was detected at a frequency of 50 percent or greater at several sites, there was little or no recorded agricultural use of that herbicide during the period of study and, as a result, no map for atrazine is presented. In all cases, these pesticide-use maps show the total amount of agricultural pesticide applications during the timeframe of April through August 2001. Nonagricultural uses of pesticides, such as for structural pest control or for roadside maintenance are not shown on these maps because exact locations of applications are not recorded. The total agricultural uses of the two organophosphorus insecticides, chlorpyrifos and diazinon, are shown in figures 17 and 18. There was a considerable amount of chlorpyrifos use within the drainage basins of the three major east-side tributaries, so it is not surprising that a large percentage of the total load in the San Joaquin River was contributed by the Stanislaus and Tuolumne Rivers (table 23). However, chlorpyrifos use in the Salt and Mud Sloughs drainage basins was much less (fig. 17).

Much more chlorpyrifos was used relative to diazinon and the use was more widespread throughout the study area. The peak applications of chlorpyrifos occurred in May, July, and August. The use of diazinon was slightly more uniform during the months of this study. Other insecticidal or nonherbicidal pesticide-use maps are carbaryl (fig. 19), carbofuran, (fig. 20), and propargite (fig. 26). Of these propargite has the greatest amount of use, with most of the use occurring in July. Although the use of propargite is high, the detection frequency is generally low. The use of carbofuran is limited in geographic area, and that for carbaryl is intermediate between that for carbofuran and propargite.

The crop that had the highest overall use of pesticides was almonds (table 21). The combined use of chlorpyrifos and propargite accounted for most of the pesticide use on almonds during the growing season. The crop with the second highest usage of pesticides during the growing season was corn (table 21). The use of propargite on corn accounted for most of the pesticide use. Other crops with relatively



Site name	Detection frequency
1. San Joaquin River near Stevinson	20
2. Salt Slough at Highway 165 near Stevinson	30
3. Mud Slough near Gustine	85
4. Merced River at River Road Bridge near Newman	50
5. Orestimba Creek at River Road near Crows Landing	75
6. San Joaquin River near Crows Landing	53
7. San Joaquin River at Patterson Bridge near Patterson	70
8. Del Puerto Creek at Vineyard Road near Patterson	60
9. Tuolumne River at Shiloh Road Bridge near Grayson	80
10. San Joaquin River at Maze Road Bridge near Modesto	70
11. Stanislaus River at Caswell State Park near Ripon	70
12. San Joaquin River near Vernalis	75

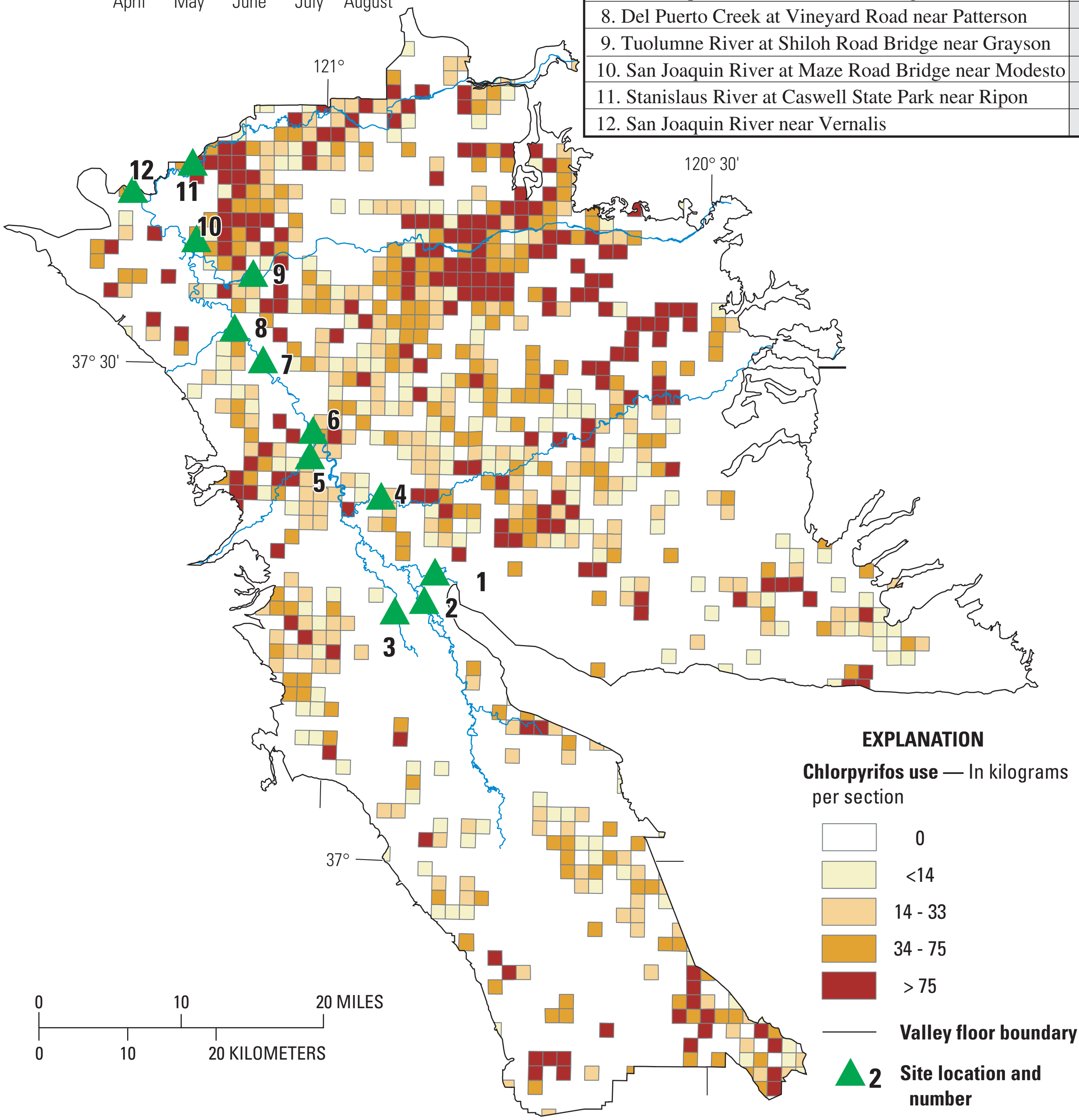
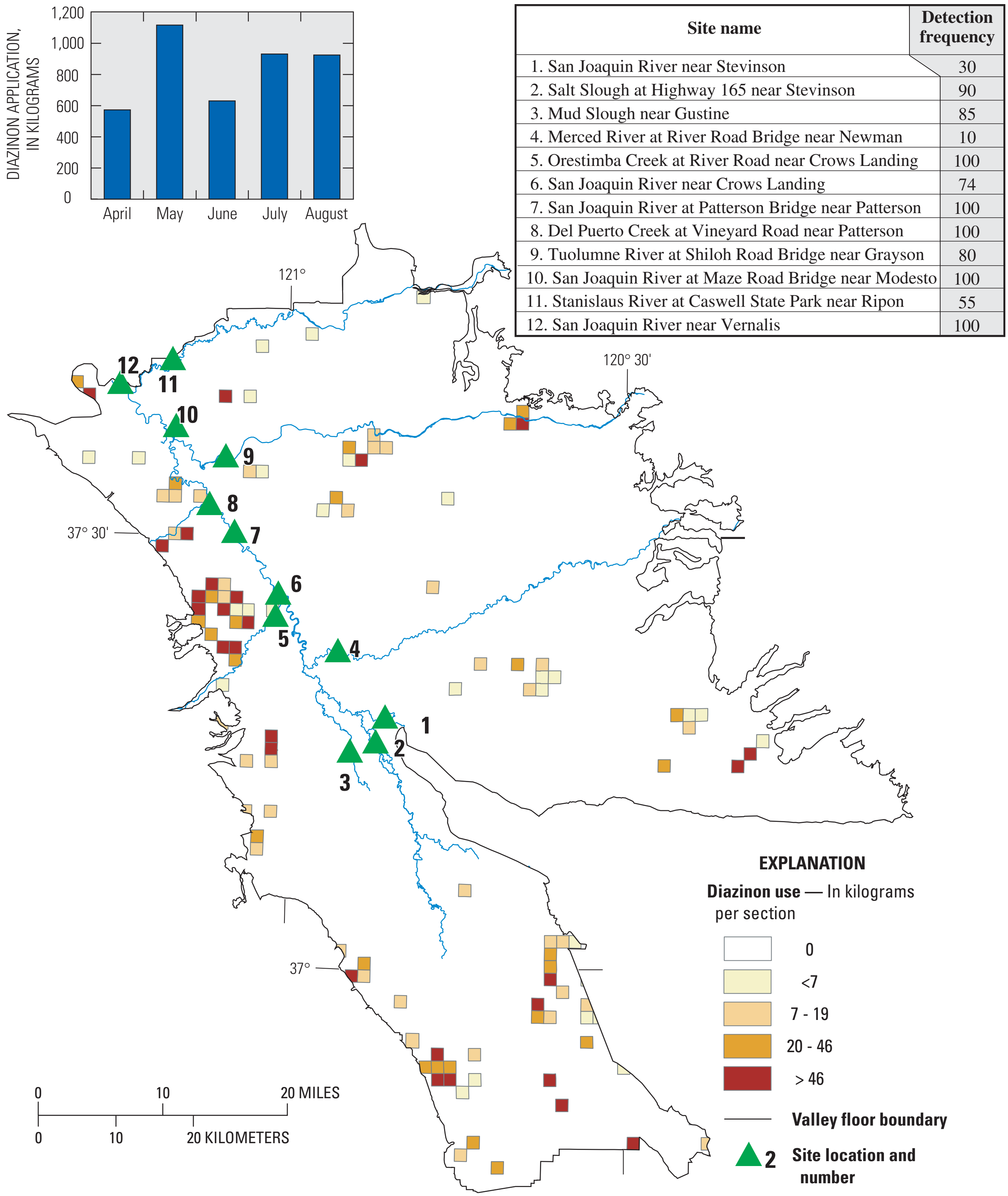
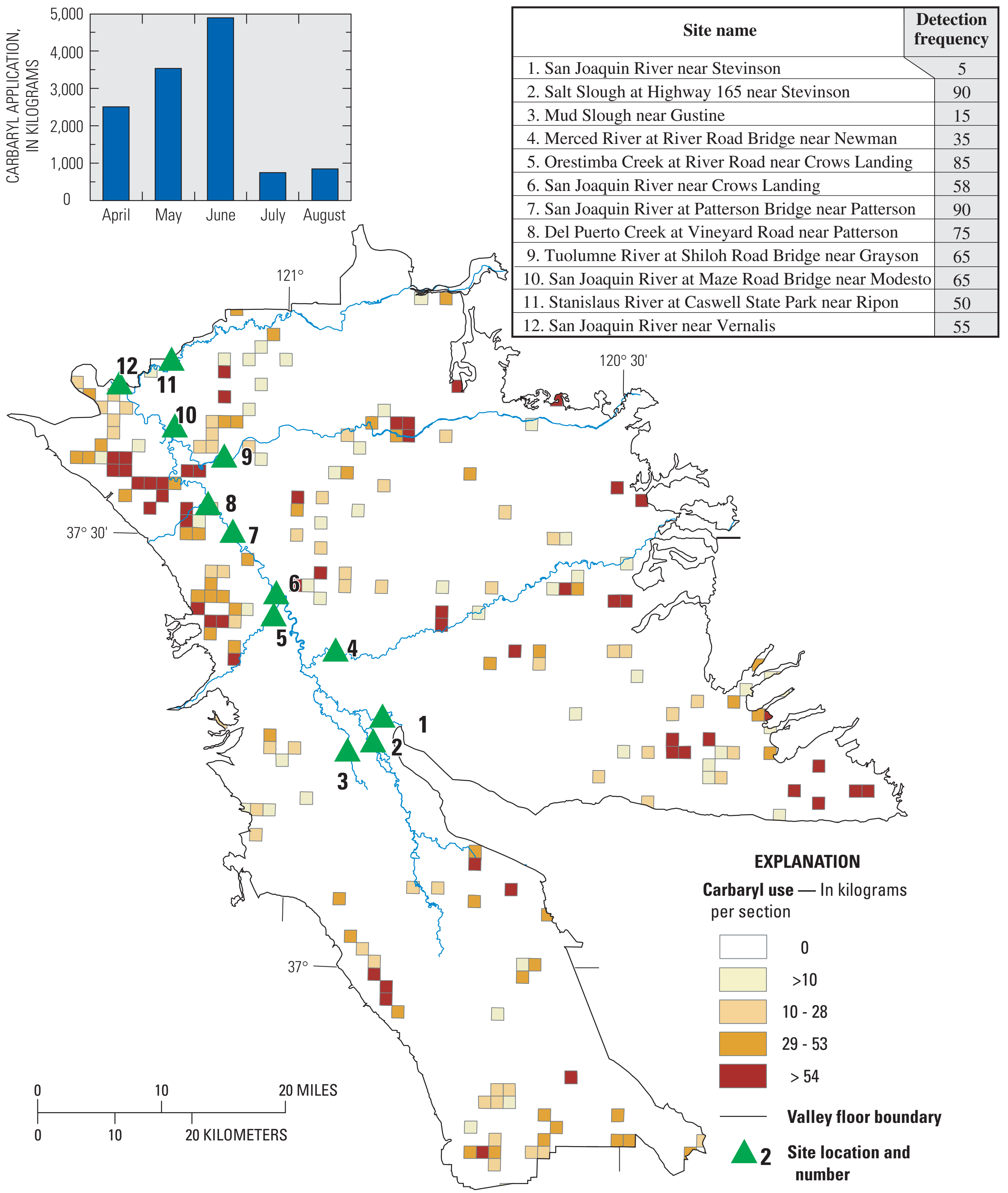


Figure 17. Use of chlorpyrifos during April through August 2001, and chlorpyrifos detection frequency at selected sites, San Joaquin Valley, California.



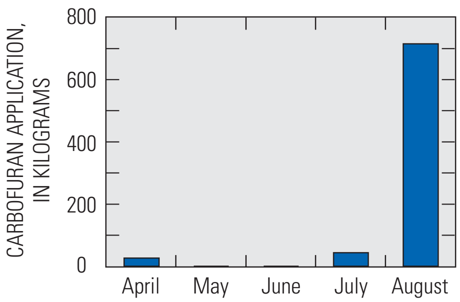
Site name	Detection frequency
1. San Joaquin River near Stevinson	30
2. Salt Slough at Highway 165 near Stevinson	90
3. Mud Slough near Gustine	85
4. Merced River at River Road Bridge near Newman	10
5. Orestimba Creek at River Road near Crows Landing	100
6. San Joaquin River near Crows Landing	74
7. San Joaquin River at Patterson Bridge near Patterson	100
8. Del Puerto Creek at Vineyard Road near Patterson	100
9. Tuolumne River at Shiloh Road Bridge near Grayson	80
10. San Joaquin River at Maze Road Bridge near Modesto	100
11. Stanislaus River at Caswell State Park near Ripon	55
12. San Joaquin River near Vernalis	100

Figure 18. Use of diazinon during April through August 2001, and diazinon detection frequency at selected sites, San Joaquin Valley, California.



Site name	Detection frequency
1. San Joaquin River near Stevinson	5
2. Salt Slough at Highway 165 near Stevinson	90
3. Mud Slough near Gustine	15
4. Merced River at River Road Bridge near Newman	35
5. Orestimba Creek at River Road near Crows Landing	85
6. San Joaquin River near Crows Landing	58
7. San Joaquin River at Patterson Bridge near Patterson	90
8. Del Puerto Creek at Vineyard Road near Patterson	75
9. Tuolumne River at Shiloh Road Bridge near Grayson	65
10. San Joaquin River at Maze Road Bridge near Modesto	65
11. Stanislaus River at Caswell State Park near Ripon	50
12. San Joaquin River near Vernalis	55

Figure 19. Use of carbaryl during April through August 2001, and carbaryl detection frequency at selected sites, San Joaquin Valley, California.



Site name	Detection frequency
1. San Joaquin River near Stevinson	15
2. Salt Slough at Highway 165 near Stevinson	50
3. Mud Slough near Gustine	30
4. Merced River at River Road Bridge near Newman	0
5. Orestimba Creek at River Road near Crows Landing	30
6. San Joaquin River near Crows Landing	32
7. San Joaquin River at Patterson Bridge near Patterson	30
8. Del Puerto Creek at Vineyard Road near Patterson	25
9. Tuolumne River at Shiloh Road Bridge near Grayson	0
10. San Joaquin River at Maze Road Bridge near Modesto	25
11. Stanislaus River at Caswell State Park near Ripon	5
12. San Joaquin River near Vernalis	15

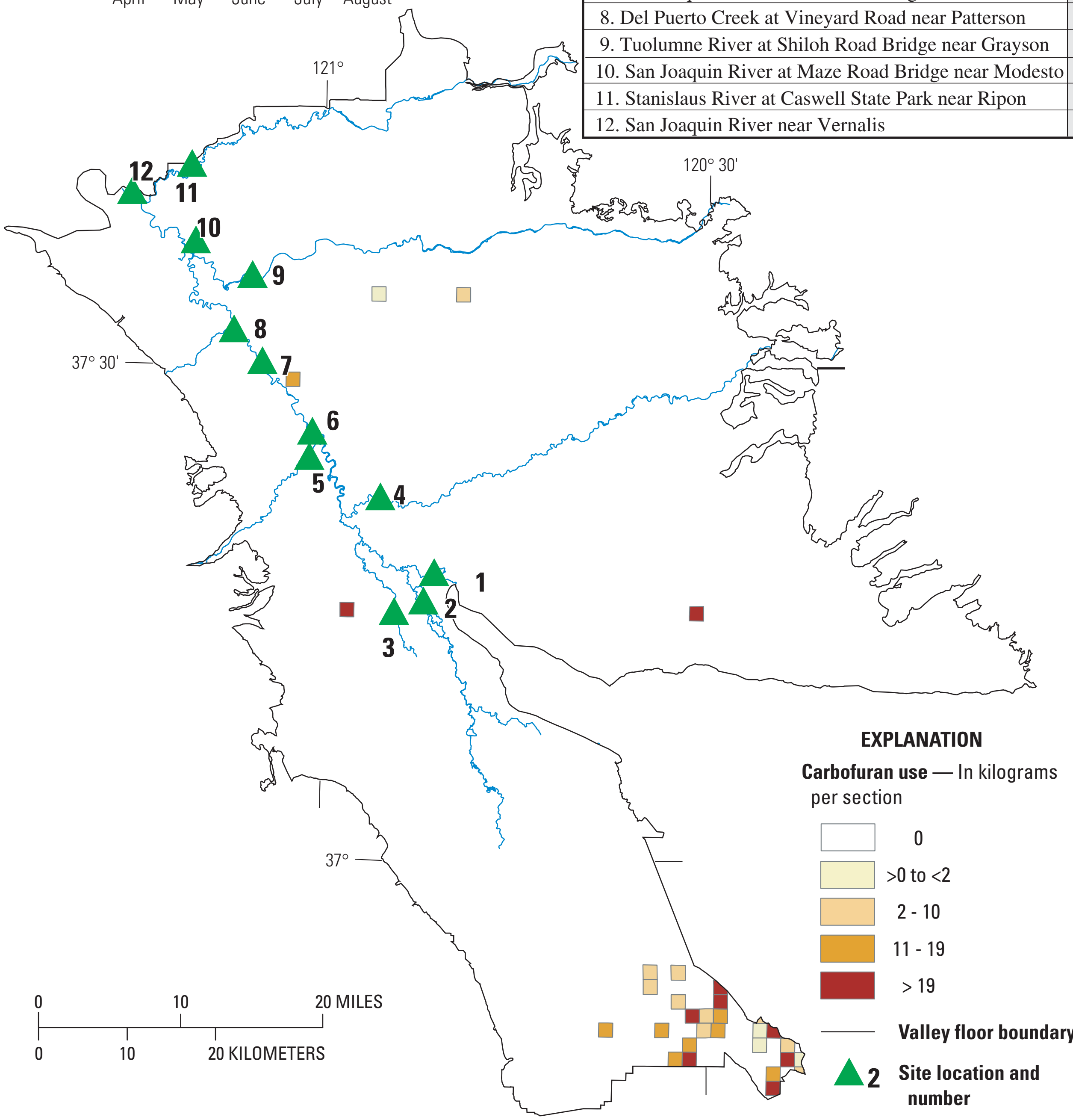
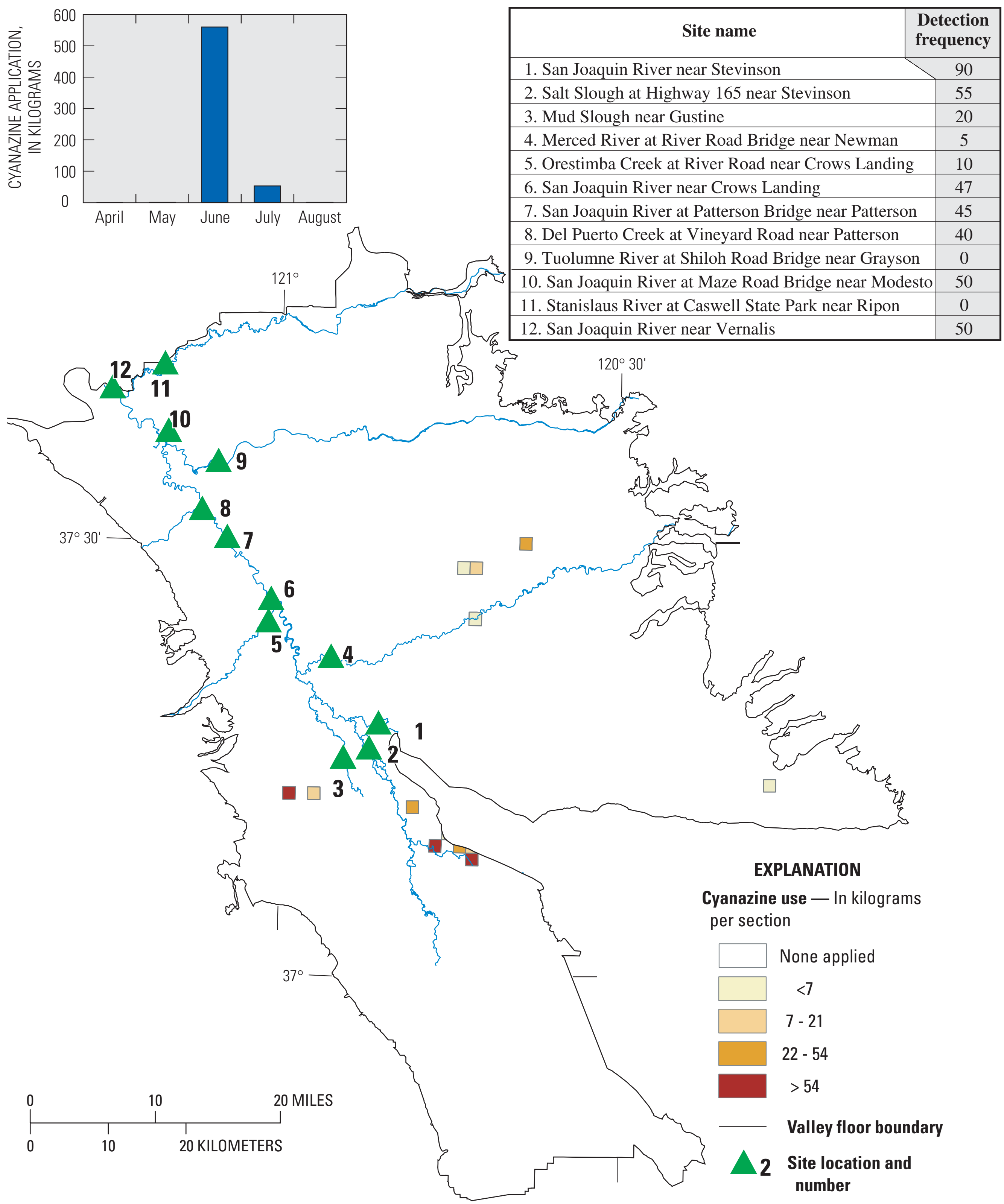
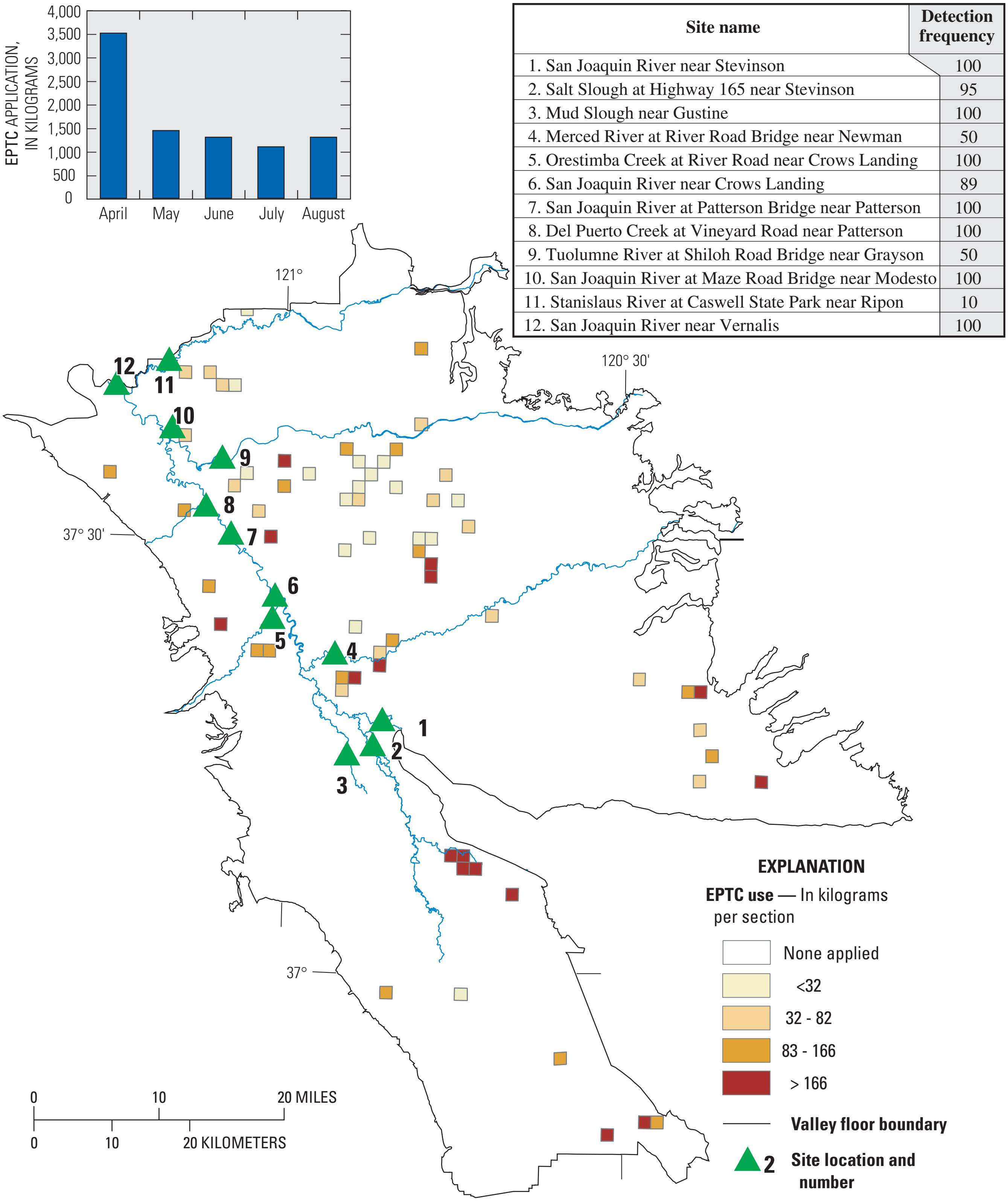


Figure 20. Use of carbofuran during April through August 2001, and carbofuran detection frequency at selected sites, San Joaquin Valley, California.



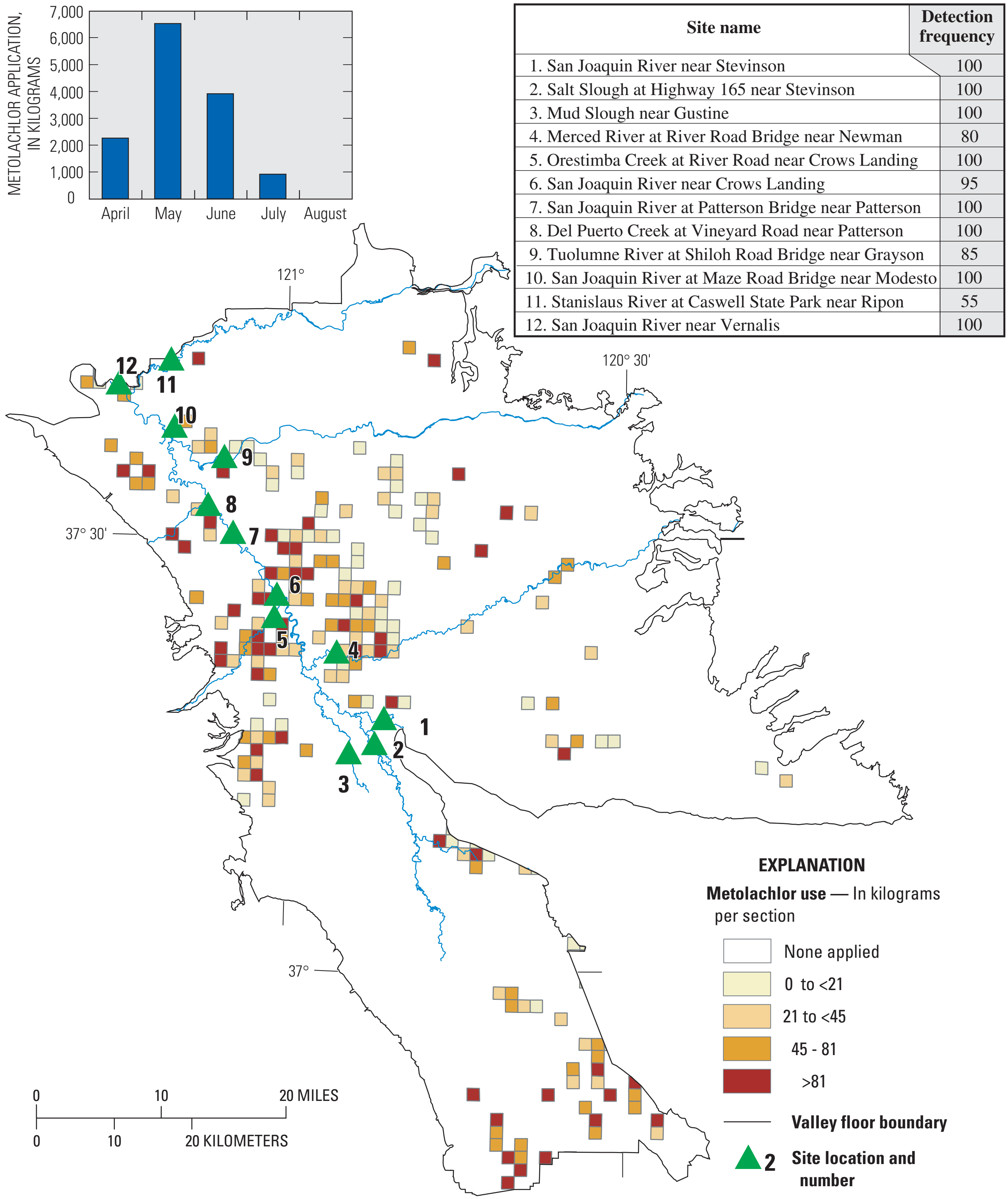
Site name	Detection frequency
1. San Joaquin River near Stevinson	90
2. Salt Slough at Highway 165 near Stevinson	55
3. Mud Slough near Gustine	20
4. Merced River at River Road Bridge near Newman	5
5. Orestimba Creek at River Road near Crows Landing	10
6. San Joaquin River near Crows Landing	47
7. San Joaquin River at Patterson Bridge near Patterson	45
8. Del Puerto Creek at Vineyard Road near Patterson	40
9. Tuolumne River at Shiloh Road Bridge near Grayson	0
10. San Joaquin River at Maze Road Bridge near Modesto	50
11. Stanislaus River at Caswell State Park near Ripon	0
12. San Joaquin River near Vernalis	50

Figure 21. Use of cyanazine during April through August 2001, and cyanazine detection frequency at selected sites, San Joaquin Valley, California.



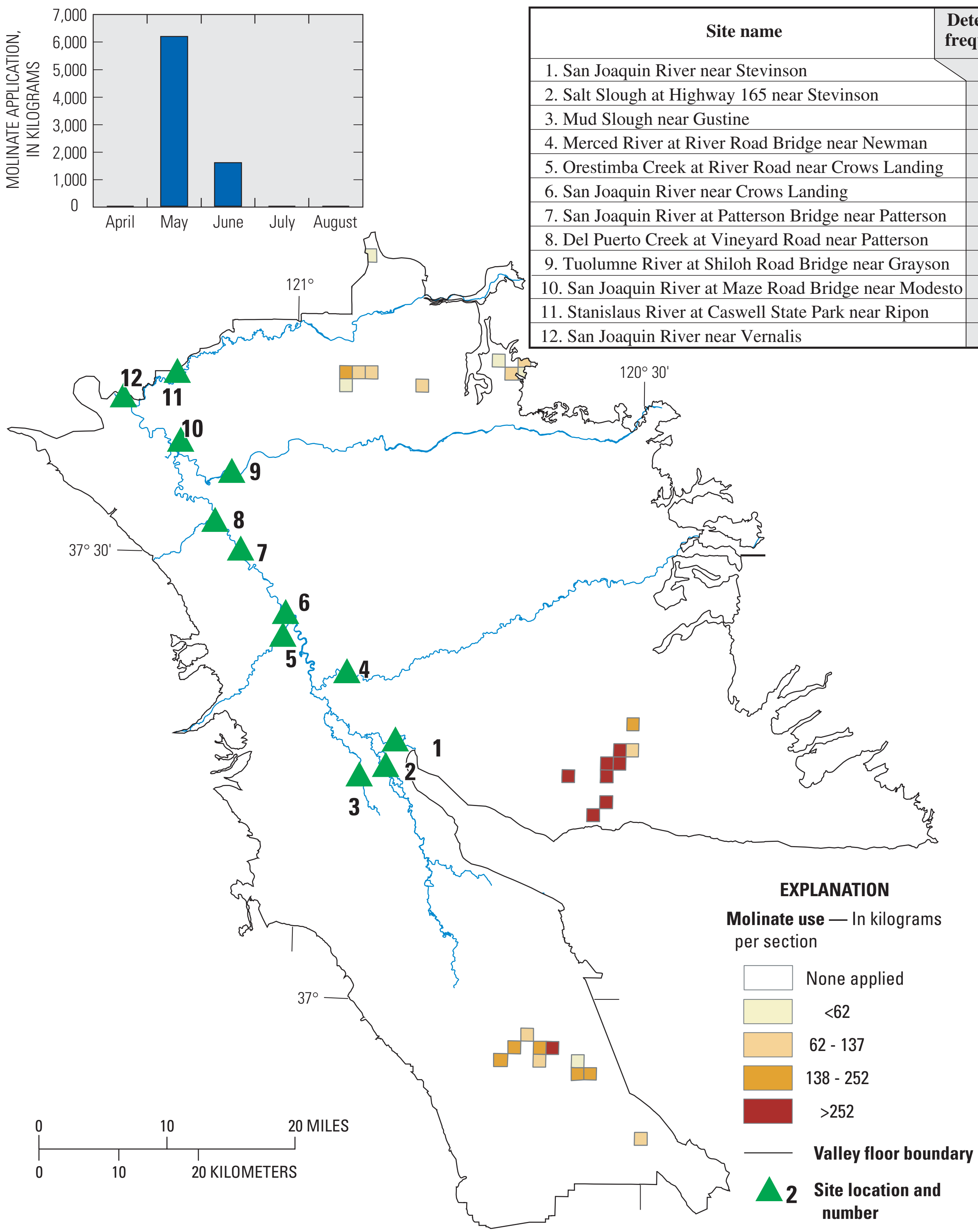
Site name	Detection frequency
1. San Joaquin River near Stevinson	100
2. Salt Slough at Highway 165 near Stevinson	95
3. Mud Slough near Gustine	100
4. Merced River at River Road Bridge near Newman	50
5. Orestimba Creek at River Road near Crows Landing	100
6. San Joaquin River near Crows Landing	89
7. San Joaquin River at Patterson Bridge near Patterson	100
8. Del Puerto Creek at Vineyard Road near Patterson	100
9. Tuolumne River at Shiloh Road Bridge near Grayson	50
10. San Joaquin River at Maze Road Bridge near Modesto	100
11. Stanislaus River at Caswell State Park near Ripon	10
12. San Joaquin River near Vernalis	100

Figure 22. Use of EPTC during April through August 2001, and EPTC detection frequency at selected sites, San Joaquin Valley, California.



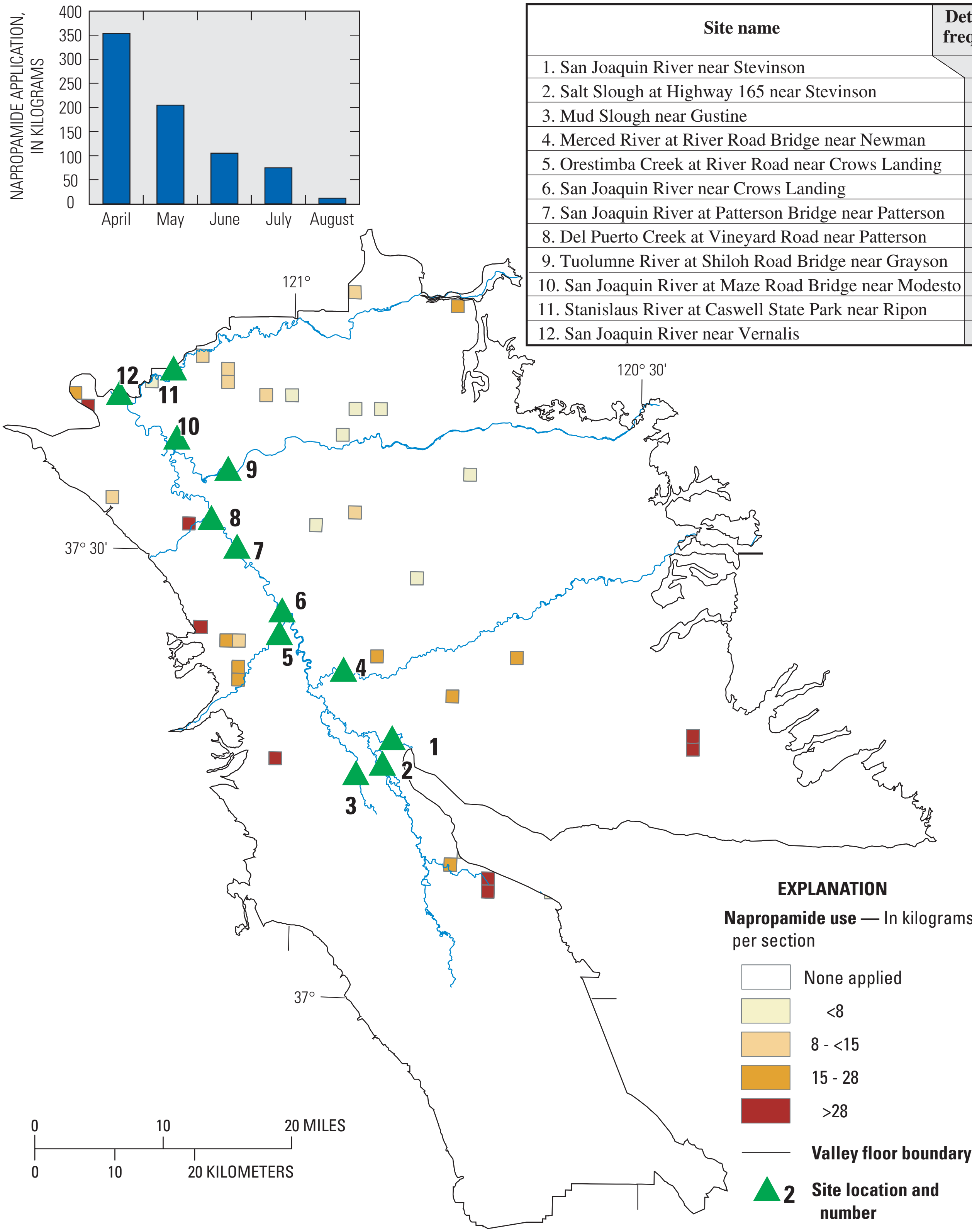
Site name	Detection frequency
1. San Joaquin River near Stevinson	100
2. Salt Slough at Highway 165 near Stevinson	100
3. Mud Slough near Gustine	100
4. Merced River at River Road Bridge near Newman	80
5. Orestimba Creek at River Road near Crows Landing	100
6. San Joaquin River near Crows Landing	95
7. San Joaquin River at Patterson Bridge near Patterson	100
8. Del Puerto Creek at Vineyard Road near Patterson	100
9. Tuolumne River at Shiloh Road Bridge near Grayson	85
10. San Joaquin River at Maze Road Bridge near Modesto	100
11. Stanislaus River at Caswell State Park near Ripon	55
12. San Joaquin River near Vernalis	100

Figure 23. Use of metolachlor during April through August 2001, and metolachlor detection frequency at selected sites, San Joaquin Valley, California.



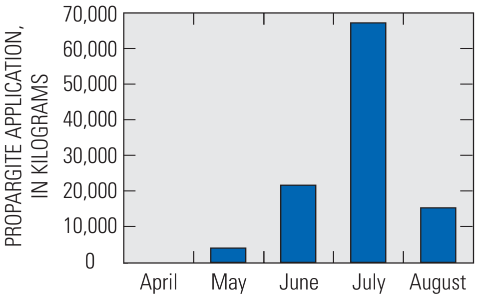
Site name	Detection frequency
1. San Joaquin River near Stevinson	20
2. Salt Slough at Highway 165 near Stevinson	50
3. Mud Slough near Gustine	90
4. Merced River at River Road Bridge near Newman	10
5. Orestimba Creek at River Road near Crows Landing	55
6. San Joaquin River near Crows Landing	53
7. San Joaquin River at Patterson Bridge near Patterson	55
8. Del Puerto Creek at Vineyard Road near Patterson	55
9. Tuolumne River at Shiloh Road Bridge near Grayson	10
10. San Joaquin River at Maze Road Bridge near Modesto	45
11. Stanislaus River at Caswell State Park near Ripon	20
12. San Joaquin River near Vernalis	35

Figure 24. Use of molinate during April through August 2001, and molinate detection frequency at selected sites, San Joaquin Valley, California.



Site name	Detection frequency
1. San Joaquin River near Stevinson	0
2. Salt Slough at Highway 165 near Stevinson	0
3. Mud Slough near Gustine	5
4. Merced River at River Road Bridge near Newman	0
5. Orestimba Creek at River Road near Crows Landing	55
6. San Joaquin River near Crows Landing	5
7. San Joaquin River at Patterson Bridge near Patterson	50
8. Del Puerto Creek at Vineyard Road near Patterson	65
9. Tuolumne River at Shiloh Road Bridge near Grayson	0
10. San Joaquin River at Maze Road Bridge near Modesto	15
11. Stanislaus River at Caswell State Park near Ripon	0
12. San Joaquin River near Vernalis	20

Figure 25. Use of napropamide during April through August 2001, and napropamide detection frequency at selected sites, San Joaquin Valley, California.



Site name	Detection frequency
1. San Joaquin River near Stevinson	0
2. Salt Slough at Highway 165 near Stevinson	5
3. Mud Slough near Gustine	0
4. Merced River at River Road Bridge near Newman	35
5. Orestimba Creek at River Road near Crows Landing	50
6. San Joaquin River near Crows Landing	21
7. San Joaquin River at Patterson Bridge near Patterson	35
8. Del Puerto Creek at Vineyard Road near Patterson	45
9. Tuolumne River at Shiloh Road Bridge near Grayson	20
10. San Joaquin River at Maze Road Bridge near Modesto	10
11. Stanislaus River at Caswell State Park near Ripon	25
12. San Joaquin River near Vernalis	10

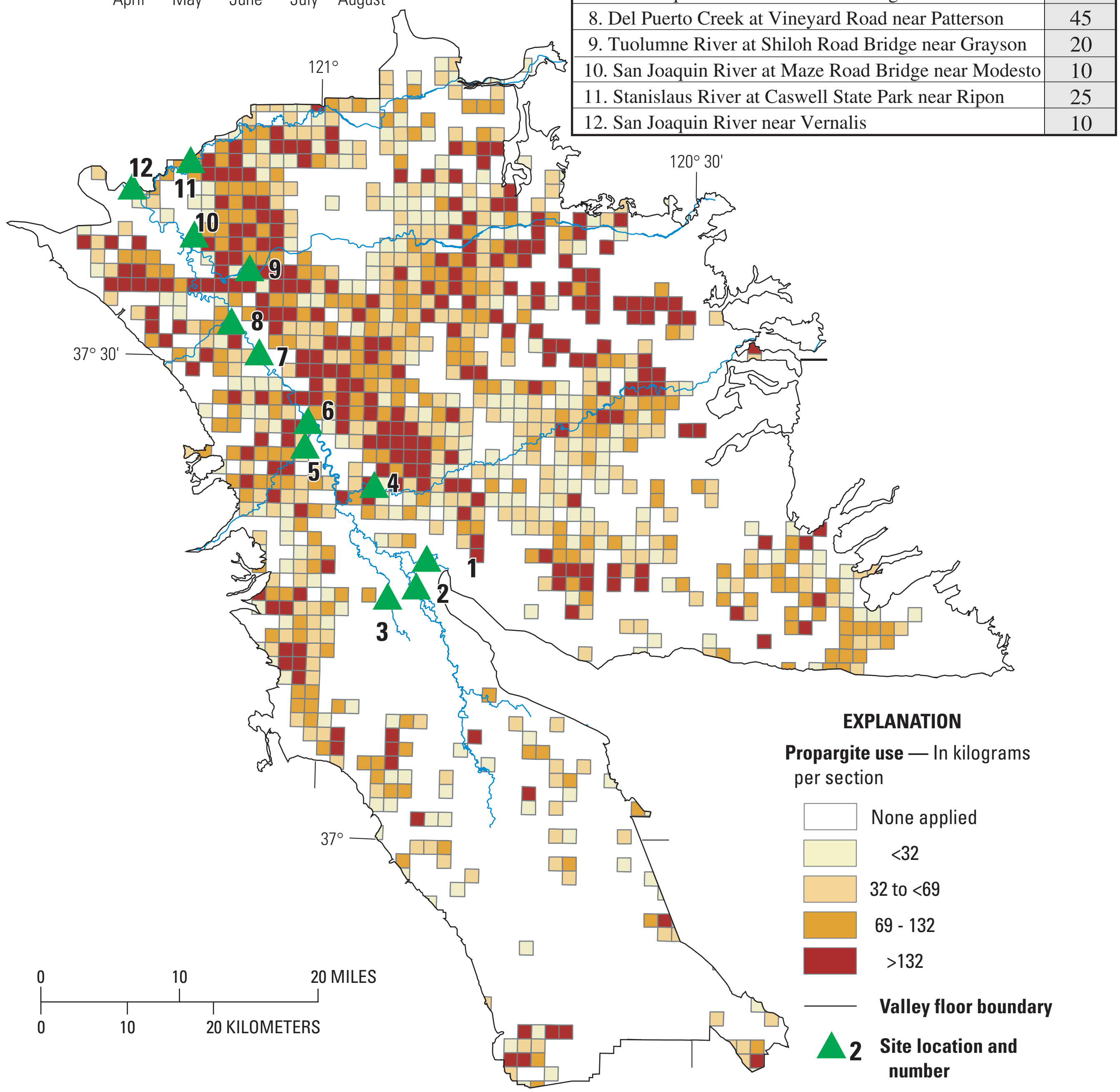
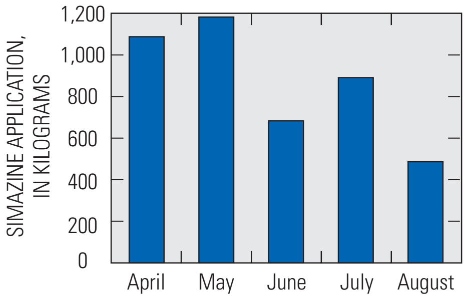


Figure 26. Use of propargite during April through August 2001, and propargite detection frequency at selected sites, San Joaquin Valley, California.



Site name	Detection frequency
1. San Joaquin River near Stevinson	100
2. Salt Slough at Highway 165 near Stevinson	100
3. Mud Slough near Gustine	100
4. Merced River at River Road Bridge near Newman	75
5. Orestimba Creek at River Road near Crows Landing	100
6. San Joaquin River near Crows Landing	95
7. San Joaquin River at Patterson Bridge near Patterson	100
8. Del Puerto Creek at Vineyard Road near Patterson	100
9. Tuolumne River at Shiloh Road Bridge near Grayson	95
10. San Joaquin River at Maze Road Bridge near Modesto	100
11. Stanislaus River at Caswell State Park near Ripon	70
12. San Joaquin River near Vernalis	100

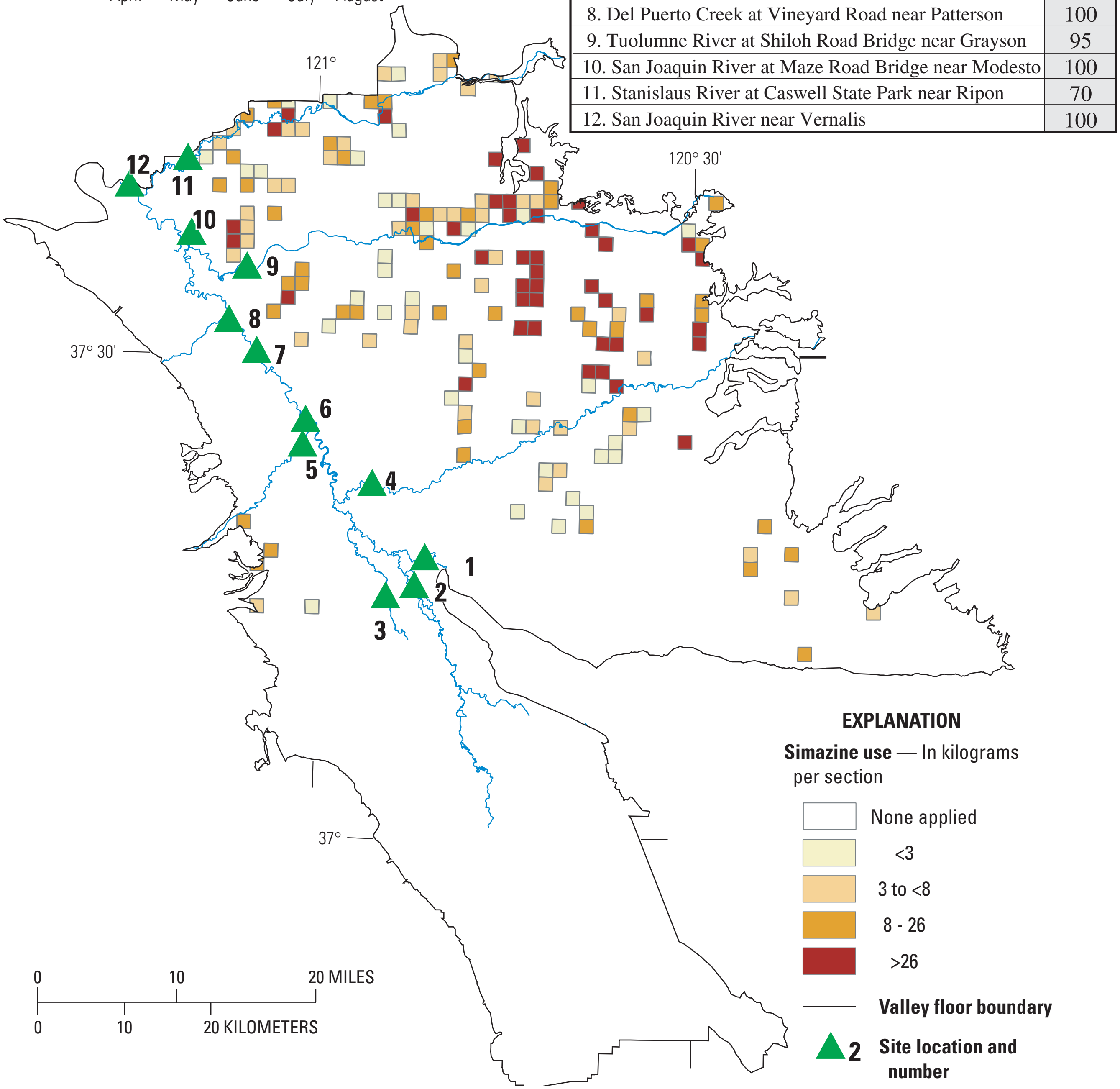
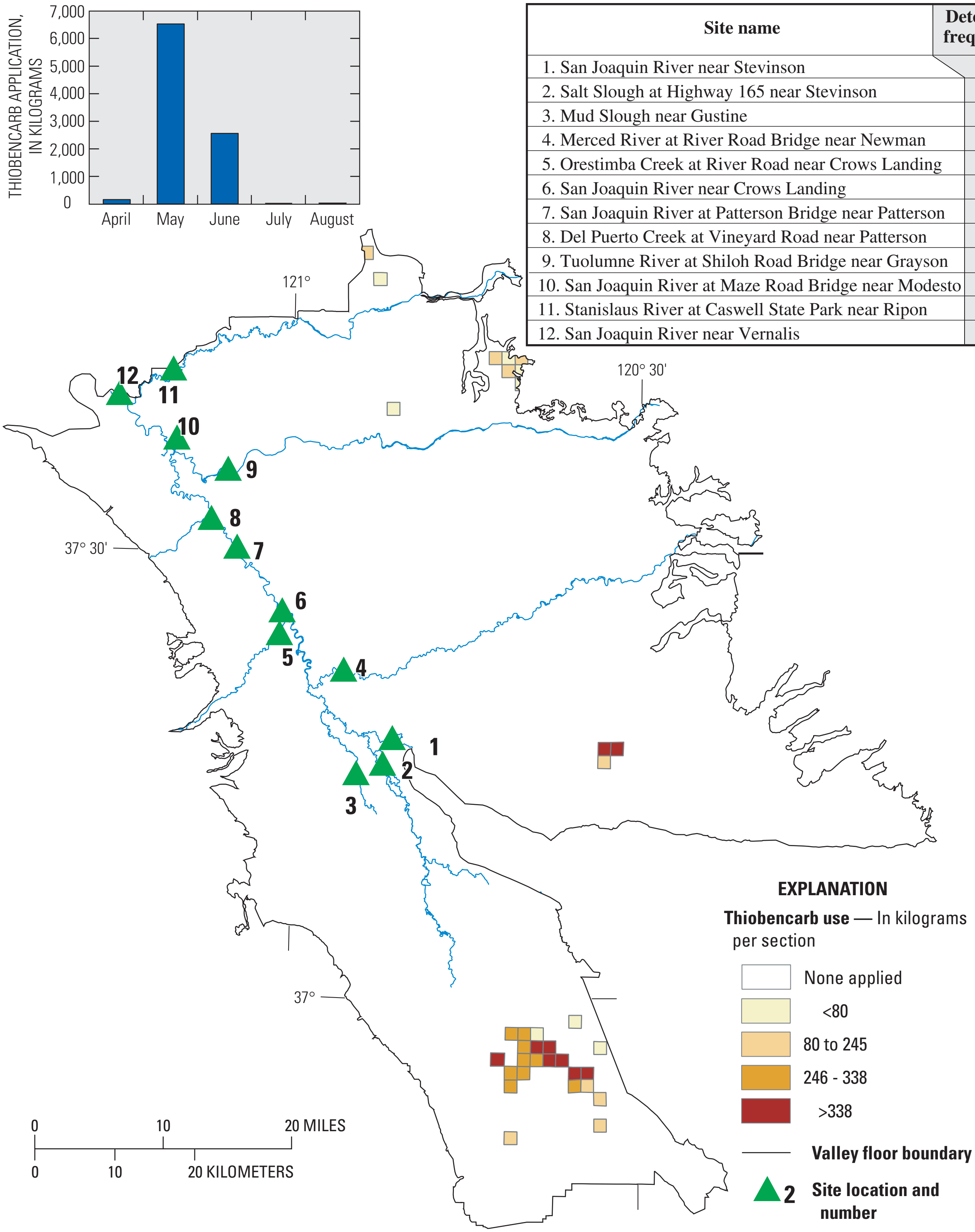
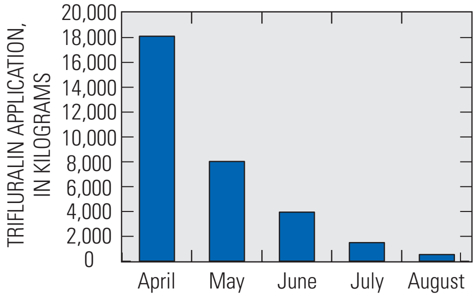


Figure 27. Use of simazine during April through August 2001, and simazine detection frequency at selected sites, San Joaquin Valley, California.



Site name	Detection frequency
1. San Joaquin River near Stevinson	0
2. Salt Slough at Highway 165 near Stevinson	25
3. Mud Slough near Gustine	80
4. Merced River at River Road Bridge near Newman	0
5. Orestimba Creek at River Road near Crows Landing	25
6. San Joaquin River near Crows Landing	26
7. San Joaquin River at Patterson Bridge near Patterson	35
8. Del Puerto Creek at Vineyard Road near Patterson	10
9. Tuolumne River at Shiloh Road Bridge near Grayson	0
10. San Joaquin River at Maze Road Bridge near Modesto	15
11. Stanislaus River at Caswell State Park near Ripon	0
12. San Joaquin River near Vernalis	10

Figure 28. Use of thiobencarb during April through August 2001, and thiobencarb detection frequency at selected sites, San Joaquin Valley, California.



Site name	Detection frequency
1. San Joaquin River near Stevinson	20
2. Salt Slough at Highway 165 near Stevinson	100
3. Mud Slough near Gustine	40
4. Merced River at River Road Bridge near Newman	50
5. Orestimba Creek at River Road near Crows Landing	100
6. San Joaquin River near Crows Landing	95
7. San Joaquin River at Patterson Bridge near Patterson	100
8. Del Puerto Creek at Vineyard Road near Patterson	100
9. Tuolumne River at Shiloh Road Bridge near Grayson	10
10. San Joaquin River at Maze Road Bridge near Modesto	100
11. Stanislaus River at Caswell State Park near Ripon	20
12. San Joaquin River near Vernalis	90

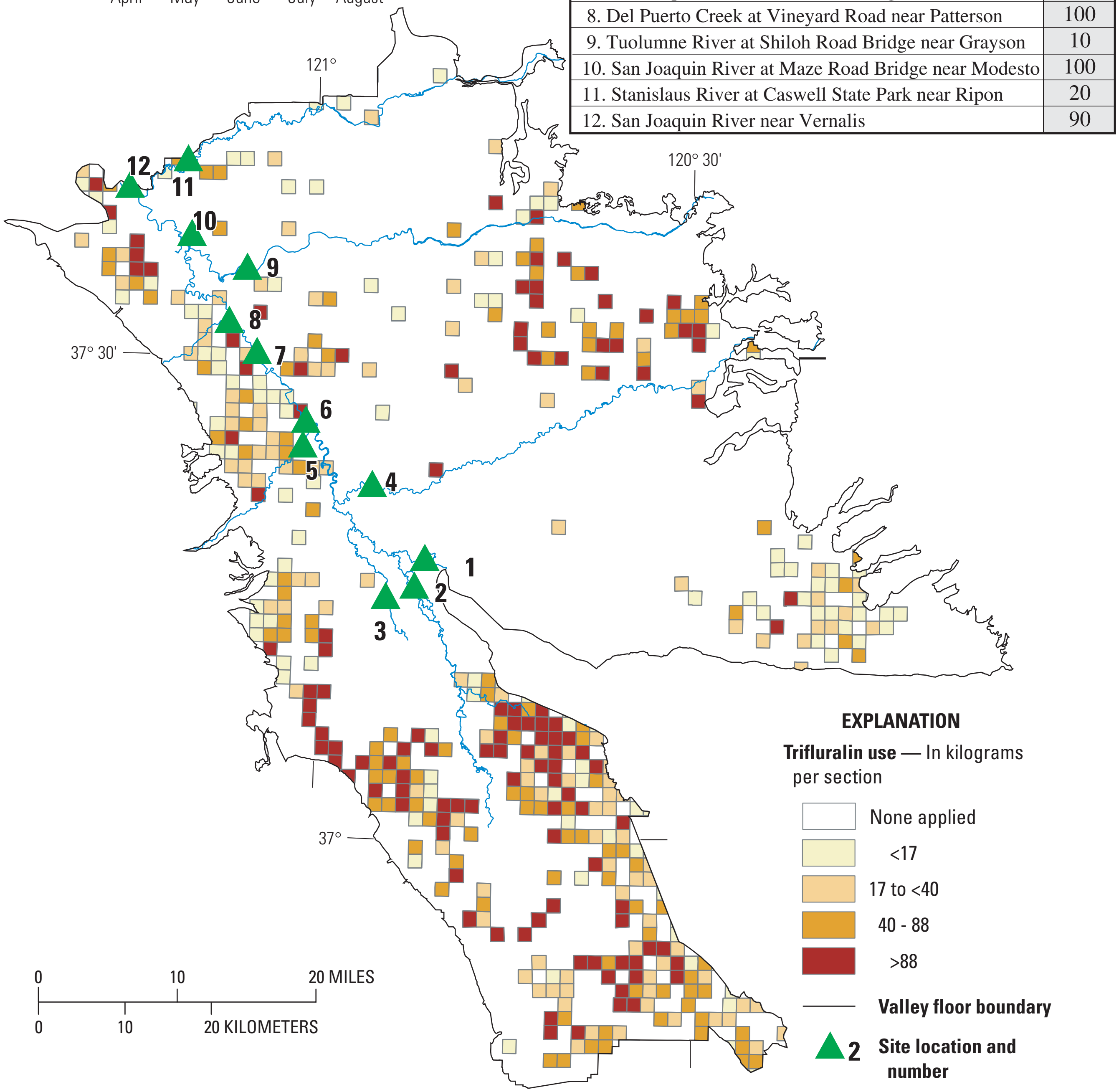


Figure 29. Use of trifluralin during April through August 2001, and trifluralin detection frequency at selected sites, San Joaquin Valley, California.

high pesticide use included walnuts and alfalfa. There was a similar pattern of pesticide usage on walnuts as for almonds. Pesticide usage on alfalfa was different in that more herbicides, especially trifluralin and EPTC were used relative to insecticides. As mentioned previously, the use of diazinon was relatively low compared with that of chlorpyrifos.

Herbicide use can be variable with respect to the types of compounds used, timing, and geographic location. The variability is mostly attributed to the large variety of crops cultivated in the San Joaquin Valley, with different needs for weed protection and different tolerance to various herbicides. For example, molinate and thiobencarb (figs. 24 and 28, table 21) are mainly applied in May. These two herbicides are used on rice and are applied for control of weeds prior to the planting of rice seeds. Other herbicides such as EPTC, metolachlor, and trifluralin (figs. 22, 23, and 29) also have a general seasonal period of applications, while simazine use (fig. 27) occurred throughout the period of study. In some cases, herbicides were detected at a sampling site even though no recorded agricultural use occurred in the basin either during the timeframe of the study, or during the preceding period, such as the winter or early spring. Molinate was detected at a frequency of 55 percent at the Orestimba Creek site, and thiobencarb was detected at a frequency of 25 percent at the same site. Rice is not grown in the Orestimba Creek Basin, and there are no other uses for those two herbicides, either for agriculture or for nonagricultural purposes. There was no use of either herbicide during the timeframe of this study in the Orestimba Creek Basin (figs. 24 and 28). It was shown in a previous study (Domagalski, 1997b) that these two compounds are transported into the Orestimba Creek Basin via the Central California Irrigation Drainage canal (fig. 1). The detections of atrazine, in spite of no use during the timeframe of the collection of the water samples, can possibly be attributed to the use of this compound at another time. It has been shown previously (Domagalski and others, 1997) that herbicide usage is high during the winter months throughout the San Joaquin Valley. Nonagricultural applications of herbicides also occur and also make the interpretation of herbicidal occurrence in water problematic. One large use of herbicides is for the control of weeds along roadways (Domagalski and others, 1997). The use of herbicides for that purpose is recorded as total amount applied for a particular county, but the actual roadways treated are not recorded.

SUMMARY AND CONCLUSIONS

The occurrence of diazinon and chlorpyrifos, and a suite of other insecticides and herbicides, in stream water was investigated during the growing season (April through August, 2001) in the San Joaquin Valley of California. Despite relatively low use of diazinon, detection frequencies were relatively high and reached 100 percent at several sites. In the vast majority of cases, the measured concentrations of diazinon were low and 90 percent of all measured concentrations were less than 0.06 micrograms per liter. The highest concentrations of diazinon tended to be measured in samples from two west-side tributaries to the San Joaquin River, Orestimba Creek, and Del Puerto Creek. Those concentrations were much lower than those previously recorded in studies of diazinon occurrence in streams following winter rainfall. The amount of diazinon transported out of the San Joaquin River Basin during the timeframe of study was 7,153 grams, which represents 0.17 percent of the total amount of diazinon applied during the April through August growing season. In contrast, the use of chlorpyrifos was much higher relative to diazinon, but the amount transported out of the basin was 3,758 grams, which represents only 0.007 percent of the total amount applied. The smaller amount of chlorpyrifos transported out of the basin was attributed mainly to the chemical properties of chlorpyrifos. Chlorpyrifos is less soluble than diazinon and more readily sorbs to sediment particles. Both properties tend to limit the transport of chlorpyrifos to water bodies. In both cases, the small tributaries of the western San Joaquin Valley, Orestimba and Del Puerto Creeks, yielded the greatest amounts of these two organophosphorus insecticides per unit area.

A fairly complex suite of other insecticides and herbicides was detected at the 12 sampling sites. Several herbicides including atrazine, EPTC, metolachlor, simazine, and trifluralin had detection frequencies greater than 50 percent at several sites. In some cases, very little or no agricultural use of a herbicide occurred in any of the tributary basins during the timeframe of this study, and the occurrence of the herbicides was attributed to either use during the preceding winter or growing season, to transport into the basin by way of one of the irrigation project canals, or to nonagricultural use.

A degradation product of DDT, *p,p′* DDE, was detected at high frequency at two sites of the western San Joaquin Valley (Orestimba and Del Puerto Creeks). The degradation product, DDE, was detected at a frequency of up to 95 percent, despite no use of the parent compound over the last few decades.

REFERENCES CITED

Bertoldi, G.L., Johnston, R.H., and Evenson, K.D., 1991, Ground water in the Central Valley, California—A summary report: U.S. Geological Survey Professional Paper 1401-A, 44 p.

de Vlaming, Victor, Connor, Valerie, Digiorgio, Carol, Bailey, H.C., Deanovic, L.A., and Hinton, D.E., 2000, Application of whole effluent toxicity test procedures to ambient water quality assessment: Environmental Toxicology and Chemistry, v. 19, no. 1, p. 42–63.

California Division of Mines and Geology, 1958, Geologic map of California, San Luis Obispo sheet: California Department of Conservation, scale 1:250,000, 2 sheets.

———1959, Geologic map of California, Santa Cruz sheet: California Department of Conservation, scale 1:250,000, 2 sheets.

———1964, Geologic map of California, Bakersfield sheet: California Department of Conservation, scale 1:250,000, 2 sheets.

———1965a, Geologic map of California, Fresno sheet: California Department of Conservation, scale 1:250,000, 2 sheets.

———1965b, Geologic map of California, Sacramento sheet: California Department of Conservation, scale 1:250,000, 2 sheets.

———1966, Geologic map of California, San Jose sheet: California Department of Conservation, scale 1:250,000, 2 sheets.

———1967, Geologic map of California, Mariposa sheet: California Department of Conservation, scale 1:250,000, 2 sheets.

———1969, Geologic map of California, Los Angeles sheet: California Department of Conservation, scale 1:250,000, 2 sheets.

Domagalski, J.L., 1997a, Pesticides in surface and ground water of the San Joaquin-Tulare Basins, California: Analysis of available data, 1966 through 1992: U.S. Geological Survey Water-Supply Paper 2468, 74 p.

———1997b, Results of a prototype surface water network design for pesticides developed for the San Joaquin River Basin, California, Journal of Hydrology, v. 192, p. 33–50.

Domagalski, J.L., Dubrovsky, N.M., and Kratzer, C.R., 1997, Pesticides in the San Joaquin River, California: Inputs from Dormant Sprayed Orchards, Journal of Environmental Quality, v. 26, no. 2, p. 454–465.

Dubrovsky, N.M., Kratzer, C.R., Brown, L.R., Gronberg, J.M., and Burow, K.R., 1998, Water quality in the San Joaquin–Tulare Basins, California, 1992–95: U.S. Geological Survey Circular 1159, 38 p.

Fitzgerald, S.A., 1997, Results of quality-control sampling of water, bed sediment, and tissue in the western Lake Michigan drainages study unit of the National Water-Quality Assessment Program: U.S. Geological Survey Water-Resources Investigations Report 97-4148, 24 p.

Gronberg, J.M., Dubrovsky, N.M., Kratzer, C.R., Domagalski, J.L., Brown, L.R., and Burow, K.R., 1998, Environmental setting of the San Joaquin–Tulare Basins, California: U.S. Geological Survey Water-Resources Investigations Report 97-4205, 45 p.

Kratzer, C.R., 1998, Pesticides in storm runoff from agricultural and urban areas in the Tuolumne River Basin in the vicinity of Modesto, California: U.S. Geological Survey Water-Resources Investigations Report 98-4017, 17 p.

———1999, Transport of diazinon in the San Joaquin River Basin, California: Journal of the American Water Resources Association, v. 35, no. 2, p. 379–395.

Kratzer, C.R., Zamora, Celia, Knifong, D.L., 2002, Diazinon and chlorpyrifos loads in the San Joaquin River Basin, California, January and February 2000: U.S. Geological Survey Water-Resources Investigations Report 02-4103, 38 p.

Kuivila, K.M., and Foe, C.G., 1995, Concentrations, transport and biological effects of dormant spray pesticides in the San Francisco Estuary, California: Environmental Toxicology and Chemistry, v. 14, no. 7, p. 1141–1150.

Lindley, C.E., Stewart, J.T., and Sandstrom, M.W., 1996, Determination of low concentrations of acetochlor in water by automated solid-phase extraction and gas chromatography with mass-selective detection: Journal of AOAC International, v. 79, no. 4, p. 962–966.

Mueller, D.K., Martin, J.D., and Lopes, T.J., 1997, Quality-control design for surface-water sampling in the National Water-Quality Assessment Program: U.S. Geological Survey Open-File Report 97-223, 17 p.

Panshin, S.Y., Dubrovsky, N.M., Gronberg, J.M., and Domagalski, J.L., 1998, Occurrence and distribution of dissolved pesticides in the San Joaquin River Basin, California: U.S. Geological Survey Water-Resources Investigations Report 98-4032, 88 p.

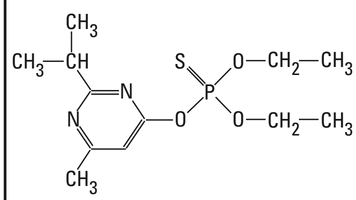
Werner, I., Deanovic, L.A., Connor, Valerie, de Vlaming, Victor, Bailey, H.C., Hinton, D.E., 2000, Insecticide-caused toxicity to *Ceriodaphnia dubia* (Cladocera) in the Sacramento–San Joaquin River Delta, California, U.S.A.: Environmental Toxicology and Chemistry, v. 19, no. 1, p. 215–227.

U.S. Environmental Protection Agency, California 1993 Section 303(d) list: California State Water Resources Control Board, accessed March 21, 2002, at http://www.epa.gov/region09/water/tmdl/calist/list5.html

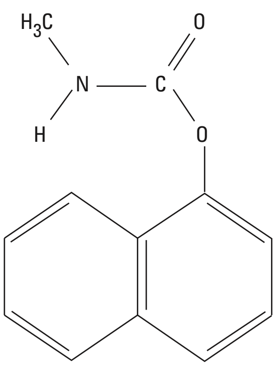
U.S. Geological Survey, Surface-water data for the nation: accessed January 12, 2002, at http://waterdata.usgs.gov/nwis/sw.

Zaugg, S.D., Sandstrom, M.W., Smith, S.G., and Fehlberg, K.M., 1995, Methods of analysis by the U.S. Geological Survey National Water Quality Laboratory—Determination of pesticides in water by C-18 solid-phase extraction and capillary-column gas chromatography/mass spectrometry with selected-ion monitoring: U.S. Geological Survey Open-File Report 95-181, 49 p.

Diazinon



Carbaryl



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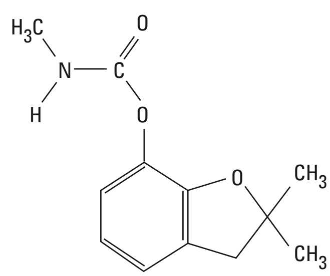

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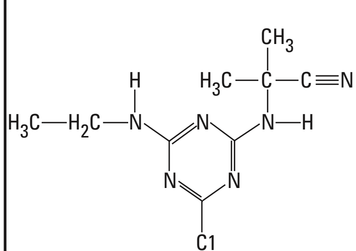

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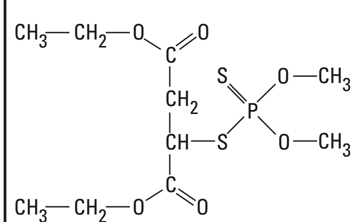
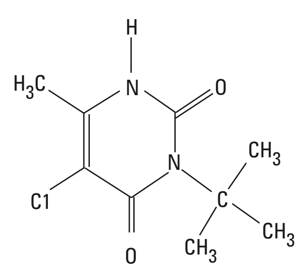


Terbacil



Domagalski and others—Evaluation of Diazinon and Chlorpyrifos Concentrations and Loads, and Other Pesticide Concentrations, at Selected Sites in the San Joaquin Valley, California, April to August, 2001—WRIR 03-4088