TEMPORAL DISTRIBUTION OF INSECTICIDE RESIDUES IN FOUR CALIFORNIA RIVERS

by

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Abstract

Several studies have indicated that certain pesticides are present in California rivers at levels which could be harmful to aquatic life. Generally, these studies have been conducted during certain seasons, but not year-round. Since year-round pesticide concentration data was limited for many California rivers having significant amounts of agricultural runoff, water was collected weekly from one sampling site along each of four rivers for a one-year period. This study was a cooperative effort between the Department of Pesticide Regulation (DPR) and the California Department of Fish and Game (CDFG). The portion conducted by DPR was an investigation of organophosphate, carbamate, and endosulfan residues in surface waters of four rivers: the Sacramento, Merced, Salinas and Russian Rivers. In addition to pesticide residue quantification by DPR, samples were tested for toxicity and ammonia concentration by CDFG on a bimonthly basis. Monitoring began on the Sacramento River in November 1993, followed by the Merced River in June of 1994 and by the Salinas and the Russian Rivers in August 1994. The primary sampling method was collecting composite samples during a 3-day period with an automatic sampler. Equal-width depth-integrated sampling and grab samples were also used. Pesticides were detected two or more times on each river. Diazinon was detected twice on the Sacramento River during periods of increased river flows. Dimethoate was detected twice, methidathion and diazinon were detected three times, and 3-hydroxy carbofuran were detected in samples collected from the Merced River. Each detection came during increased flows and with the exception of the dimethoate detections, the detections occurred during the rainy season. Chlorpyrifos was detected during the first major runoff event of the rainy season along the Salinas River. Samples were also collected monthly at the Salinas River Lagoon. Diazinon and dimethoate were detected in one sample collected in early summer. Samples collected from the Russian River yielded two detections: diazinon during the first runoff event in the fall and dimethoate during a winter rain event. CDFG found no apparent relationship between the presence of pesticide residues and mortality observed in the samples tested for toxicity.

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Introduction

Pesticide residues in surface water are of concern to the Department of Pesticide Regulation (DPR) due to their potential to contaminate drinking water and their possible effects on California's fish and wildlife. Studies conducted on the San Joaquin and Sacramento Rivers (Ross et al., 1996; Foe and Sheipline, 1993; Lee et al., 1993, Wofford and Lee, 1995), as well as regional studies (Shelton and Miller, 1988), indicated that certain pesticides are present in California rivers at levels which could be harmful to aquatic life. In these studies, however, samples were only collected once per month, or more frequently during certain seasons. Year-round pesticide concentration data is lacking for many California rivers which receive significant amounts of agricultural runoff that could contain pesticide residues. A more consistent sampling approach is required in order to identify potential problems caused by pesticides throughout the year.

This study was a cooperative effort between DPR and the California Department of Fish and Game (CDFG). Water was collected weekly from one sampling site along each of four rivers for a one-year period. DPR collected water samples and analyzed them for pesticide residues. CDFG tested the water for acute toxicity to fathead minnows, *Pimephales promelas* and cladoceran, *Ceriodaphnia dubia* on a bimonthly basis. The objective of this study was to identify rivers and seasons requiring more detailed pesticide investigation. Monitoring was conducted as reconnaissance to be used to indicate if more intense monitoring in the future will be needed. This study was not designed to derive statistical correlations between pesticide detections and rainfall, discharge, or pesticide use; however, useful information regarding tendencies was obtained.

The 3-day (72-hour) composite sampling method was chosen as a compromise between sampling for an entire week, which would likely create diluted samples, and sampling only a small portion of the flow each week. Monitoring for residues on a daily basis would have been optimal, but the travelling distance to three of the rivers prevented this. Composite sampling with the autosamper was chosen to sample a representative portion of the river's flow each week, yet without causing too much dilution that detections would be impossible.

The four rivers selected for this study include the Sacramento, Merced, Salinas, and Russian Rivers. Watersheds for these rivers have high density agriculture and associated pesticide use. The Sacramento River was selected since pesticides were detected during several studies conducted by DPR and other agencies on the river and its tributaries (Wofford and Lee, 1995; Kuivila and Foe, 1995; Lee et al., 1993; MacCoy et al., 1995). The Merced River was chosen because organophosphate residues were detected in river samples collected in 1993 by DPR (Ross et al., 1996) and by U.S. Geological Survey (Domagalski, 1995); however, year-round pesticide contamination data for these rivers were lacking.

The Salinas and Russian Rivers were chosen because few surface water monitoring studies of pesticide residues have been conducted in each of these watersheds. The studies that were conducted suggested a need for further study. Pesticide residues were detected in clam and fish tissue collected from both watersheds for the State Mussel Watch Program (SMWP) and the Toxic Substances Monitoring Program (TSMP) (Rasmussen, 1995a; Rasmussen, 1995b). In the Salinas River Watershed, chlorpyrifos, chlorthal-dimethyl, dicofol, endosulfan, and oxadiazon were detected in clam tissue and chlorpyrifos and chlorthal-dimethyl were detected in fish tissue. In the Russian River Watershed, chlorpyrifos, diazinon, endosulfan sulfate, chlorthal-dimethyl, and oxadiazon were detected in clam tissue and oxadiazon and ethyl parathion were detected in fish tissue. Other than SMWP and TSMP, the only pesticide sampling in the Salinas River watershed consisted of sediment sampling for endosulfan and chlorthal-dimethyl (Oakden and Oliver, 1988; Fleck et al., 1988). According to the Water Quality Control Plan for the Central Coast Region of the Regional Water Quality Control Board (CCRWQCB), the Salinas River is listed as water body needing an intensive survey for pesticides (1994). In the Russian River Watershed, studies have focused mainly on water quality issues other than pesticide residues. However, one of the studies conducted in the watershed found DDVP, 2,4-D and dichloprop (NCRWQCB, 1992). EPA priority pollutants, including some pesticides were also sampled; however, no pesticides were detected (Goodwin, 1993). Additional surface water monitoring of these two rivers was needed. The Salinas River Lagoon was also included in the study because it represents the lower portion of the Salinas River where water is present year-round.

The format of this report is as follows: sampling and analytical methods generic to all four rivers can be found in the materials and methods section, detailed description of each watershed and the sampling sites plus results and discussion can be found listed under each watershed, a general conclusion section covering all four rivers follows the river sections and a recommendation section for all four rivers concludes the report. This report will use the data collected to determine the temporal distribution of pesticide residues in each of the four rivers in order to make recommendations for further monitoring. Results of this study will be compared with previous studies and the physical-chemical properties of the more highly used pesticides will be examined to assess their environmental fate.

MATERIALS AND METHODS

Sampling Methods

Monitoring began on the Sacramento River in November 1993, followed by the Merced River in June 1994 and then by the Salinas and the Russian Rivers in August 1994. Each river was monitored weekly for an entire year.

Sampling sites were located downstream from agricultural areas and upstream from major sources of dilution water. Care was taken to select sites along the river that were well mixed. Accessibility of sites, safety for sampling crews and presence of year-round flow narrowed the choices of possible sites.

At the Sacramento, Merced and Russian Rivers, composite water samples were collected over a 3-day period using an ISCO® model 2700R/2740 refrigerated, automatic sampler The automatic sampler was placed on a platform or dock with a Teflon® intake line either set in a fixed position or on a flexible sampling arm. In all cases, the Teflon® line with a stainless-steel strainer attached was at least 2 feet below the water surface. The sampling schedule spanned three consecutive days per week, generally occurring over a weekend. The 3-day composite-sampling method was chosen as a compromise between sampling during as much of the week as possible, and preventing dilution of any pesticide residues that may have been present for a short duration During the 3-day period, a total of 20 L of water were collected by programming the automatic sampler to collect one subsample per hour, for a total of 72 hours of sampling. The sample was refrigerated at 4°C in the automatic sampler until retrieved by DPR staff. On a few occasions the automatic sampler failed to operate properly and instead, grab samples were collected. During such times, water was collected using a Teflon® bottle or a 1-gallon amber glass bottle, by submerging, removing the cap, filling, and replacing the cap before surfacing the bottle.

One drawback of using the 3-day sampling period is possible degradation of pesticide residues during sample collection and during transport time. River water subsamples collected during the beginning of the sampling period sat refrigerated and unacidified for up to 4 days including travel time, and subsamples collected near the end of the 72-hour period, sat for a much shorter time. The results of a storage stability study conducted on carbamates and organophosphates by Ross et al. (1995) showed that a few pesticides may begin to degrade during this length of time. The storage stability study was conducted by spiking two sets of test samples with a basic pH of 8.5 and one set of samples of acidified water at pH 3.0 One set of basic water samples were refrigerated and the other were frozen and the acidic water samples were refrigerated. All of the organophophates (OPs), carbamates (CBs), and respective breakdown products included in the screens, as well as endosulfan and its breakdown products were used to spike these samples. Then each sample was analyzed and recovery was determined over time. Our samples from the Sacramento, Merced and Russian Rivers were generally about pH 7, which reduces the potential for degradation. The Salinas River had a pH closer to 8 or greater. Based on the storage stability study, the OPs that might have degraded during collection and shipping are DDVP, malathion, phosmet, and the breakdown products: malathion OA (oxygen analog), methidathion OA, methyl parathion OA, chlorpyrifos OA and phosmet OA. The CBs that might have been affected are methiocarb, oxamyl, and the breakdown products: aldicarb sulfoxide and 3-hydroxy carbofuran.

During the winter months organophosphate insecticide use within the watershed is intensified along the Merced River due to dormant spray of chlorpyrifos, diazinon, and methidathion on almonds. These three OPs were detected during the dormant spray season in the Merced and San Joaquin Watershed in past studies (Domagalski, 1995; MacCoy et al., 1995; CVRWQCB, 1995a; Ross et al., 1996). To better determine the temporal distribution of dormant sprays in the Merced River, sample collection frequency was increased during the the dormant spray season to twice weekly from January 31 through March 6. A sample volume of 20 L was collected over a 48-hour period (versus 72 hours) and the second sample of the week (no pH adjustment) was analyzed for OPs only. CDFG conducted acute toxicity tests once per week during this period instead of every other week.

The automatic sampler was used throughout the year on the Sacramento River. However, the autosampler was not used year-round along the Merced and Russian Rivers and not used at all along the Salinas River. Heavy rains resulted in regional flooding in the Merced River watershed rendered the automatic sampler inoperative the third week of March. A contingency plan called for the collection of samples using the depth-integration method as described by Guy and Norman (1970). However, the equipment needed for this method was unavailable due to another project being conducted in another region of the state. Consequently, as an interim collection method, grab samples were collected from the center of the river during March 13 to April 17 from the old River Road bridge, located approximately 100 yards downstream of the automatic sampler. Grab samples reflect instantaneous concentrations, similar to a l-hour water quality criterion. Due to continued large amounts of precipitation in the watershed, Merced River discharge remained greater than normal and we were unable to use the automatic sampler to collect further samples. However, the equipment required to conduct depth-integrated sampling became available in April. Samples were collected weekly from April 24 through the end of the study, from the old River Road bridge, using the equal-width depth-integration method (Guy and Norman, 1970).

Due to the lack of available power and security, and the necessity to move the automatic sampler often due to fluctuations in the water level, the automatic sampler could not be used to sample the Salinas River. Instead, water was collected weekly for an entire year using the equal-width increment, depth-integration method (Guy and Norman, 1970). To provide a representative water sample, depth-integrated samples were taken at 10 to 30 verticals across the width of the river using a USGS model DH-81 sampler. The procedure took approximately 1 hour. A total of 20 L of water were collected and stored at about 4°C until analyzed. The monthly Salinas River Lagoon samples were collected by submersing l-gallon amber-glass bottles in the water, uncapping and recapping the bottles underwater when full.

Similar to the Merced River, flooding prevented the use of the automatic sampler on the Russian River. The autosampler was removed from its location on January 5, 1995. Subsequent samples were collected weekly from January 17 through May 1 from the Hacienda Bridge located 4 miles upstream of the original sampling site. Two methods were used; a grab sample was collected from the center of the river during the extreme flows to avoid equipment damage, and the equal-width depth-integration method (Guy and Norman, 1970). From May 8 to August 8, samples were again to be collected using the automatic sampler that was returned to the site near Guerneville. However, due to mechanical failure of the autosampler on May 8 and June 26, grab samples were collected from the river’s edge.

Within one day of collection, samples from the Sacramento, Merced and Russian Rivers were split with a ten-port splitter (Geotech® dekaport) into 6 discrete samples. Salinas River samples were split within 3 days of collection. For each sampling date, 14.5 L of water were sent to CDFG for toxicity testing with *C.dubia* and *P. promelas.* DPR retained three I-L samples for pesticide analyses by the California Department of Food and Agriculture (CDFA) Center for Analytical Chemistry. Water samples were kept at about 4°C on ice or refrigerated until analyzed.

Environmental Measurement Methods

Water quality and environmental parameters measured were pH, dissolved oxygen (DO), electrical conductivity (EC), water, and air temperature. Weekly *in situ* pH and DO measurements were made on the days samples were collected. A Sentron pH meter (model 1001) was used for pH measurements and DO was measured with a Yellow Springs Instruments (model 57) or a Corning (Check Mate 90 model) dissolved oxygen meter. DO and electrical conductivity were also measured by the Aquatic Toxicology Laboratory (ATL) on samples submitted for toxicity testing. Water and air temperatures were measured *in situ* with a Cole-Palmer temperature meter (model 90201-10) or a Whatman Lo-Temp µ-Sensor meter.

In addition to parameters measured by DPR, discharge data were obtained from DWR (Department of Water Resources) or USGS (U.S. Geological Survey) gauging stations. At the Salinas River at Gonzales, a gauging station was not available, discharge was measured by DPR staff weekly from August to December, 1994, using the six-tenths-depth method (Buchanan and Somers, 1969).

Pesticide Analytical Methods

Pesticides included in the screens for this study were not necessarily those with the greatest number of pounds of active ingredient (lb a.i.) applied in a given river watershed. Due to the large volume of water needed for the biotoxicity tests and the limitations of the automatic sampler, approximately 4 L of water from each composite sample was available for chemical analysis. Since the amount of water for chemical analysis was limited, pesticides that were generally more toxic to aquatic organisms and that have previously been detected in surface water were selected for analysis. Organophosphate and carbamate insecticides were included since both types are acetyl cholinesterase inhibiting pesticides, have been detected in surface water in the past, and can affect aquatic organisms at low concentrations. Endosulfan isomers I and II and the endosulfan breakdown product, endosulfan sulfate, were included in the analyses since each are still detected in fish and mussel tissue in state surface waters (Rasmussen, 1995a; Rasmussen, 1995b). Endosulfan is highly toxic to certain fish species (Mayer and Ellersieck, 1986). In addition, endosulfan was analyzed to assess the effects of recent changes to permit conditions which restrict the use of endosulfan in areas where it may run off directly into surface water.

Many other pesticides were applied in large amounts in one or more of the river basins but were not included in the analyses. For example, herbicides make up a large portion of pesticide use in each watershed but herbicides are generally not as toxic to aquatic invertebrates as insecticides (Mayer and Ellersieck, 1986). Many pesticides, such as sulfur and methyl bromide that are heavily used in the basins, are not expected to reach surface water due to their physical properties such as low water solubility or high volatility, respectively, or in the case of sulfur, it may be naturally occuring in an area. Fungicides vary in toxicity and some may be the focus of future studies. The fungicide ziram and the insecticide permethrin were considered for inclusion, but due to the poor reliability of detection methods and the requirement for special handling during sampling and storage, these two chemicals were excluded. Thiobencarb and molinate were not included in this study, because they have been extensively monitored in previous and ongoing studies and are only used in the Sacramento River Watershed.

Three I-L samples were retained for chemical analysis at 1 L for each of the following: organophosphates, carbamates, and endosulfan (I, II, and sulfate forms) (Table 1). To preserve samples prior to analysis, the OP and CB samples were acidified with hydrochloric acid to a pH of 3.0 to 3.5. In most cases, the pesticides listed in Table 1 were adequately preserved under acidic conditions for at least 2 weeks in storage at 4°C. However, in past studies, diazinon was found to degrade rapidly under acidic conditions (Ross et al., 1996). Therefore, diazinon was analyzed using a portion of the endosulfan sample, which was not acidified. Pesticides analyzed in the OP and CB screens and reporting limits (RL) for each pesticide are listed in Table 1. Extraction and analysis dates for samples are listed in appendix I.

Organophosphate Screen

For OP analysis, the river water was extracted with 100 ml methylene chloride by shaking for 2 min. The methylene chloride layer was drained through 20 g sodium sulfate and transferred to a 500-ml round bottom flask. The sample was extracted two more times. The solvent was evaporated to dryness on a rotary evaporator at 35°C and transferred with one 5-ml rinse and two 2-ml rinses with acetone, to a calibrated tube. The extract was reduced to 0.5 ml under N_2 without heat, and brought to a final volume of 1 ml with acetone. Analysis was performed by gas chromatography (GC) using a Hewlett Packard GC model HP-5890 (Wilminton, DE), equipped with a flame photometric detector. Oven temperature was 150°C, held for one min, and increased to 200°C by 10°C/min, and held for two min. This temperature was then increased to a final temperature of 250°C by 20°C/min and held for five min. Injector temperatures

Table 1. List of active ingredients and their breakdown products analyzed by the California Department of Food and Agriculture, Center for Analytical Chemistry, for the Four-River Monitoring Study

Organophosphate (OP) Screen[a]

Method: Gas chromatography/ Flame photometric detector

Compound	RL[b]
Azinphos-methyl	0.05
Azinphos-methyl OA[c]	0.05[e]
Chlorpyrifos	0.05
Chlorpyrifos OA	0.05[e]
DDVP	0.05
Diazinon	0.05
Diazinon OA	0.05[f]
Dimethoate	0.05
Ethoprop	0.05
Ethyl Parathion	0.05
Ethyl Parathion OA	0.05[g]
Fonofos	0.05
Malathion	0.05
Malathion OA	0.05[e]
Methidathion	0.05
Methidathion OA	0.05[f]
Methyl Parathion	0.05
Methyl Parathion OA	0.05[g]
Phosalone	0.05
Phosalone OA	0.05[f]
Phosmet	0.05
Phosmet OA	0.05[h]

N-methyl Carbamate (CB) Screen[a]

Method: High performance liquid chromatography/ Post Column derivitization with fluorescence detector

Compound	RL
Aldicarb	0.05
Aldicarb Sulfone	0.05
Aldicarb Sulfoxide	0.05
Carbaryl	0.05
Carbofuran	0.05
3-Hydroxycarbofuran	0.05
Methiocarb	0.05
Methiocarb Sulfone	0.05
Methiocarb Sulfoxide	0.05
Methomyl	0.05
Oxamyl	0.05

Endosulfan

Method: Gas chromatography/ Electron capture detector

Compound	RL
Endosulfan I	0.005
Endosulfan II	0.005
Endosulfan Sulfate	0.01

Diazinon[d]

Method: Gas chromatography/ Nitrogen phosphorus detector

Compound	RL
Diazinon	0.05
Diazinon OA	0.05

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a) Preserved by acidification. b) Reporting limit in ppb. c) Oxygen analog. d) Diazinon and diazinon OA were extracted from the same water sample as endosulfan I, endosulfan II and endosulfan sulfate. e) analyzed until 5/25/95. f) analyzed until 4/25/95. g) analyzed until 8/16/94. h) analyzed until 2/6/95.

were 220°C and **250°C,** respectively. The complete analytical method and method validation recoveries are in Appendix II and Appendix III, respectivley.

Carbamate Screen

For the CB screen, the water samples (about 100 g) were extracted using three 100-ml aliquots of methylene chloride, shaking vigorously for one minute. Solvent layers from all three extractions were poured into a 500-ml round bottom flask and concentrated to 3-5 ml on a rotary evaporator at 30-35°C. About one g of sodium sulfate was used to remove any water from the concentrate and then filtered through a 0.45µm filter into a calibrated tube. The flask was rinsed with two 2-ml aliquots of methylene chloride and filtered through the same filter into the same tube. The extract was evaporated to dryness under N_2 at 35°C, and brought to final volume of 0.2 ml with methanol, and mixed for about 15 sec using a vortex. Immediately prior to high performance liquid chromatography analysis, 0.8 ml of water were added and the sample was mixed for about 15 sec using a vortex, and transferred to an autosampler vial. Analysis was performed using a Hewlett Packard 1090 Liquid Chromatograph equipped with a C18 column (4.6 mm by 25 cm by 5µm) Pickering Labs post-column derivatization system (Pickering Labs, Mountain View CA) and a Hitachi F1000 Flourescence spectrometer set at 340 and 450 nm excitation and emission wavelengths, respectively. A water-acetonitrile gradient was used to separate the analytes. Complete analytical method and method validation recoveries are in Appendix II and Appendix III, respectivley.

Diazinon and Endosulfan

Endosulfan I, II, and sulfate and diazinon residues were extracted from water samples (1 L) twice with 100 ml and once with 80 ml aliquots of methylene chloride, shaking for 1.5 min, venting often. Solvent layers were drained through 30-g sodium sulfate into a 500-ml flat-bottomed boiling flask. The sodium sulfate was rinsed with three 10-ml aliquots of methylene chloride and added to the flask. The extract was evaporated to dryness on a rotary evaporator at 40°C and transferred to a calibrated tube using 8 to 10 ml of acetone and brought to a final volume of 2 ml under N_2 at 40°C.

Diazinon residue quantification was performed with a GC Hewlett Packard 5890 equipped with a flame photometric detector and a HP-1, methyl silicone gum column (10 m by 0.53 mm by 2.65 µm). Initial oven temperature was 150°C, held for two min, and increased to a final temperature of 200°C (held for one min) by 10°C/min. Injector and detector temperatures were 220°C and 250°C, respectively.

For Endosulfan, a florisil column clean-up prodedure was used, when necessary, prior to analysis. The extract solvent was exchanged from acetone to hexane under N_2 at 35°C. Extract was poured into a column filled with 10 cm heat-activated florisil, topped witha 12 mm sodium sulfate and pre-wet with 50 ml hexane. The extract was loaded quantitatively to the column and eluted with 200 ml of a 50% diethyl ether:hexane (containing 10-25 g anhydrous sodium sulfate) and collected in a 500 ml flat-bottomed boiling flask. The eluant was reduced to 2 ml on a rotary evaporator at 40°C, transferred to a calibrated tube using 8 to 10 ml hexane, and brought to final volume of 2 ml under N_2 at 40°C. Analysis was performed by GC (Varian Model 6000) equipped with an electron capture detector and a HP-1 capillary column, 25 m by 0.2mm by 0.33 µm. Initial oven temperature was 150°C, held for two min, and increased to 250°C by 25°C/min, and held for six min . Injector and detector temperatures were 230°C and 300, respectively. Complete analytical method and method validation recoveries are in Appendix II and Appendix III, respectivley.

Quality Control Methods

As part of our quality control (QC) program, data generated during method validation (see Appendix III) were used to assess all subsequent study results. Specifically, the data were used to establish warning and control limits similar to that described by Miller and Miller (1988). A warning limit is the mean ±2s, where the mean is the average % recovery found in method validation and the s is the standard deviation. A control limit is the mean ±3s. Continuing QC samples consisted of clean river water (background water determined to be pesticide free prior to analysis) from each river spiked with one or more analytes at given concentrations, extracted and analyzed with each extraction set. An extraction set consists of one to 14 field samples, and depends on how many samples are received in the laboratory for processing at any one time. During the course of the study, continuing QC samples are compared to the warning and control limits. If a continuing QC sample exceeds the warning limit the chemist is notified. If the continuing QC sample exceeds the control limit, corrective measures are taken in the lab. In addition, blank background water samples were analyzed with each extraction set. American River water was substituted as background water when there was any detectable pesticides in background collected from any of the four rivers. Average spike recoveries of individual OP parent compounds ranged from 93% to 107%. Spike recoveries for CB parent compounds ranged from 81% to 91%. Recoveries for endosulfan I, II, and endosulfan sulfate were 92%, 95% and 96%, respectively. Diazinon had an average recovery of 95%. Average spike recoveries, standard deviations and coefficients of variation of the QC data are summarized in appendix IV. The entire table of continuing QC results is filed at the Department of Pesticide Regulation and copies are available upon request. In addition, blind spikes were analyzed. A blind spike is a surface water sample that is spiked by one chemist and submitted to another for analysis. The analyte and concentration of blind spikes is therefore not known by the chemist performing the analysis.

As a quality assurance procedure in the field, equipment rinse samples were prepared for each river approximately every IO weeks. Equipment rinse procedures involved pouring deionized water sequentially into or through each piece of equipment used in the splitting procedure after a typical cleaning was performed. Sufficient deionized water was used to obtain three I-L samples which were stored and analyzed for pesticide residues the same way as river water samples. Equipment rinse samples for the Salinas River also included rinse water poured through the DH-81 sampler, then analyzed for pesticide residues.

Each autosampler was equipped with a 7-day temperature recorder. The records document that storage temperature remained near 4°C (±2°C), and are filed at DPR

CDFG Toxicity Testing Methods

Acute toxicity tests were performed by the **CDFG's** Aquatic Toxicology Laboratory. The toxicity tests were performed with fathead minnows *Pimephales promelas* larvae and cladoceran *Ceriodaphnia dubia* neonates on a bi-monthly basis on samples from each of the four rivers. Ten fathead minnow larvae were place into 1.0-L glass test chambers containing undiluted river water under static conditions with daily renewal. There were two replicates per treatment. Cladoceran neonates were also exposed to undiluted samples under static conditions with daily renewal solutions. Five cladocerans were placed in each of four 20-ml glass vials, containing river water. ATL well water and commercial spring water were used as the water in control samples. Mortality and water quality measurements for each test chamber were recorded daily for each test organism. A thorough description of the toxicity testing methods is presented in Appendix V.

Sacramento River

Sacramento River Watershed

The Sacramento River is the largest river in California both in flow (volume of water transported) and in drainage area (Domagalski and Brown, 1994). The river flows for 327 miles, from Mount Shasta in the north to the Sacramento-San Joaquin Delta in the south (Figure 1). Approximately 27,000 square miles (mi^2) of agricultural, urban and undeveloped land are drained, with over 21,000 mi^2 of that land located upstream of the sampling site used in this study (Mullen et al., 1994b). The Sacramento River provides a major source of the State's water supply, both drinking and agricultural (Domagalski and Brown, 1994), and is also an important resource for recreation and wildlife.

The primary source of water entering the system is surface runoff from the Sierra Nevada Mountains to the east. Runoff from rain events occurring in the Sacramento Valley provides significant short term increases in river flow. Seasonal rains occur from October to March with little significant rain from June to September. River flow during the summer is composed of dam releases of snowmelt water for irrigation and return flows from agricultural land. Due to the seasonal nature of rainfall in the Sacramento River Watershed, most agriculture is heavily dependent on irrigation from spring through fall.

The Feather River is the largest tributary of the Sacramento River. It contributes up to 47% of the discharge at the Verona gauging station and is the last major source of agricultural runoff flowing into the Sacramento River above the confluence of the Sacramento and American Rivers, 17 miles downstream. The sampling site used in this study was located at a private dock approximately 2.5 miles downstream of the confluence of the Sacramento and Feather Rivers and was located 1 mile downstream of the DWR gauging station at Verona (Figure 1).

The main flow of the Sacramento and Feather Rivers and their tributaries are heavily regulated by dams and water transfers. The Sacramento River's main flow is regulated by Shasta Dam and by water transfers from the Trinity River (CSLC, 1993). The Feather River is regulated by releases from Oroville Dam. Release rates are driven by demand and water availability. For example, discharge is increased during August and September to aid salmon swimming upriver at that time.

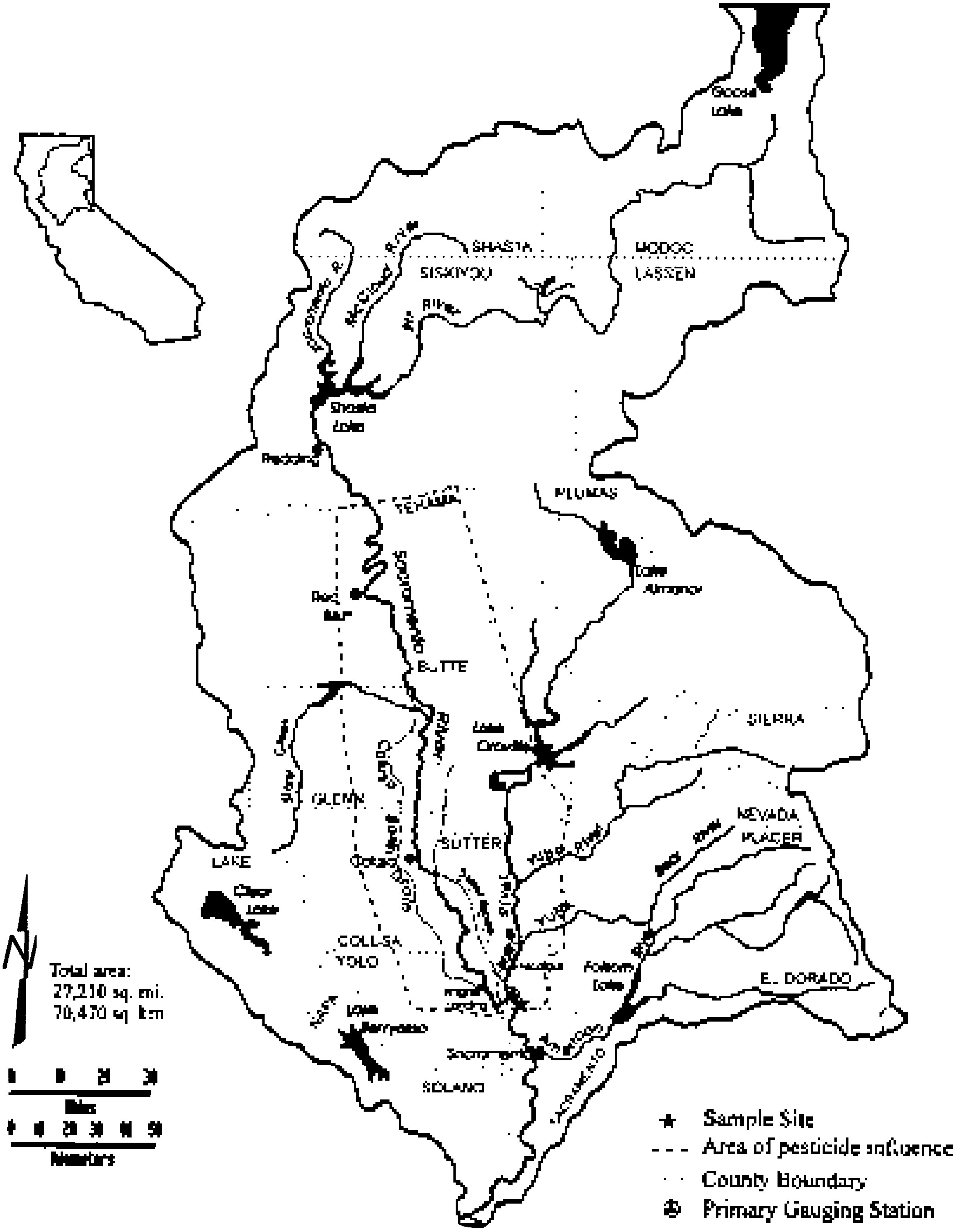


Figure 1. Map of the Sacramento River Watershed.

In the Sacramento River watershed water for agricultural use is dispersed through a system of canals and drains. Two major sources of agricultural return water to the Sacramento River above the sampling site are the Sacramento Slough (3.5 miles above the sampling site) and the Colusa Basin Drain (13.5 miles above the sampling site) (Figure 1). The Sacramento Slough flows east across the southern end of the Sutter By-pass and is formed from the merging of the Reclamation Slough and the western edge of the Sutter By-pass at Karnak. During the irrigation season, this flow is dominated by agricultural return water. The Colusa Basin Drain, which originates north of the city of Willows, discharges into the Sacramento River at Knights Landing. The Colusa Basin Drain captures waters from the two major diverters located on the west side of the Sacramento River, the Tehama-Colusa and Glenn-Colusa irrigation districts. These systems carry water originally diverted from the Sacramento River. Much of this water is used multiple times for irrigation by the time it is returned to the Sacramento River at Knights Landing. The Sacramento Slough captures most of the agricultural runoff from the area between the Sacramento and Feather Rivers. As much as 16% of the daily flow at the sampling site from August through September was supplied via the Colusa Basin Drain and the Sacramento Slough. Historically, during low water years, agricultural drains may contribute as much as 30% of the total river flow above the American River (SWRCB, 1990).

The Sacramento Valley is predominanly agricultural and roughly bounded by Shasta Dam to the north, Oroville Dam to the west, Black Butte Reservoir to the east and the Sacramento Delta to the south (Figure 1). The counties located upstream of the sampling site, where the bulk of pesticide use occurs, are Butte, Colusa, Glenn, Sutter Tehama, Yolo, and Yuba. Only the northern portion of Yolo County drains into the Sacramento River upstream of the sampling site, so only the data for the northern townships are included in this report. According to 1993 Agricultural Commissioners' Data, there were over 410,000 acres of rice, 120,000 acres of wheat, 80,000 acres of almonds 70,000 acres of prunes, and 60,000 acres each of sugar beets and walnuts grown in the Valley (CDFA, 1994). A great variety of other crops of lesser acreage were also grown. Pesticide use is as varied as the crops grown since 290 registered pesticides were used within the seven county region during 1993 (DPR, 1993).

Figures included in this report describe locations of pesticide applications and lb a.i. applied each month, and the major crops receiving the applications. The watersheds as depicted in these figures were reduced to the area of pesticide influence at our sampling site. This pesticide influence boundary excludes the watershed area downstream of our sites, upstream of large reservoirs and areas where pesticides analyzed in this study are not generally applied.

Environmental Measurements

Dissolved Oxygen was initially monitored weekly *in situ* but the frequency was reduced to random checks due to the consistently high oxygen levels in the Sacramento River. Daily rainfall measurements during the sampling period were obtained from the Sacramento Metropolitan Airport (4.5 miles south of the sampling site) and from the Colusa DWR weather station (40 miles northwest of the sampling site). When rain data from the selected monitoring station was absent, data from the closest operating weather station was substituted.

Water samples collected during the 12 month period had pH values ranging from 6.1 to 7.8 and DO values were between 8.3 to 11.2 mg/L (78 to 98% saturation, respectively) (Table 2). Both pH and DO met the water quality criteria set by the Central Valley Regional Water Quality Control Board (CVRWQCB,1995b) and the U.S. Environmental Protection Agency (U.S. EPA, 1986) (Table 3), except for the pH value on November 15. This low reading, pH 6. 1, may be an anomaly as the pH for the next 3 weeks exceeded 7.4 and no other value during the year fell below 6.9. Water temperatures on sample pick-up days ranged from 7.5” to 23.5” C and air temperatures from 4.7” to 29.0” c.

During the first quarter of the study there were 7.9 inches of rain recorded at the Colusa weather station and the Sacramento River discharge rate fluctuated between 10,600 to 29,100 cubic feet per second (cfs) (Figure 2). In the second quarter there were 2.3 inches of rain at Colusa and discharge ranged from 6,200 to 27,428 cfs (Figure 3). During the last 6 months there were 1.4 inches of rain at Colusa and discharge was between 5,400 and 13,953 cfs (Figures 4 and 5). Total annual discharge for the year was 70% of the mean historical discharge for the Sacramento River (Mullen et al., 1994b). Rainfall, however, was sufficient to allow for surface runoff from agricultural areas in the Sacramento Valley in December, January and February.

Pesticide Detections

During the 12-month sampling period, only two of the 52 samples (3.8%) had a pesticide concentration above the reporting limit (Table 2). Diazinon was detected at a concentration

Table 2. Sacramento River Water Quality Data and Pesticide Detections

Start Sample Date	End Sample Date	Air Temperature	Water Temperature	Dissolved Oxygen (mg/L)	% saturation	pH (in lab)	Detections
11/12/93	11/15/93	17.4	10.4	10.8	98%	8.1	
11/19/93	11/22/93	14.4	9.6	12.4	92%	7.8	
Grab	11/29/93	12	8.7	NT	NT	7.5	
12/3/93	12/6/93	13.7	9.4	10.18	89%	7.4	
12/10/93	12/13/93	12.5	9.3	13.8	94%	7.8	
12/17/93	12/20/93	4.7	8	10.3	89%	7.2	
Grab	12/27/93	9.4	7.5	11.2	93%	7.2	
12/31/93	1/3/94	6.9	8.3	10.7	92%	7.2	
1/7/94	1/10/94	9.8	8.5	NT	NT	7.3	
1/14/94	1/17/94	18	9	9.7	84%	7.2	
1/21/94	1/24/94	NT	NT	NT	NT	7.7	
1/28/94	1/31/94	11.3	8.3	10.8	91%	7.4	Diazinon (0.11 ppb)
2/4/94	2/7/94	10.8	9.5	NT	NT	7.7	
2/11/94	2/14/94	13.8	9	NT	NT	7.1	Diazinon (0.07 ppb)
2/18/94	2/21/94	10.4	8.5	NT	NT	7.8	
2/25/94	2/28/94	15.6	11.4	NT	NT	7.7	
3/4/94	3/7/94	21	13.3	NT	NT	7.4	
3/11/94	3/14/94	18.7	14.3	NT	NT	7.6	
3/18/94	3/21/94	17.5	14.3	NT	NT	7.8	
3/25/94	3/28/94	21.2	14.6	9.09	89%	7.5	
4/1/94	4/4/94	17	9	10.6	93%	7.4	
4/8/94	4/11/94	19.9	15.5	8.3	83%	7.5	
4/15/94	4/18/94	27.1	19.4	NT	NT	7.3	
4/22/94	4/25/94	NT	14.8	NT	NT	7.1	
4/29/94	5/2/94	22.3	17.8	8.8	90%	7.3	
5/6/94	5/9/94	21.9	17.2	NT	NT	6.9	
5/13/94	5/16/94	17.5	17.8	NT	NT	7.3	
5/20/94	5/23/94	25.3	20.5	NT	NT	7.5	
5/26/94	5/31/94	21.7	22.4	NT	NT	7.5	
6/3/94	6/6/94	22.5	20.5	NT	NT	7.5	
6/10/94	6/13/94	28	23.4	7.6	91%	7.8	
6/17/94	6/20/94	24	22.4	NT	NT	7.5	
6/24/94	6/27/94	24.8	23.5	7.4	91%	7.8	
7/1/94	7/4/94	24.2	22.8	7.7	90%	7.8	
7/8/94	7/12/94	24	22.2	NT	NT	7.3	
7/15/94	7/18/94	23.1	21.9	NT	NT	8.1	
7/22/94	7/25/94	20	21.4	NT	NT	NT	
7/29/94	8/1/94	23.5	21.5	NT	NT	7.6	
8/5/94	8/8/94	29	22.7	NT	NT	7.4	
Grab	8/15/94	27.7	22.3	NT	NT	7.3	
8/19/94	8/22/94	25.8	21.2	NT	NT	7.0	
8/26/94	8/29/94	22.9	19.9	7.85	84%	7.5	
9/2/94	9/5/94	23.0	20.1	NT	NT	7.5	
9/9/94	9/12/94	21	14.5	NT	NT	7.6	
9/16/94	9/19/94	25.3	19.7	7.9	87%	7.6	
9/23/94	9/26/94	26.5	20	NT	NT	7.5	
9/30/94	10/3/94	23	16.4	7.4	79%	7.4	
10/7/94	10/10/94	22.2	17.7	NT	NT	7.5	
Grab	10/17/94	18	16.7	8.4	83%	7.6	
10/21/94	10/24/94	18.1	14.3	8.2	81%	7.8	
10/28/94	10/31/94	17.6	13.8	NT	NT	8.3	
11/4/94	11/7/94	13.4	11.2	8.95	85%	8.5	

NT=measurement not taken

Table 3. Acute water quality objectives and criteria for the protection of freshwater aquatic life

Constituent	Central Valley Regional Water Quality Control Board[a]	Central Coast Regional Water Quality Control Board[b]	North Coast Regional Water Quality Control Board[c]	U.S. EPA Criteria[d]
pH	6.5-8.5	7.0-8.5	6.5-8.5	6.5-9.0
Dissolved Oxygen	5.0 mg/L (warm) 7.0 mg/L (Cold) 7.0 mg/L (spawn)[e]	5.0 mg/L (warm) 7.0 mg/L (Cold)	Specific for the Russian River Minimum: 7.0 mg/l 90% lower limit: 7.5 mg/l 50% lower limit: 10 mg/l	4.0 mg/L (Cold)

[a] Objectives are from: Central Valley Regional Water Quality Control Board. 1994. Water Quality Control Plan (Basin Plan), Central Valley Region, Sacramento and San Joaquin River Basins. Third Edition. Sacramento, CA.

[b] Central Coast Regional Water Quality Control Board. 1994. Water Quality Control Plan, Central Coast Region

[c] North Coast Regional Water Quality Control Board. 1994. Water Quality Control Plan for the North Coast Region (Basin Plan). Revised 1987. Santa Rosa, CA.

[d] Criteria are from: United States Environmental Protection Agency. 1986. Quality criteria for water 1986.

[e] Dissolved oxygen objectives and criteria are dependent on habitat type (warm, cold, or spawning habitat).

[f] Minimum of values: 90% or more of the values collected in a calendar year must be greater than the 90% lower limit. 50% or more of the values must be greater than the 50% lower limit. North Coast Basin Plan.

Sacramento River

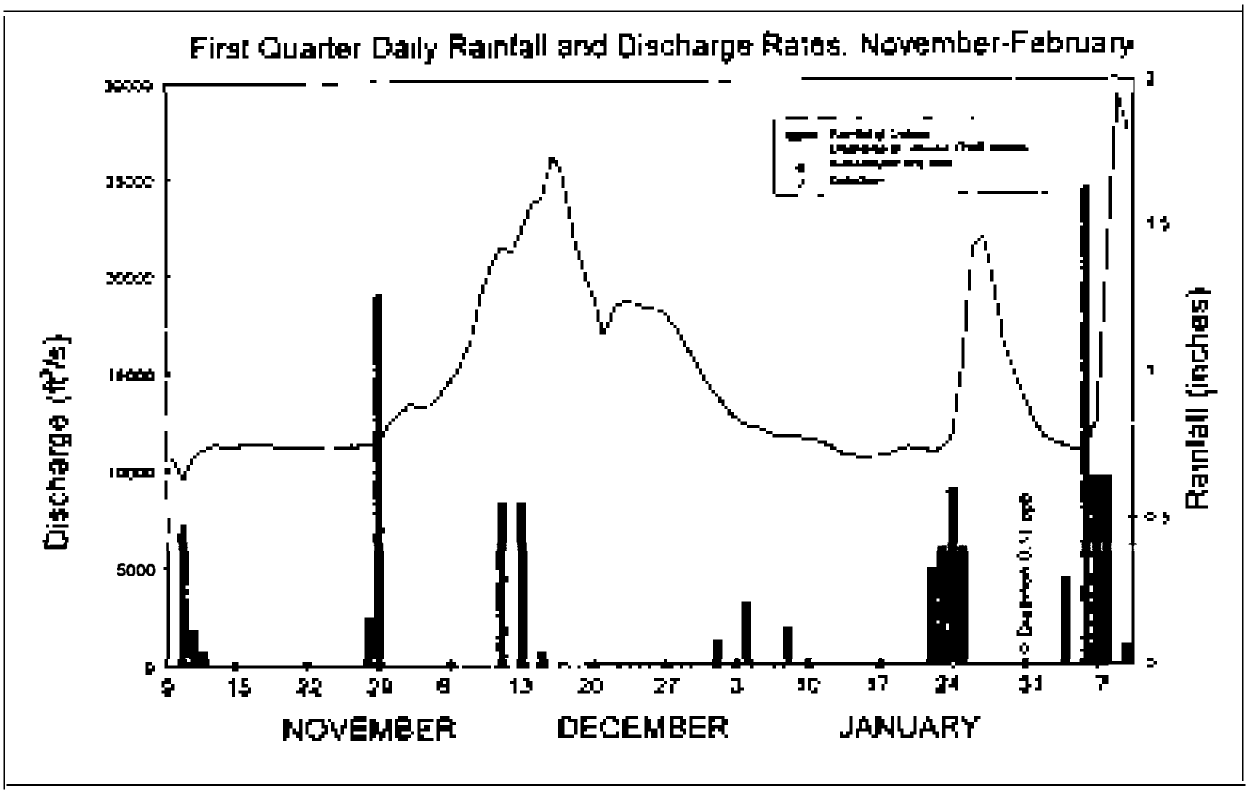

First Quarter Daily Rainfall and Discharge Rates. November-February

Figure 2. Daily rainfall and Sacramento River discharge (river flow) for November 9, 1993 through February 11, 1994.

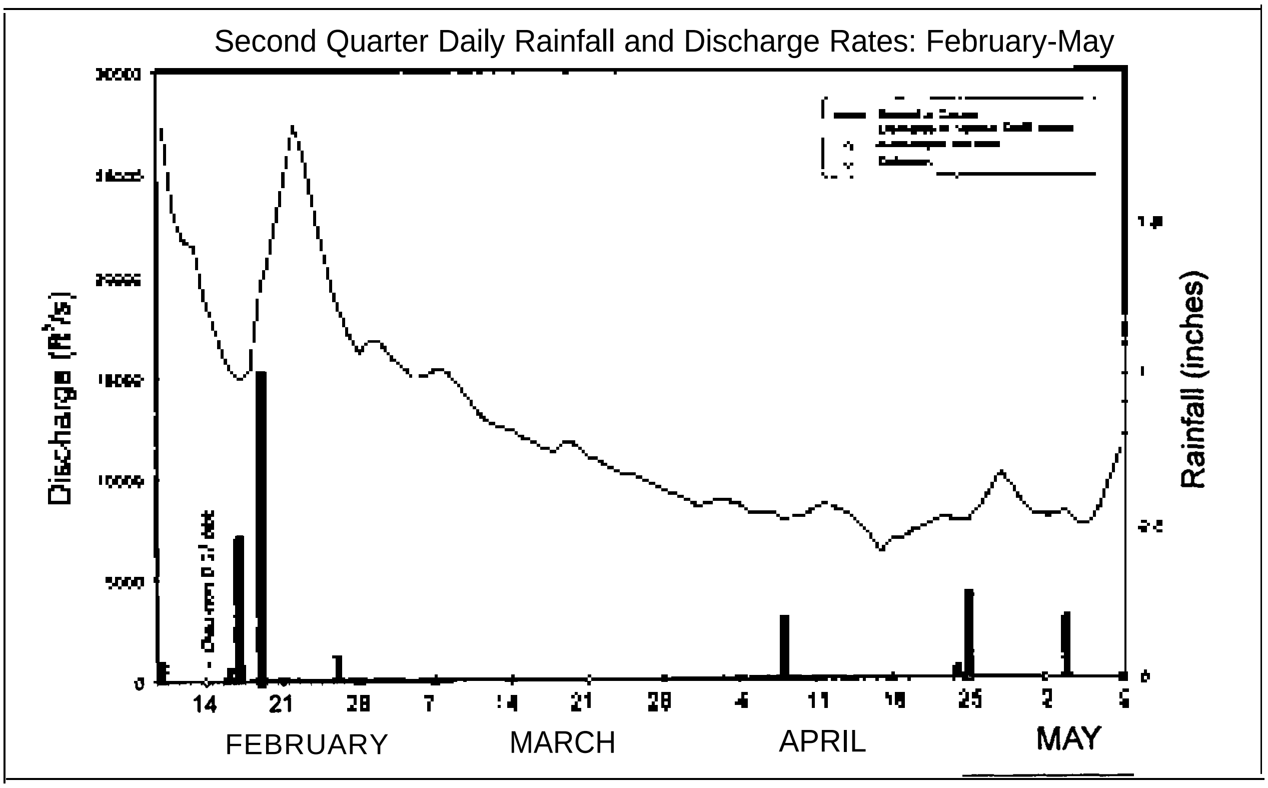

Second Quarter Daily Rainfall and Discharge Rates: February-May

Figure 3. Daily rainfall and Sacramento River discharge for February 10, 1994 through May 10, 1994

Sacramento River

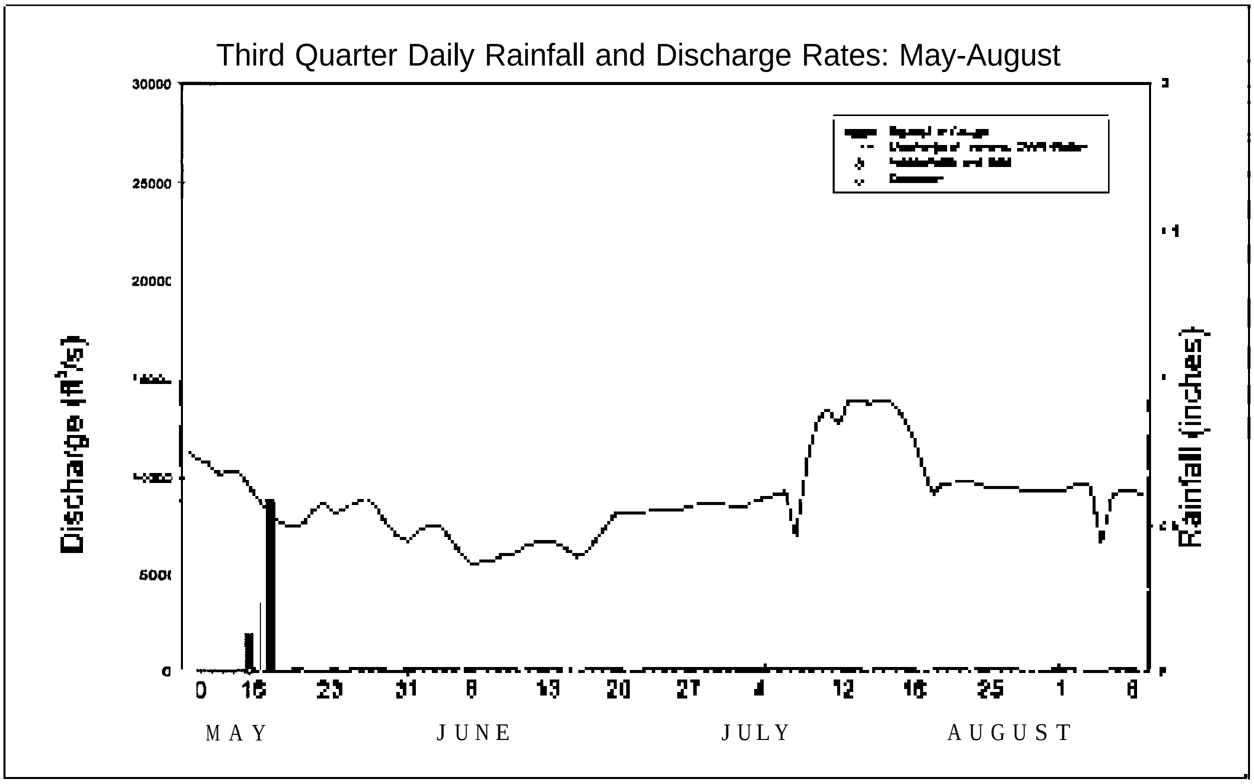


Figure 4. Daily rainfall and Sacramento River discharge for May 10, 1994 through August 10, 1994.

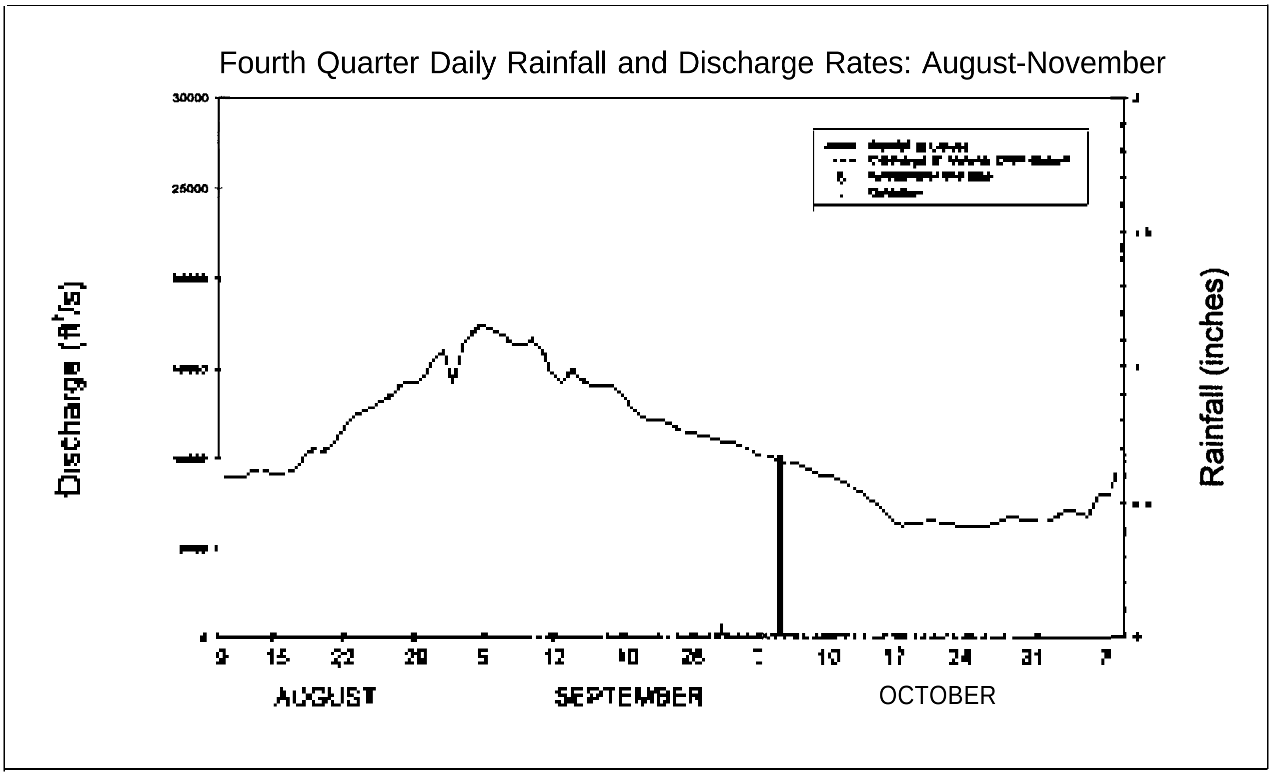


Figure 5. Daily rainfall and Sacramento River discharge for August 9, 1994 through November 10, 1994.

of 0.11 ppb in the January 28-31 sample, and was detected again in the February 11-14 sample at a concentration of 0.07 ppb. There were no detections reported from the six equipment rinse samples. U.S. EPA has not yet determined a water quality criterion for the protection of freshwater aquatic organisms. However, CDFG recently developed acute and chronic freshwater criteria for diazinon (Menconi and Cox, 1994). According to CDFG, freshwater organisms "should not be affected unacceptably if the four-day average concentration of diazinon does not exceed 0.04 μg/L (0.04 ppb) more than once every 3 years..."(Menconi and Cox, 1994; Stephan, et al., 1985) (Table 4). The levels of diazinon detected are far below those determined harmful for human health but may exceed those considered harmful for freshwater aquatic organisms.

The above criteria are presented for comparison purposes since the sample period in this study represents a 3-day average, not a 4-day average. The amount of diazinon detected if our sample was collected over 4-days may have been greater or less than the amounts detected in this study conducted for . The amount detected depends on the distribution of pesticide residues during our sampling period. However, given that both concentrations exceeded 0.04 ppb indicates the need for further chronic and acute monitoring in the Sacramento River Watershed during the winter months.

In the Sacramento River Watershed, over half of the diazinon used is applied during winter months as a dormant spray on prunes, almonds, and walnuts (Figure 6). Most of these sprays are ground applications made predominately in Butte, **Colusa,** Glenn, Sutter, Tehama, Yolo, and Yuba Counties. Applications were made throughout the year and the majority of the dormant spray applications of diazinon **occured** in two regions: 1) along the Feather River in Yuba and Sutter Counties and in the southern portion of Butte County, and 2) along the Sacramento River in the northern portion of Glenn and Butte Counties. These are the major stone fruit growing areas of the valley. Figure 7 presents the lb a.i. of diazinon applied each week and the application locations by section for the period preceding the two reported detections.

During October 1993 through April 1994, USGS conducted a pesticide study of the Sacramento River concurrently with our study. Their sample collection method and detection limit were different from ours; the results provide us with an opportunity to compare findings. USGS staff collected water three times or more per week from the I Street bridge in the city of Sacramento, 17 miles downstream from our sampling site. Their method detection limit was 0.038 ppb for diazinon (RL for DPR study was 0.05 ppb) (**MacCoy** et al., 1995).

Table 4. Water quality criteria for pesticide residues in water for the protection of freshwater aquatic life

insecticide	CDFG suggested acute criteria (1 hour average)[a]	CDFG suggested chronic criteria (4-day average)[a]	U.S. EPA recommended criteria (1-hour average maximum concentration)[c,d]	U.S. EPA recommended criteria (4-day average continuous concentration)[c,d]
Diazinon	0.08[b]	0.04[b]	NA	NA
Dimethoate	NA	NA	NA	NA
Methidathion	NA[e]	NA	NA	NA
3-hydroxycarbofuran	NA	NA	NA	NA
Chlorpyrifos	NA[f]	NA	0.083	0.04[b]

[a] California Department of Fish and Game's suggested criteria; see Menconi and Cox, 1994 for diazinon hazard assessment

[b] Not to be exceeded more than once in three years

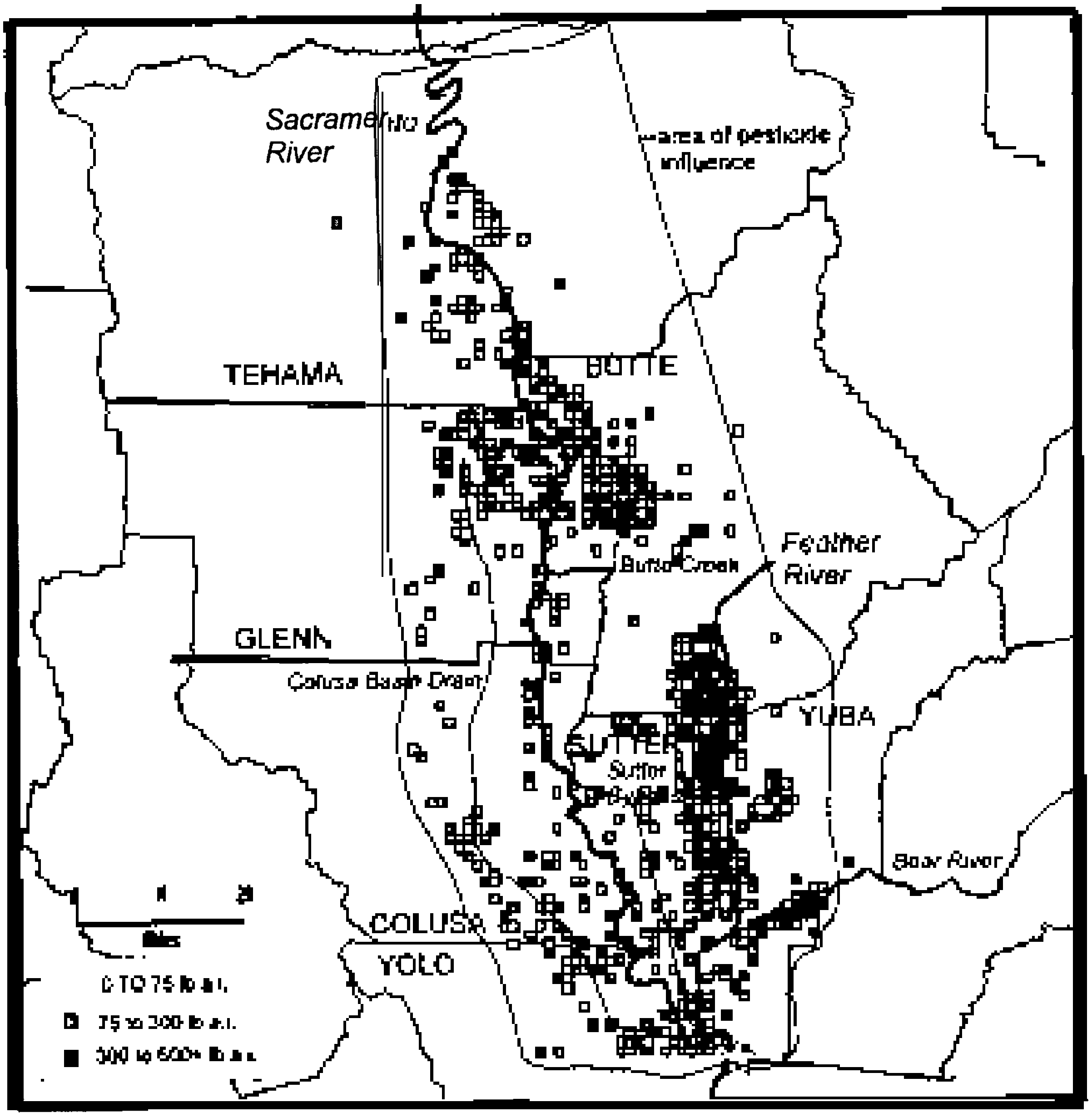
[c] U. S. EPA National Ambient Water Quality Criteria

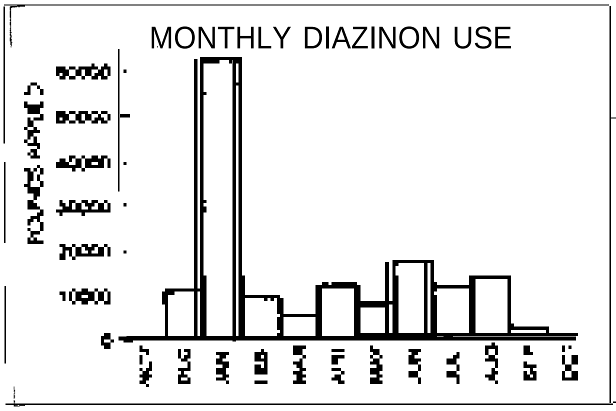
[d] Marshack, 1995

[e] Due to a lack of data, CDFG could not develop criteria for methidathion using accepted U.S. EPA methods (Menconi and Siepmann, 1996).

[f] The suggested criterion in CDFG's chlorpyrifos hazard assessment (Menconi and Paul, 1994) was a combined fresh and salt water value and is not included here.

DIAZINON USE IN THE SACRAMENTO RIVER WATERSHED





☆ **Sampling site**

❑ Each square represents one or more applications within a one square mile section

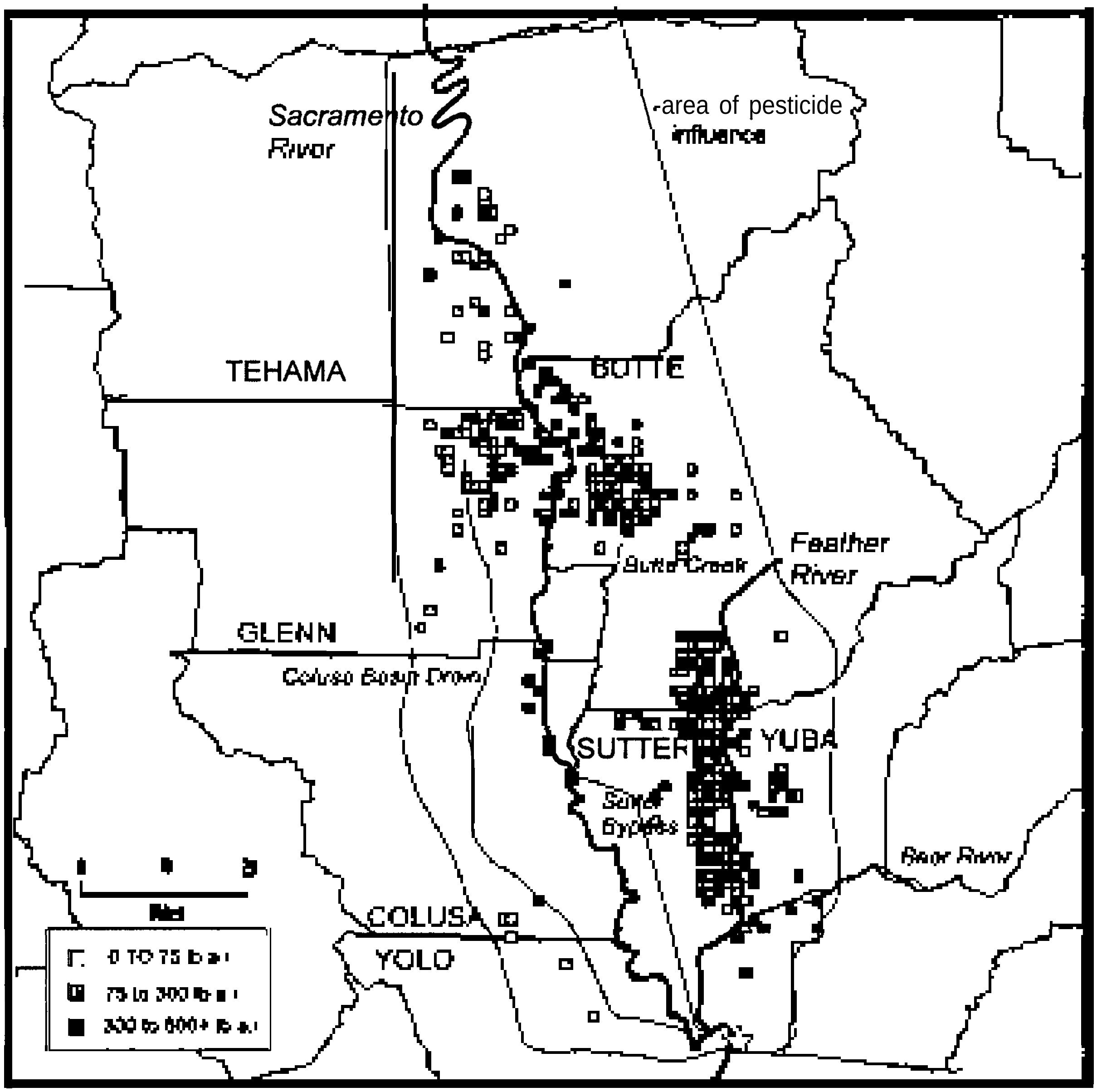
Primary Crop	Pounds
1. Prune	50,525
2. Almonds	35,558
3. Walnut	32,786
4 Peach	14,133
5 Tomato	12,080
Total pounds applied during the sampling year.	150,01[illegible]

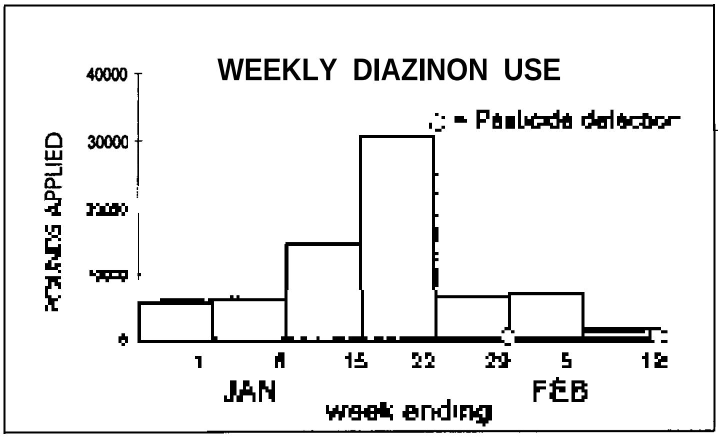
Figure 6. Applications of diazinon in seven counties of the Sacramento River watershed upstream of the sampling site near Verona, from November 1993 through October 1994

More diazinon (about 55,000 lb a.i.) was applied in the Sacramento River watershed during January 1994 prior to the first significant rainfall (Figure 6 and 2) However no detections occurred in the samples collected during the three-day sampling periods ending January 3, 10, 17 and 24, 1994. USGS detected diazinon in a grab sample collected on January 17 at 0.046 ppb which was just below our reporting limit (MacCoy et al., 1995). The DPR sample collection period January 21-24 yielded no detectable diazinon even though the first storm had begun and 0.7 inches of rain had fallen during the last 2 days of the collection period. Results of the USGS study showed that diazinon (0.042 ppb) was present at a level below our reporting limit, in a sample collected on January 24 (MacCoy et al., 1995). Data from the Verona gauging station indicated that a rise in discharge did not begin at our sampling site until 1 day after the January 21-24 sample was collected (Figure 5). With the increased flows, DPR detected diazinon at 0.11 ppb in the next sample. This sample was collected January 28-31, during declining flows after peak discharge on January 27. USGS detected levels of diazinon above our reporting limit in each of their daily samples collected from January 26 through January 31 (MacCoy et al., 1995). Their highest detection for that storm was on the day of peak discharge, January 27 at 0.236 ppb, which was a day prior to the start of our sampling period. In fact, when the USGS daily detections were averaged for January 28, 29, 30, and 31, the value was 0.11 ppb, the same as the level detected in our 3-day composite sample during the same period. However, there are sources of dilution water, mainly the American River, and possible urban sources of diazinon residues between our site near Verona and the USGS site at Sacramento.

More diazinon was applied during the dry period, January 26 through February 5, prior to the second storm (Figures 2, 3 and 7). The amount applied was much less than during the dry period before the first storm, but more than the periods preceding the following storms. Once again there was no detection in the sample collected on February 4-7. This was probably because, despite the occurrence of rainfall, the sampling period ended prior to an increase in river discharge. Discharge started to increase February 8, peaked on February 9-10 and continued to decline until February 17 (Figures 2 and 3). Diazinon was detected in the February 11-14 sample which was collected during the decline in discharge that followed this rain event. Again, detections by USGS were comparable to our detections. During our February II-14 sampling period, USGS detected diazinon concurrently on each day, averaging 0.07 ppb, the same as our detection. The USGS data indicated peak diazinon levels occurred February 10, a day after peak river discharge (Figure 6) and prior to the start of the DPR sample period (MacCoy et al., 1995).

DIAZINON USE IN THE SACRAMENTO RIVER WATERSHED
DECEMBER 26, 1993 TO FEBRUARY 12, 1994





☆ Sampling site

□ Each square represents one or more applications within a one square mile section

Primary Crops	Pounds
1. Prune	35,801
2. Almond	25,236
3. Peach	11,442
4. Apple	331
Total pounds applied during the sampling period.	73,112

Figure 7. Applications of diazinon in seven counties of the Sacramento River watershed upstream of the sampling site near Verona, from December 26, 1993 through February 12, 1994.

Since detections coincided with peak discharge, the amount of rain runoff was probably as critical as the quantity of pesticide applied in producing detectable levels of diazinon in the Sacramento River. About 60,000 lb a.i. of diazinon were applied prior to the second storm beginning January 22 and another 9,000 lb a.i. were applied prior to the third storm beginning February 6 (DPR, 1994). Diazinon has an average field dissipation half-life of 14 days (Table 5), and Ross et al. (1997) reported a 5 or 6 day half-life in the Sacramento Valley. However, total persistence is reported at anywhere between 3 and 12 weeks (Howard, 1991). Diazinon is not expected to bind strongly to soil and is expected to exhibit moderate mobility. Wauchope (1978) calculated that total pesticide losses are 0.5% or less of the amount applied, unless severe rainfall events occur within 1 to 2 weeks after application. He described a critical runoff event as one which “occurs within 2 weeks of application, has at least one cm (0.4 inches) of rain, and a runoff volume which is 50% or more of the precipitation.” He found that “these events almost always produce the bulk of the runoff loses for an entire season unless the chemical is incorporated or extremely persistent.”

Approximately 1.7 inches of rain fell in the week prior to January 28-31, 1994 which provided sufficient runoff to raise river flow rates by 102% at the peak on January 27, 1994 (calculated using daily average discharge). The second detection of diazinon on February 1 I-14 was preceded by 3.16 inches of rainfall at Colusa and a 166% increase in flow volumes at the peak which occurred on February 9, 1994. From these data, with the exception of diazinon residues in rainfall itself, which has not been quantified, rain runoff appears to be the principal means by which diazinon reached the Sacramento River. Part of the same study by USGS was conducted year-round from October 1992 through September 1993. Diazinon was detected in the Sacramento River only during the rainy season, except for a detection on 1 day in July (MacCoy et al., 1995).

Toxicity Results

CDFG found that two of the 22 Sacramento River water samples caused significant mortality to fathead minnows. Those samples were not correlated with any pesticides detected. In addition, CDFG toxicity tests showed no significant mortality to cladocerans. See Appendix V for the results and discussion.

Table 5. Physical-chemical properties of selected pesticides

Insecticide	Field dissipation half-life[a]	K_d[a]	Solubility[b]
diazinon	7 to 30	8.20 to 17.8	60.0
dimethoate	6 to 10	0.0255 to 0.740	39.800
carbofuran	13 to 13	not reported	351
methidathion	5	0.154 to 8.69	221
chlorpyrifos	33 to 56	68.8 to 253	1.39
phosmet	5 to 18	11.7 to 15.8	20.0
azinphos-methyl	5 to 11	4.24 to 13.4	28.0
malathion	1	0.230 to 10.1	125
methomy	5 to 54	0.230 to 1.40	5,400
carbaryl	7 to 12	0.20 to 11.3	115
endosulfan	77 to 83	63.0 to 523	0.325

[a] range of numbers reported in Kollman and Segawa (1995)

[b] reported number or average of numbers reported in Kollman and Segawa (1995)

Other Pesticides Used In The Watershed

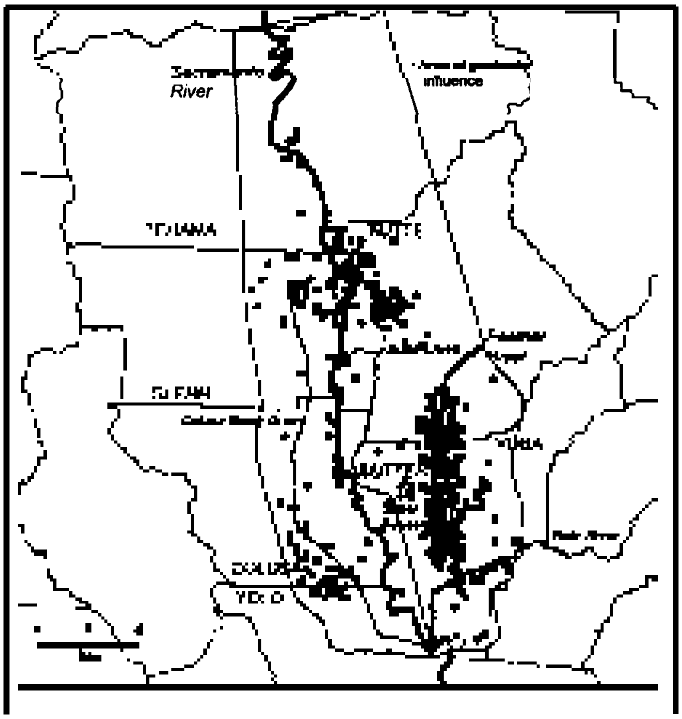
Several other highly used pesticides, which have previously been detected in surface water, were applied in the Sacramento Valley during this study but were not detected. Due to the quantities used and timing of applications, methidathion had the greatest potential of all the pesticides included in the screens to move offsite into the Sacramento River. During January, 42,000 lb a.i. of methidathion were applied to areas and crops that were similar to diazinon uses (Figure 8). Methidathion is more soluble and has less affinity for binding to soil than diazinon; therefore, it should have greater runoff potential. The primary difference between the two is that methidathion has a shorter field-dissipation half-life of 6.4 days (Ross et al., 1997). Methidathion was detected by USGS during the same sampling periods when diazinon was detected. However, the USGS detections were below our RL (0.05 ppb) on all but one of our collection days, when their concentration was at our RL (MacCoy et al., 1995).

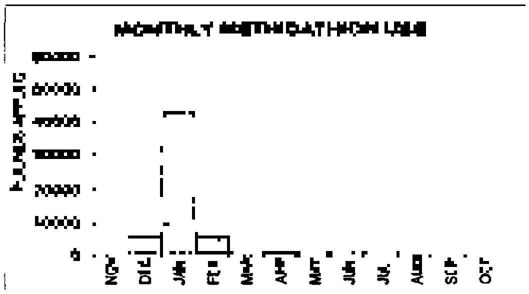
Over 52,000 lb a.i. of carbaryl were applied from January through September with a peak application period in July (Figure 9). Carbaryl has a moderate water solubility (113 to119 ppm) and a low soil adsorption coefficient (average K_d 2.66), and therefore has potential to move offsite (Table 5). However, it was applied only in low amounts during the rainy months to peaches, prunes and almonds. Most of the applications occurred throughout the dry months, which combined with a short half-life (average 10 days) made carbaryl unlikely to reach the sample site at measurable concentrations.

Carbofuran (Figure 10) is applied to rice predominantly in April and May and methyl parathion (Figure 11) in May and June to rice. Both have a moderate water solubility at 351 and 70.3 ppm, respectively (Table 5). When rice water is released there is potential for river contamination from these two pesticides. However, growers are required to hold water on the fields for at least 24 days prior to release. With a half-life of 3 weeks in water, most of the carbofuran applied will have undergone degradation prior to release back into the river system. Methyl parathion is reported to degrade by photolysis in a natural water in 8 days in the summer (Howard, 1991), and most likely would be degraded prior to release.

Azinphos-methyl (Figure 12) and chlorpyrifos (Figure 13) represent another typical use pattern for pesticides in the Sacramento River Watershed. Both are applied during the summer months, largely to tree and nut crops. Neither is particularly soluble but they have greatly different field dissipation half-lives (8 and 45 days, respectively) and

METHIDATHION USE IN THE SACRAMENTO RIVER WATERSHEC





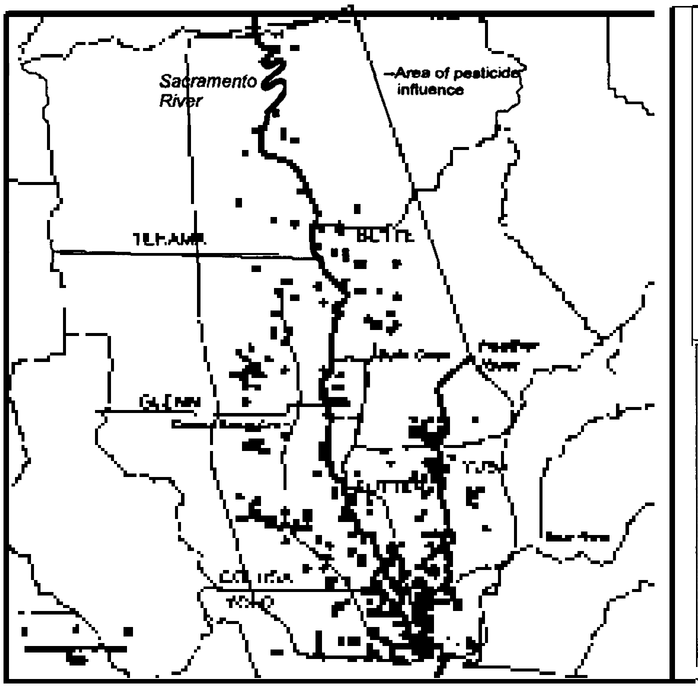
Primary Crops	Pounds
1. Almonds	22,19
2. Prune	21,290
3. Peach	8,31
4. Walnut	2,97
5. Pear	1,08
Total pounds applied during sampling year:	57,528

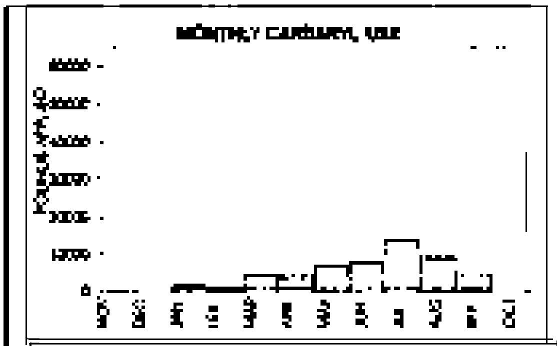
☆ **Sampling site**

☐ Each square represents one or more applications within a one square mile section

Figure 8. Applications of methidation in seven counties of the Sacramento River watershed upstream of the sampling site near Verona, from November 1993 through October 1994 .

CARBARYL USE IN THE SACRAMENTO RIVER WATERSHED



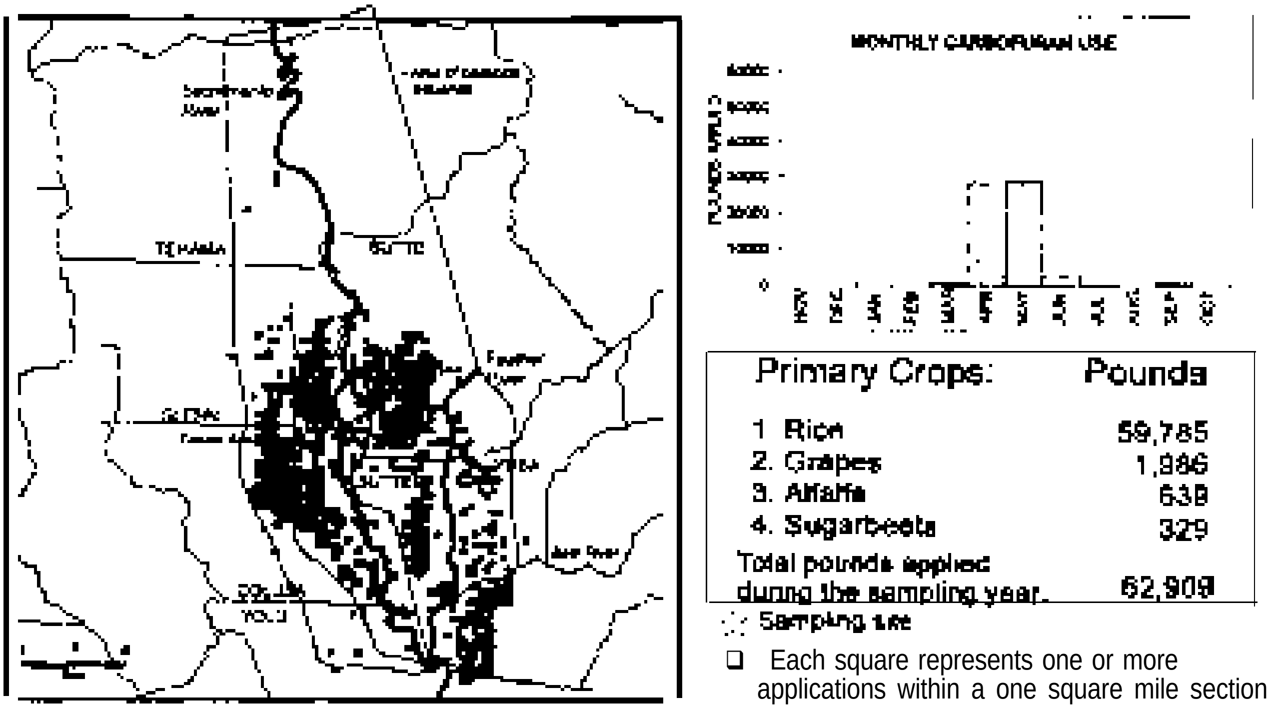


Primary Crops	Pounds
1. Tomato	8,305
2 Pear	7,093
3 Melons	6,433
4 Peach	5,448
5 Walnut	4,390
6 Beans	4,289
7 Almond	3,749
8 Apple	3,154
9 Sugarbeet	2,014
Total pounds applied during the sampling year	52,851

☆ Sampling site

Figure 9. Applications of carbaryl in seven counties of the Sacramento River watershed upstream of the sampling site near Verona, from November 1993 through October 1994 .

CARBOFURAN USE IN THE SACRAMENTO RIVER WATERSHED



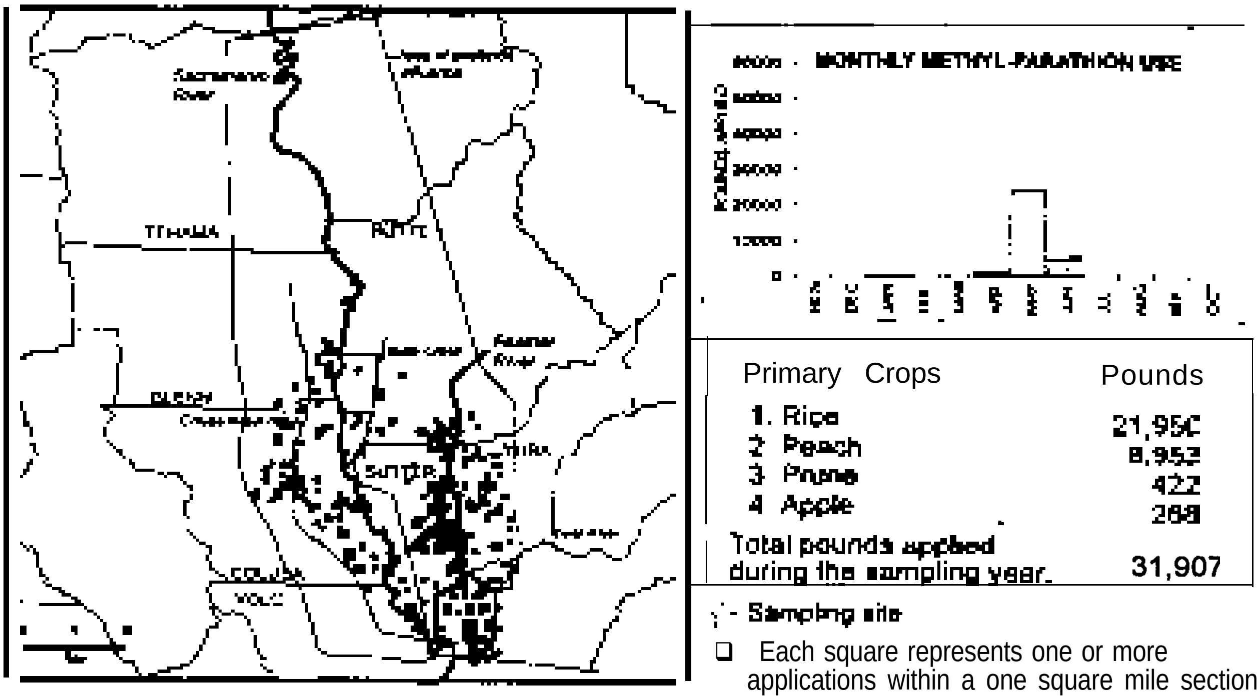
Primary Crops:	Pounds
1 Rice	59,785
2. Grapes	1,986
3. Alfalfa	639
4. Sugarbeets	329
Total pounds applied during the sampling year.	62,909

Sampling site

☐ Each square represents one or more applications within a one square mile section

Figure 10. Applications of carbofuran in seven counties of the Sacramento River watershed upstream of the sampling site near Verona, from November 1993 through October 1994 .

METHYL PARATHION USE IN THE SACRAMENTO RIVER WATERSHED

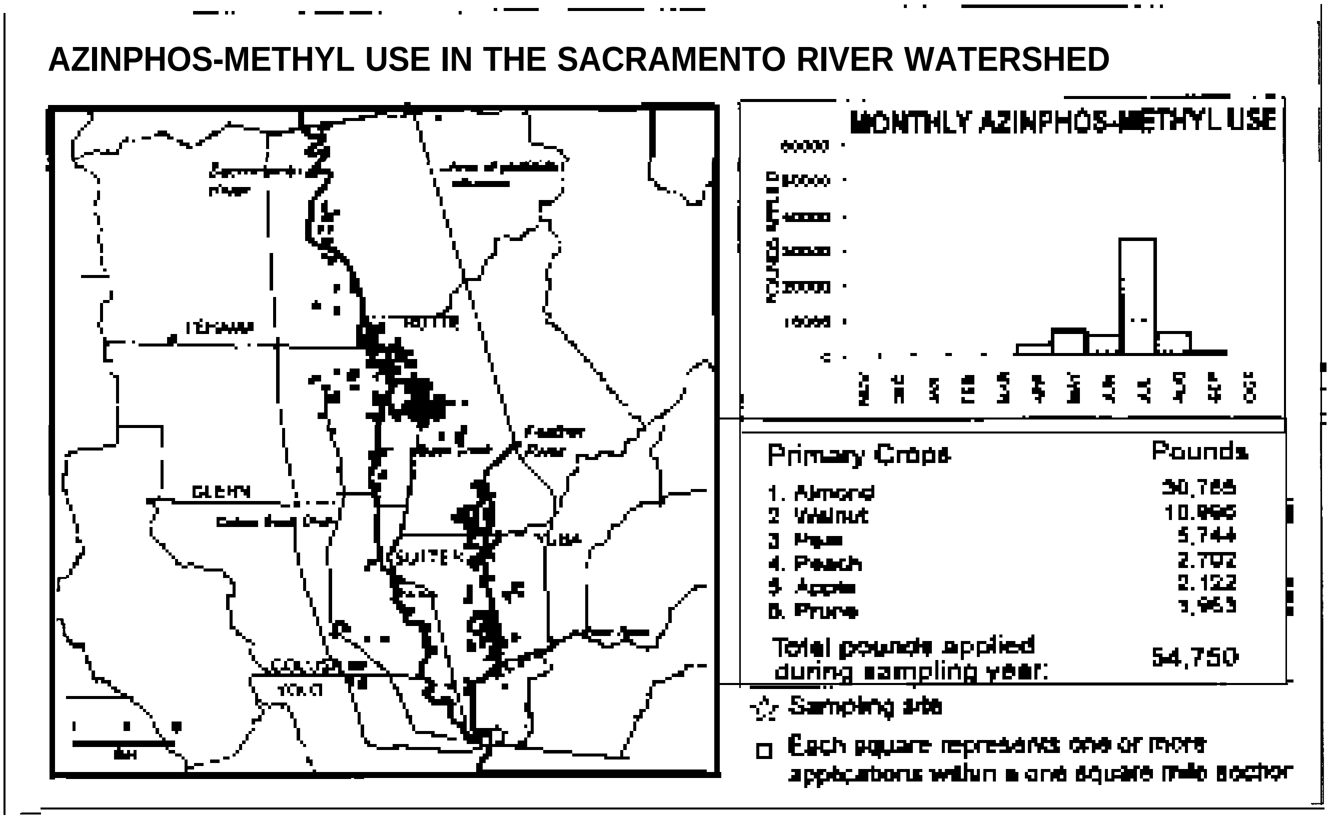


Primary Crops	Pounds
1. Rice	21,950
2 Peach	8,952
3 Prune	422
4 Apple	268
Total pounds applied during the sampling year.	31,907

Sampling site

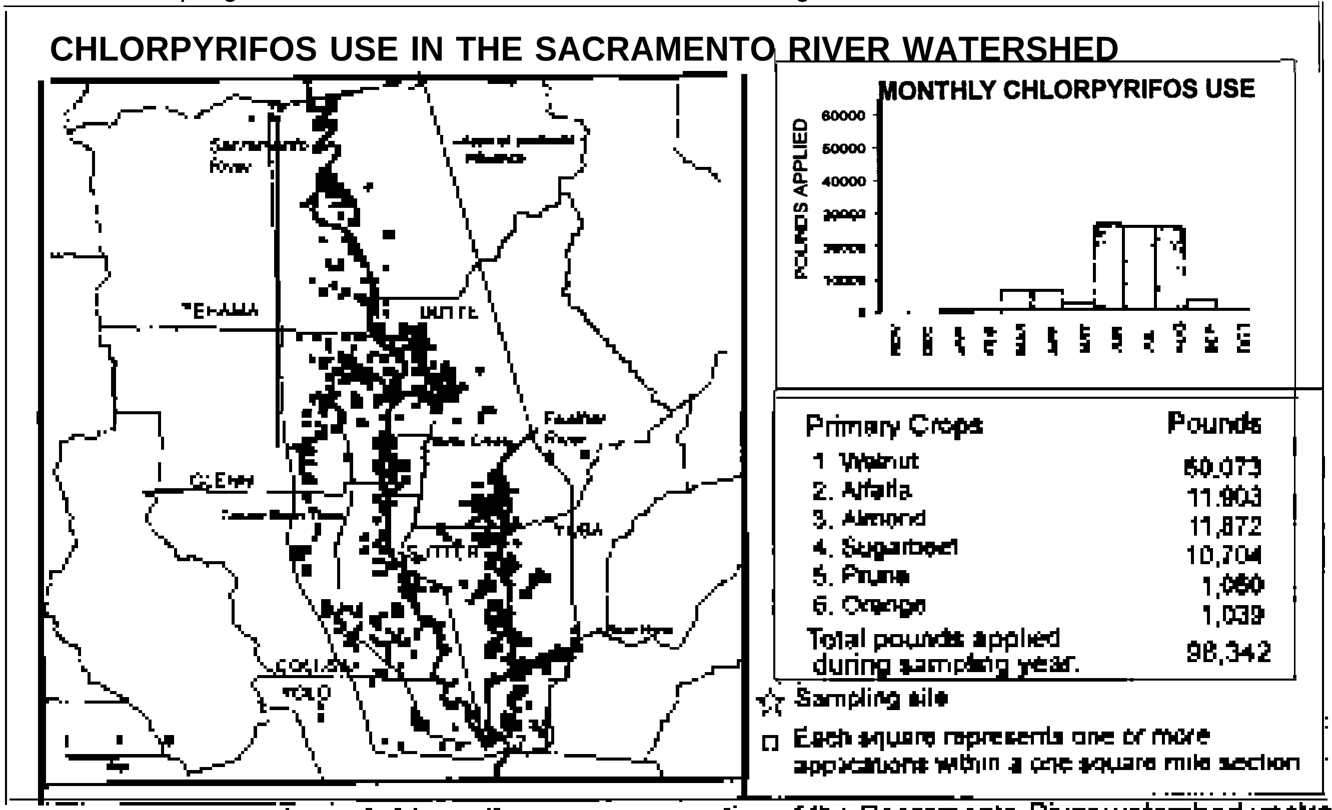
☐ Each square represents one or more applications within a one square mile section

Figure 11. Applications of methyl parathion in seven counties of the Sacramento River watershed upstream of the sampling site near Verona, from November 1993 through October 1994



Primary Crops	Pounds
1. Almond	30,765
2 Walnut	10,966
3 Plum	5,744
4. Peach	2,792
5 Apple	2,122
6. Prune	1,963
Total pounds applied during sampling year:	54,750

Figure 12. Applications of azinphos-methyl in seven counties of the Sacramento River watershed upstream of the sampling site near Verona, from November 1993 through October 1994 .



Primary Crops	Pounds
1 Walnut	60,073
2. Alfalfa	11,903
3. Almond	11,872
4. Sugarbeet	10,704
5. Prune	1,060
6. Orange	1,039
Total pounds applied during sampling year.	98,342

Figure 13. Applications of chlorpyrifos in seven counties of the Sacramento River watershed upstream of the sampling site near Verona. from November 1993 through October 1994 .

different soil adsorption characteristics (K_d 8.4 and 125, respectively) (Table 5). However, without rain to move the compounds offsite, current irrigation practices may be adequate in preventing these pesticides from reaching the Sacramento River at detectable levels.

If rain runoff is the primary vector for moving pesticides into surface water, pesticides applied during the rainy winter months have the greatest likelihood of entering river systems. Diazinon, for example, was applied nearly year round at significant levels but was only detected during the rainy season. However, most pesticides are applied during the dry season. Since the primary water source during the dry season for most California crops is irrigation, only the more soluble pesticides or pesticides applied on highly erodible soil are susceptible to transport off-site. Since growers control irrigation volume to save water, generally runoff is avoided. Our 3-day sampling method at one site along the Sacramento River would detect those pesticides that move easily off the site of application. Some of the chemicals not detected in this study may be important in localized areas where discharge is less and therefore dilution is less.

Merced River

Merced River Watershed

With its headwaters in the central portion of the Sierra Nevada Mountain range, the Merced River flows approximately 125 miles west through the central valley to where it meets the San Joaquin River (Figure 14). It is characterized by a complicated system of dams and diversion canals that provide water for Merced and Mariposa Counties. Within the first 28-miles of the river upstream from the junction with the San Joaquin River, there are 14 discharge points and 49 points of water diversion (CVRWQCB, 1989). This large system of diversion canals and discharge points makes it difficult to determine which areas drain into the Merced River downstream of the Merced and Mariposa County line. The USGS has made an attempt to delineate the watershed in this area. The Merced River watershed depicted in figure 14 was copied from USGS (Kratzer, USGS). The Merced River watershed drains roughly 1,280 mi^2, a large portion of which is used for agriculture

Agricultural influence on the Merced River stretches approximately 45 miles from near the town of Snelling to the Merced River's confluence with the San Joaquin River at Hills Ferry (Figure 14). Agricultural influence on the river from Snelling to Cressey consists of management practices involved with orchard crops, predominantly almonds and peaches, though apples are also grown in the area. From Cressey to the River's end, crops within the watershed become more diverse adding alfalfa, grapes and assorted row crops to the mix of nut and fruit crops.

The sampling site chosen for the Merced River was located approximately 1 mile upstream from the river's confluence with the San Joaquin River, at Hatfield State Recreation Area (Figure 14). The site was selected because it is downstream from all sources of agricultural runoff along the Merced River and it has been used in previous studies (Ross et al., 1996). Discharge data were obtained from the USGS gauging station at Stevinson, located 4 miles upstream of the sampling site.

Environmental Measurements

Water samples collected during the 12 month study had pH values ranging from 6.3 to 8.2 (Table 6). The pH values fell outside the CVRWQCB (1995b) criteria on two occasions, January 30 at pH 6.3 and February 9 at pH 6.4 (Table 3). Measurements of

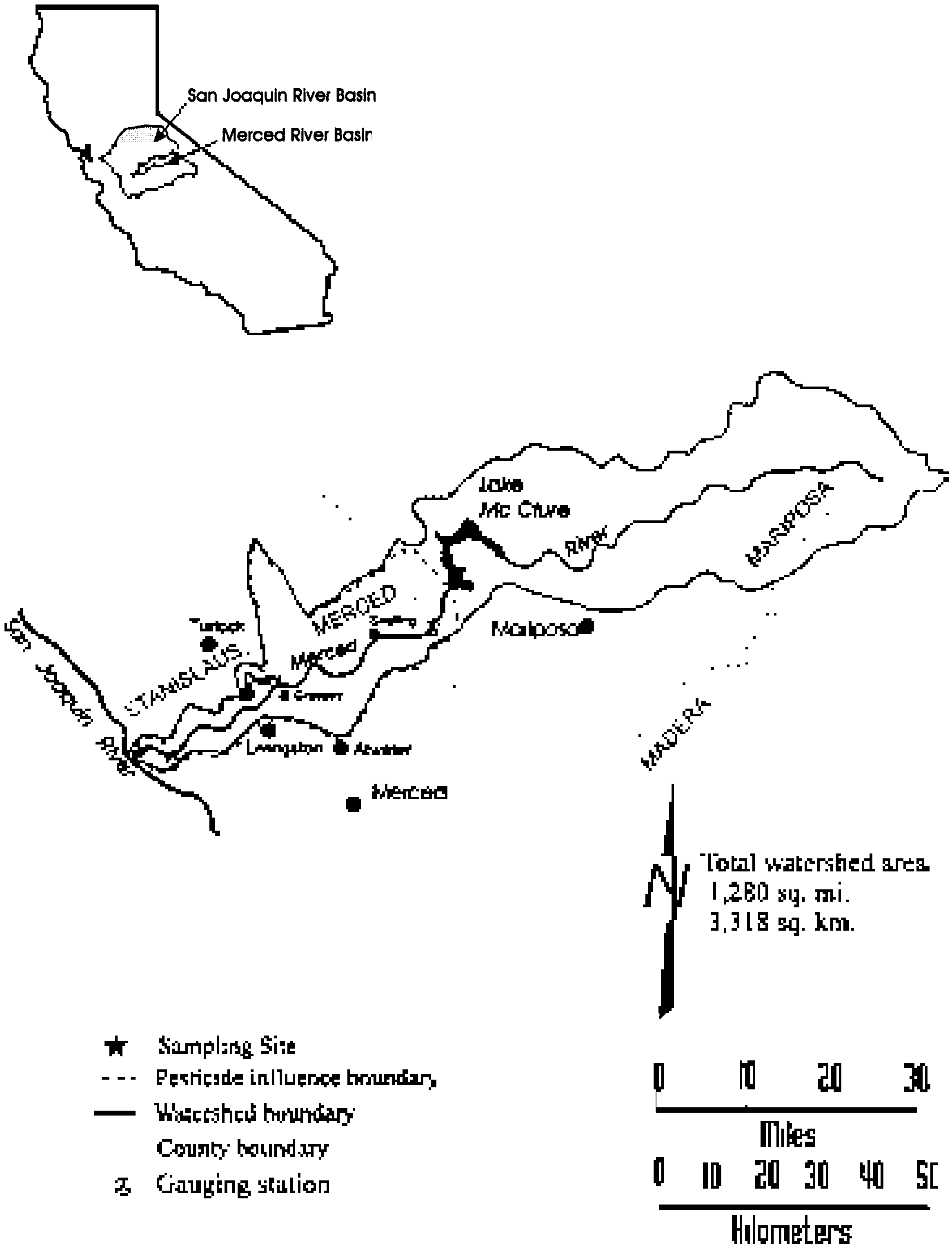


Figure 14. Map of the Merced River watershed. The California map inset indicates the relationship to the San Joaquin River watershed.

Table 6. Merced River Water Quality Data and Pesticide Detections

Start Sample Date	End Sample Date	Air Temperature	Water Temperature	Dissolved Oxygen (mg/L)	% Saturation	pH (in field)	pH (in lab)	Detections
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	NT	[illegible]	
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	NT	[illegible]	
[illegible]	[illegible]	[illegible]	[illegible]	NT	NA	NT	[illegible]	
[illegible]	[illegible]	[illegible]	[illegible]	NT	NA	NT	[illegible]	
[illegible]	[illegible]	[illegible]	[illegible]	NT	NA	NT	[illegible]	
[illegible]	[illegible]	[illegible]	[illegible]	NT	NA	NT	[illegible]	
[illegible]	[illegible]	[illegible]	[illegible]	NT	NA	NT	[illegible]	
[illegible]	[illegible]	[illegible]	[illegible]	NT	NA	NT	[illegible]	
[illegible]	[illegible]	[illegible]	[illegible]	NT	NA	NT	[illegible]	
8/19/94	8/22/94	27	22	NT	NA	NT	7.5	
8/26/94	8/29/94	30	24	NT	NA	NT	7.6	
9/2/94	9/5/94	34	24	8.3	99	NT	7.7	Dimethoate 0.13 ppb
[illegible]	[illegible]	[illegible]	21	[illegible]	[illegible]	NT	[illegible]	
[illegible]	[illegible]	[illegible]	[illegible]	NT	NA	NT	[illegible]	
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	NT	[illegible]	[illegible] ppb
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	NT	[illegible]	
[illegible]	[illegible]	[illegible]	21	NT	NA	NT	[illegible]	
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	NT	[illegible]	
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	NT	[illegible]	
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	
[illegible]	[illegible]	[illegible]	14	[illegible]	[illegible]	[illegible]	[illegible]	
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[illegible]	[illegible]	[illegible]	11	[illegible]	[illegible]	[illegible]	[illegible]	
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	
[illegible]	12/5/94	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	
12/16/94	12/19/95	11	10	9.2	81	7.2	7.4	
12/23/94	12/26/95	14	9	11.0	95	7.0	7.4	
12/30/94	1/2/95	7	9	9.4	80	7.2	7.2	
1/6/95	1/9/95	19	12	9.0	84	7.0	7.0	Diazinon (0.11) and Methidathion (0.22)
[illegible]	[illegible]	26	13	7.6	71	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	15	11	11.0	102	[illegible]	[illegible]	
[illegible]	[illegible]	15	12	7.2	67	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	14	14	8.5	82	[illegible]	[illegible]	[illegible]
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[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	
2/11/95	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	
2/14/95	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	
2/18/95	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	
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[illegible]	[illegible]	[illegible]	15	[illegible]	[illegible]	[illegible]	[illegible]	
[illegible]	[illegible]	22	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	
[illegible]	[illegible]	NT	15	8.0	79	[illegible]	[illegible]	
[illegible]	Grab Sample	18	16	8.0	80	[illegible]	[illegible]	[illegible]
3/22/95	Grab Sample	12	12	7.7	71	[illegible]	[illegible]	
[illegible]	Grab Sample	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	
[illegible]	Grab Sample	[illegible]	14	11.0	[illegible]	[illegible]	[illegible]	
4/10/95	Grab Sample	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	
[illegible]	Grab Sample	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	
[illegible]	Grab Sample	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	
[illegible]	Grab Sample	[illegible]	21	[illegible]	[illegible]	[illegible]	[illegible]	
[illegible]	Grab Sample	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	
[illegible]	Grab Sample	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	
[illegible]	Grab Sample	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	
[illegible]	Grab Sample	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	
6/5/95	Grab Sample	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	
[illegible]	Grab Sample	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	

[illegible]

[illegible]

DO were made *in situ* when equipment was available. The DO readings ranged from 5.1 to 11 mg/L (54 to 106% saturation). DO measurements fell below the CVRWQCB cold water minimum of 7.0 mg/L for this river on September 30 (6.8), February 6 (6.9), May 1 (6.9), and June 5 (5.1) (Table 3 and 6). The measurement of 5.1 mg/L on June 5 had rebounded to 9.1 mg/L by the next sampling period on June 12, 1995. Water temperatures on sample collection days varied from 8.6 to 29°C and air temperatures ranged from 7.1 to 40°C (Table 6).

During the first and second quarters discharge at the Stevenson gauge ranged from 24 to 1,080 ft³/s (cfs) and rainfall at Modesto totaled 1.71 inches (Figures 15 and 16). Daily rainfall measurements for the first half of the study (June 1994 to December 1995) were obtained from the Modesto field station, 20 miles north of the site. Data from this station were unavailable in 1995, thus rainfall measurements for the remainder of the study were obtained from the Merced Municipal Airport, located 25 miles east of the sampling site. During the winter and spring, unusually large amounts of precipitation fell in the watershed, resulting in regional flooding. In the third quarter there were 10.5 inches of rain recorded at the Merced Municipal Airport and the Merced River average daily discharge ranged from 214 to 3,200 cfs (Figure 17). As a comparison, the peak discharge during the 1986 flood was measured in March at 4,750 cfs (Mullen et al., 1994a) Rainfall totaled 3.6 inches during the final quarter of the study (Figure 18), and discharges remained considerably higher than those of 1993 (Mullen et al., 1994a) and 1992 (Anderson et al., 1993) for the same period due to dam releases. The annual runoff for the 1995 calendar year was about 200% of the average during the years 1941 to 1995 (USGS, 1995)

Pesticide Detections

There were pesticide detections in seven of the 57 (12.3%) samples collected and analyzed from the Merced River (Table 6). Three of the samples had multiple pesticide detections. None of the equipment rinse samples had detectable residues. During the year of sampling, three different pesticides: dimethoate, diazinon, and methidathion, and one breakdown product, 3-OH carbofuran, were detected.

Two detections of the OP, dimethoate at a concentration of 0.13 ppb were reported for the sampling periods of September 2-5 and September 23-26 (Table 6). The California Department of Health Services (DHS) has set an action level of 140 ppb for dimethoate in drinking water (Marshack, 1993); currently, there is no U.S. EPA, CDFG or

Merced River

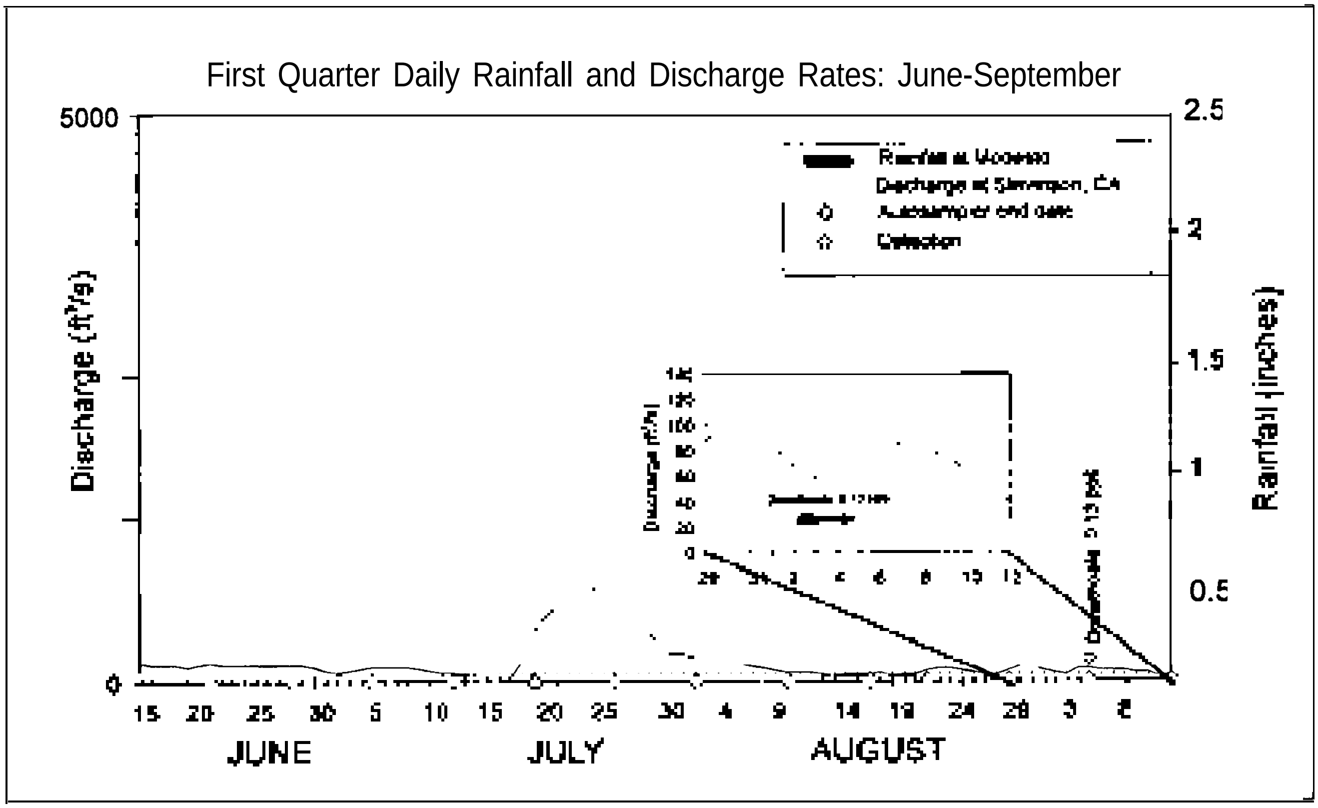


Figure 15 . Daily rainfall and Merced River discharge (river flow) for June 15 through September 12, 1994

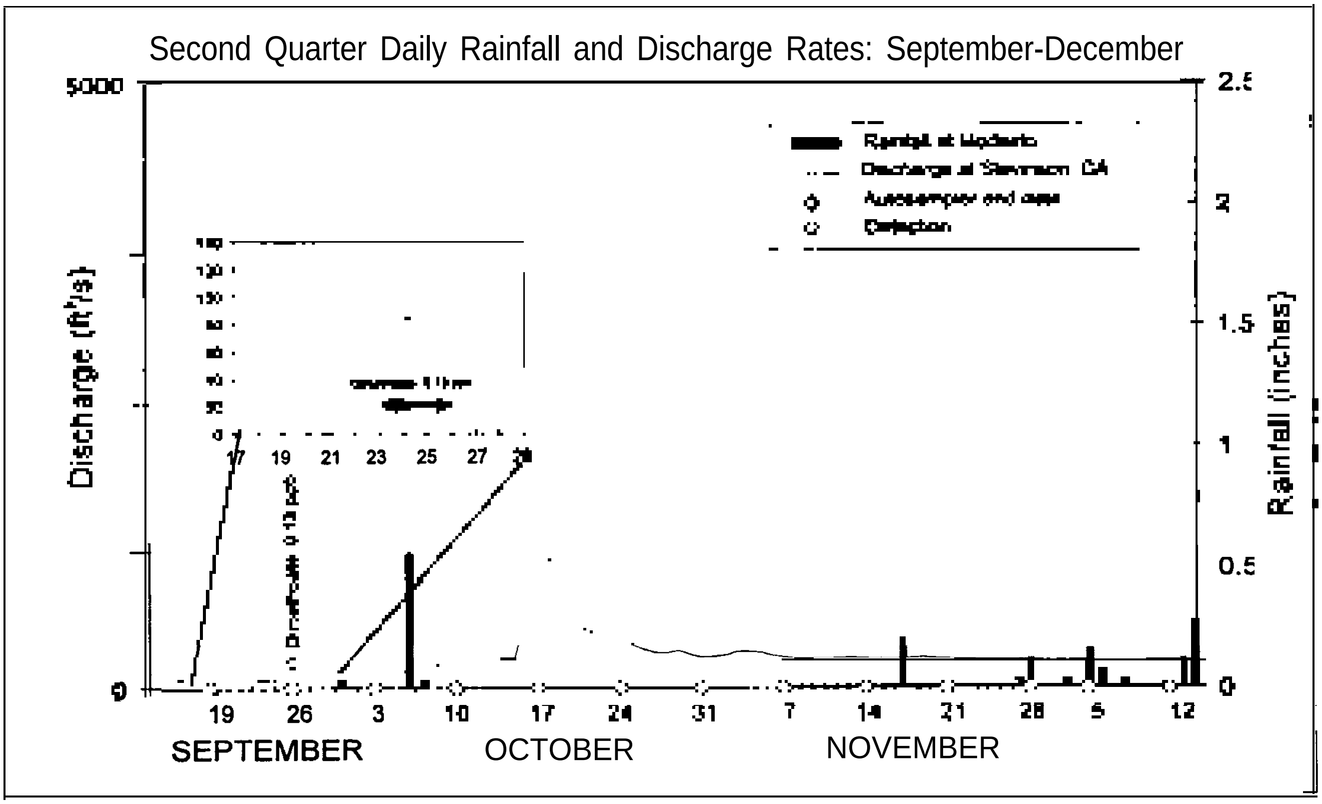


Figure 16. Daily rainfall and Merced River discharge for September 13 through December 12, 1994

Merced River

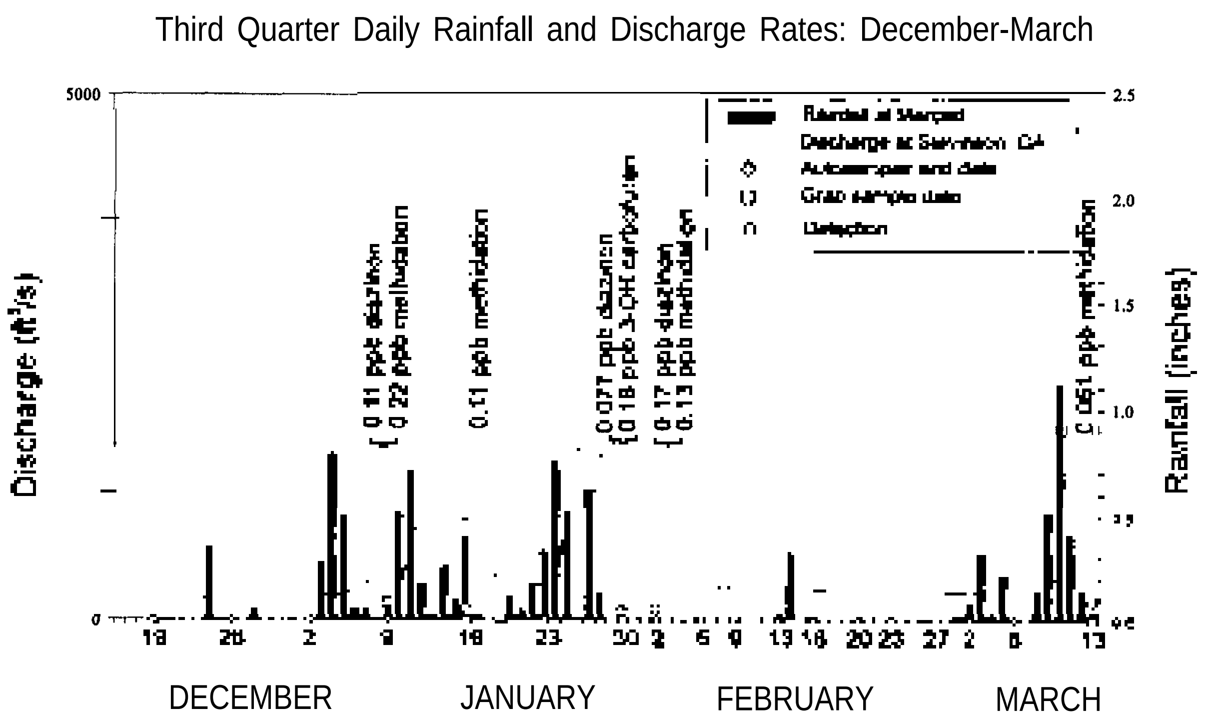


Figure 17. Daily rainfall and Merced River discharge for December 18, 1984 through March 13, 1995

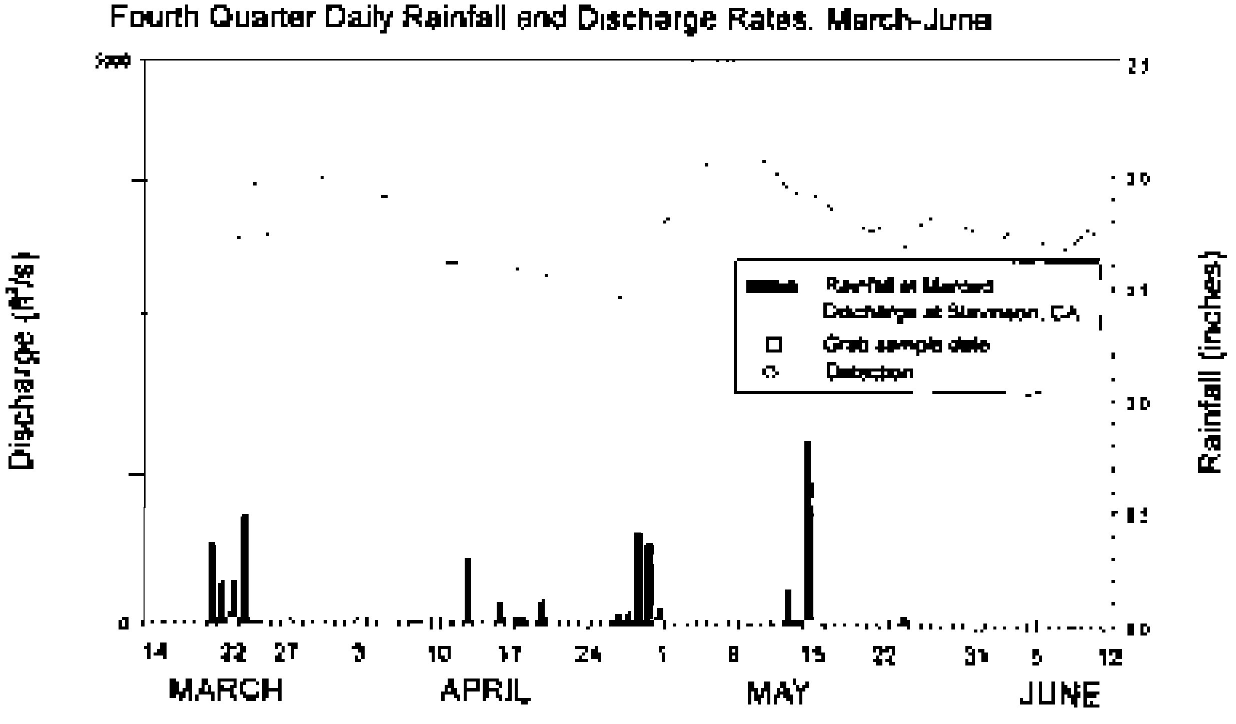


Figure 18. Daily rainfall and Merced River discharge for March 19 through June 12, 1995

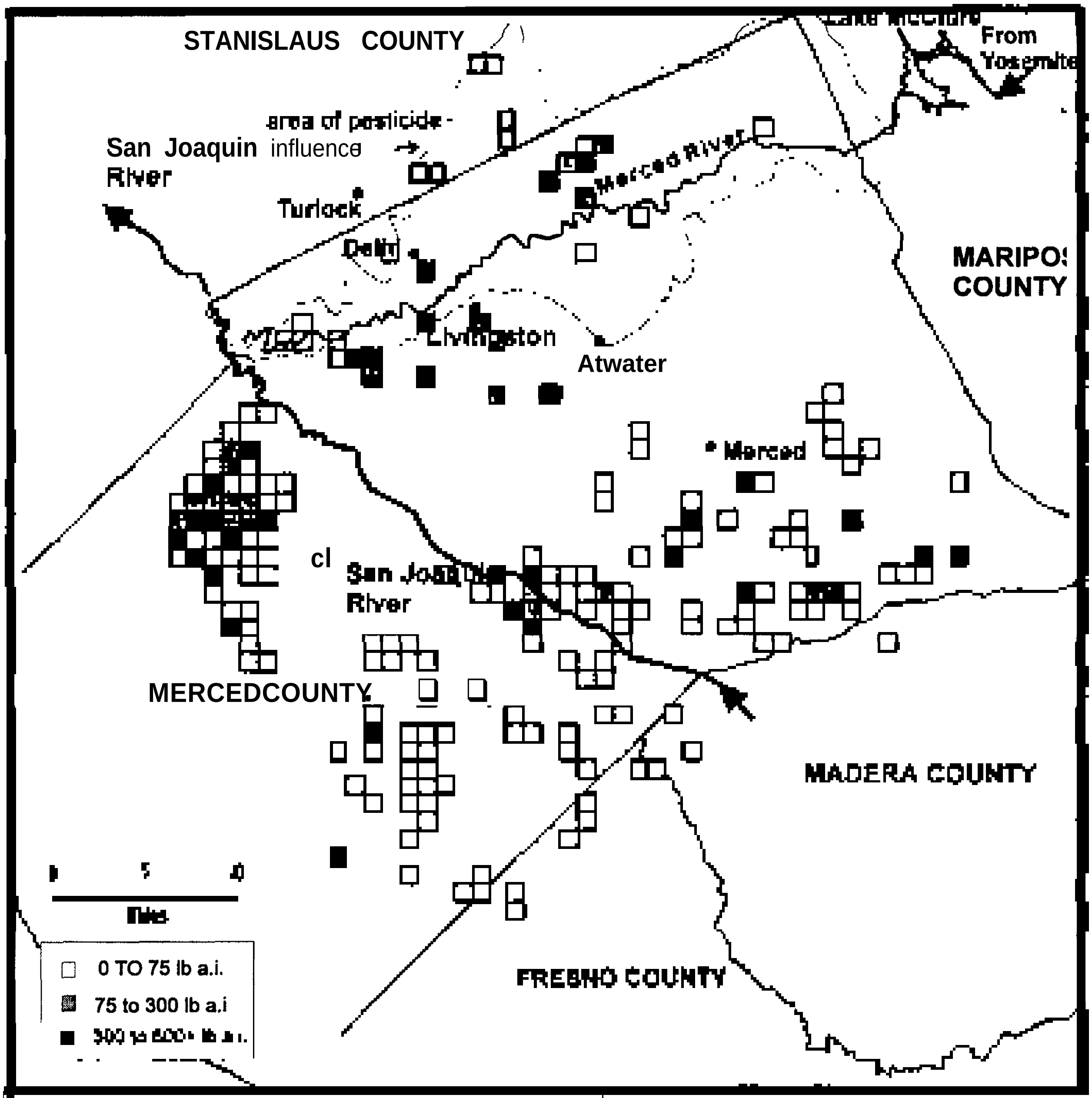
CVRWQCB water quality criterion established for the protection of freshwater aquatic organisms (Table 4).

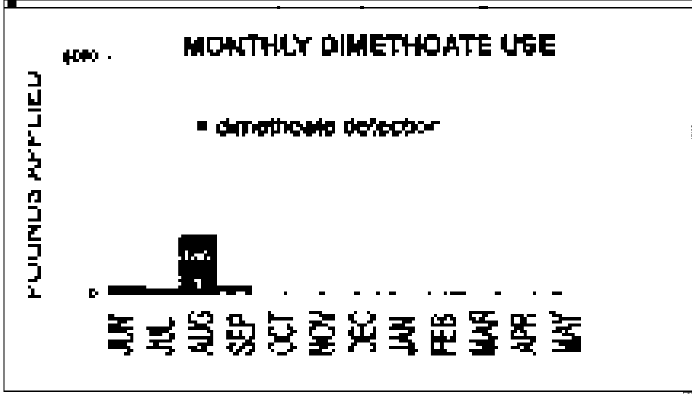
In the Merced River watershed, the majority of dimethoate is used on beans, grapes, and corn and is applied from June to September with peak use in August (Figure 19). During the 4 month period the applications within the watershed add up to slightly greater than 1,600 lb a.i.. The first detection, September 2-5, 1994, occurred during the last week that dimethoate was applied in the watershed (Figure 20). Two applications were made to corn within 3 miles East of the sampling site during the sampling period. These applications were made in a section of land that the river transects and were less than a mile from the river itself. Within the 2 weeks before the first detection, dimethoate was applied to crops in other sections of land that the Merced River also transects. The second detection, September 23-26, 1994, happened over 2 weeks after all reported applications.

Direct runoff from flooded fields and/or aerial drift to the river may have been the transport mechanism. The discharge data for the Merced River showed that the flow was increasing during both 3-day sampling periods (Figures 15 and 16). Since discharge was less than 120 cfs during September, irrigation runoff could easily increase the flow. For instance, 12 cfs of runoff would increase the flow by 10%. In fact the flow increase during the 3-day sampling periods was 44% and 66%, respectively. However, flow may appear to increase when a diversion pump is turned off. The field dissipation half-life of dimethoate is approximately 8 days (Table 5) and thus the second detection could have been from residues still remaining on site. The detections were probably due to an irrigation event occurring one to two weeks after application. This is likely scenario since irrigation water could carry dimethoate from a field because it does not adsorb well to soil, has a high water solubility (39,800 ppm), low average Kd (0.339 g/cm^3) (Table 5) and is expected to be highly mobile. In water, dimethoate tends not to sorb to sediment and is subject to hydrolysis and possibly biodegradation (Howard, 1991).

These data are consistent with prior data collected in the San Joaquin River watershed indicating that dimethoate is present during late summer (Ross 1992, 1993b). Prior concentrations in samples collected in the San Joaquin River upstream of the mouth of the Merced River ranged from 0.05 to 0.14 ppb in 1991 and 0.07 to 2.4 ppb in 1992. Due to a lack of available data, CDFG was unable to develop water quality criteria for dimethoate (Siepmann and Yargeau, 1996). However, when compared with known

DIMETHOATE USE IN THE MERCED RIVER WATERSHED





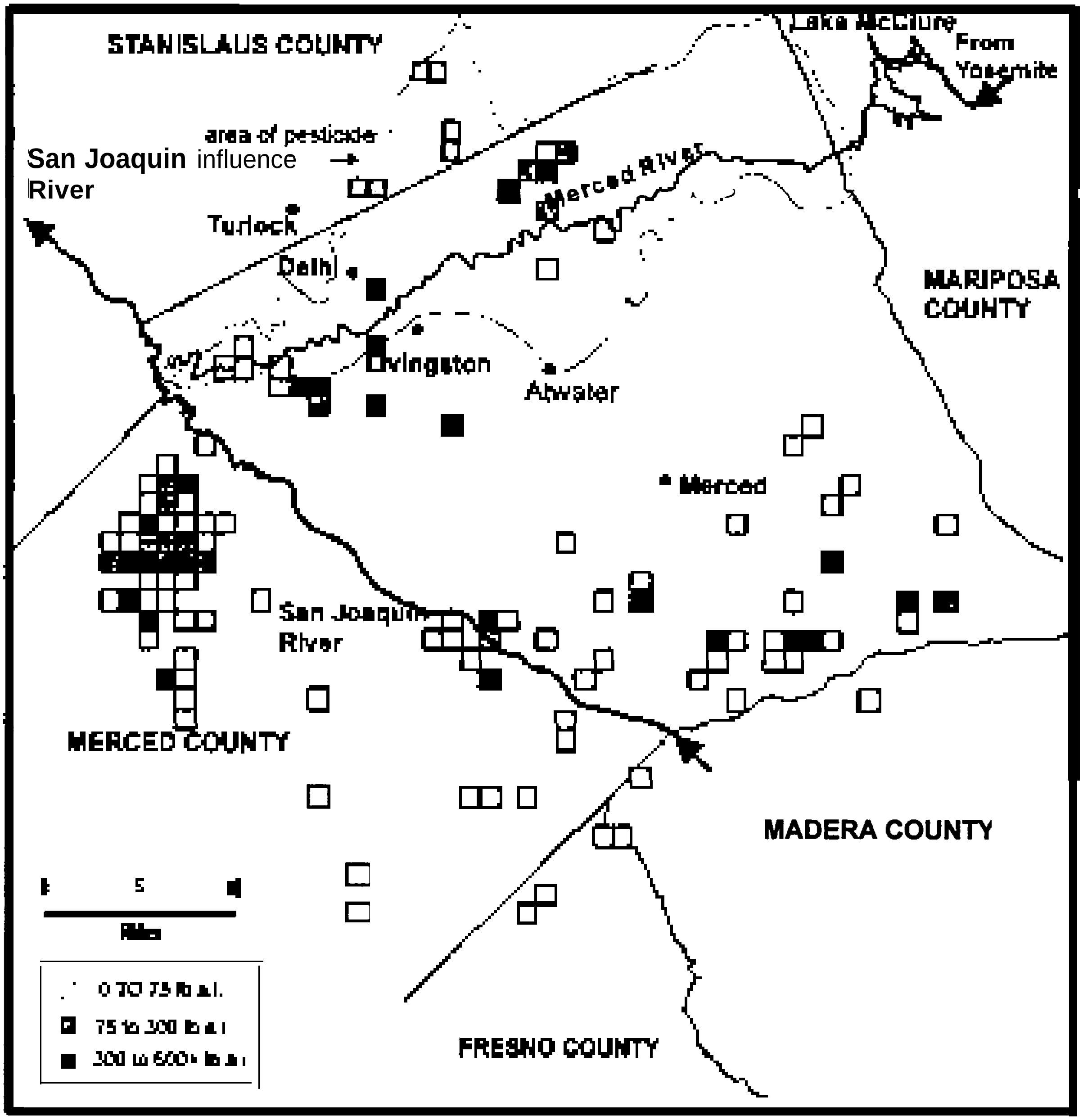
☆ Sampling site

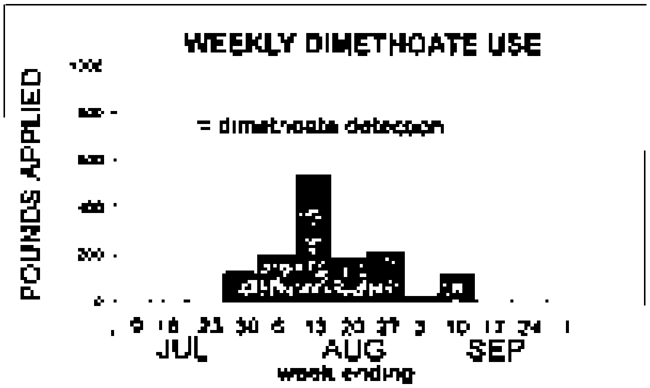
☐ Each square represents one or more applications within a one square mile section

Primary Crops	Pounds
1. Beans	1,128
2. Grapes	282
3. Corn	211
Total pounds applied during sampling year:	1,655

Figure 19 Applications and pounds of dimethoate used in the Merced River watershed, June 1994 through May 1995.

DIMETHOATE USE IN THE MERCED RIVER WATERSHED
JULY-SEPTEMBER 1994





∴ Sampling site

☐ Each square represents one or more applications within a one square mile section

Primary Crops	Pounds
1. Bean	1,075
2. Corn	211
3. Grapes	155
4. Tomato	13
Total pounds applied during sampling period:	1,419

Figure 20. Applications and pounds of dimethoate used in the Merced River watershed, July through September 1994

toxicity data, CDFG noted that dimethoate levels detected in previous studies of the San Joaquin River system indicate that dimethoate does not appear to pose an acute or chronic hazard to aquatic organisms (Seipman and Yargeau, 1996). The most sensitive species LC,, for a 96-hr toxicity test listed in Mayer and Ellersieck (1986) was stoneflies *(Pteronarcys californica)* at 43 µg/L. The level we detected during our 72-hr samples was much lower and does not appear to pose a hazard.

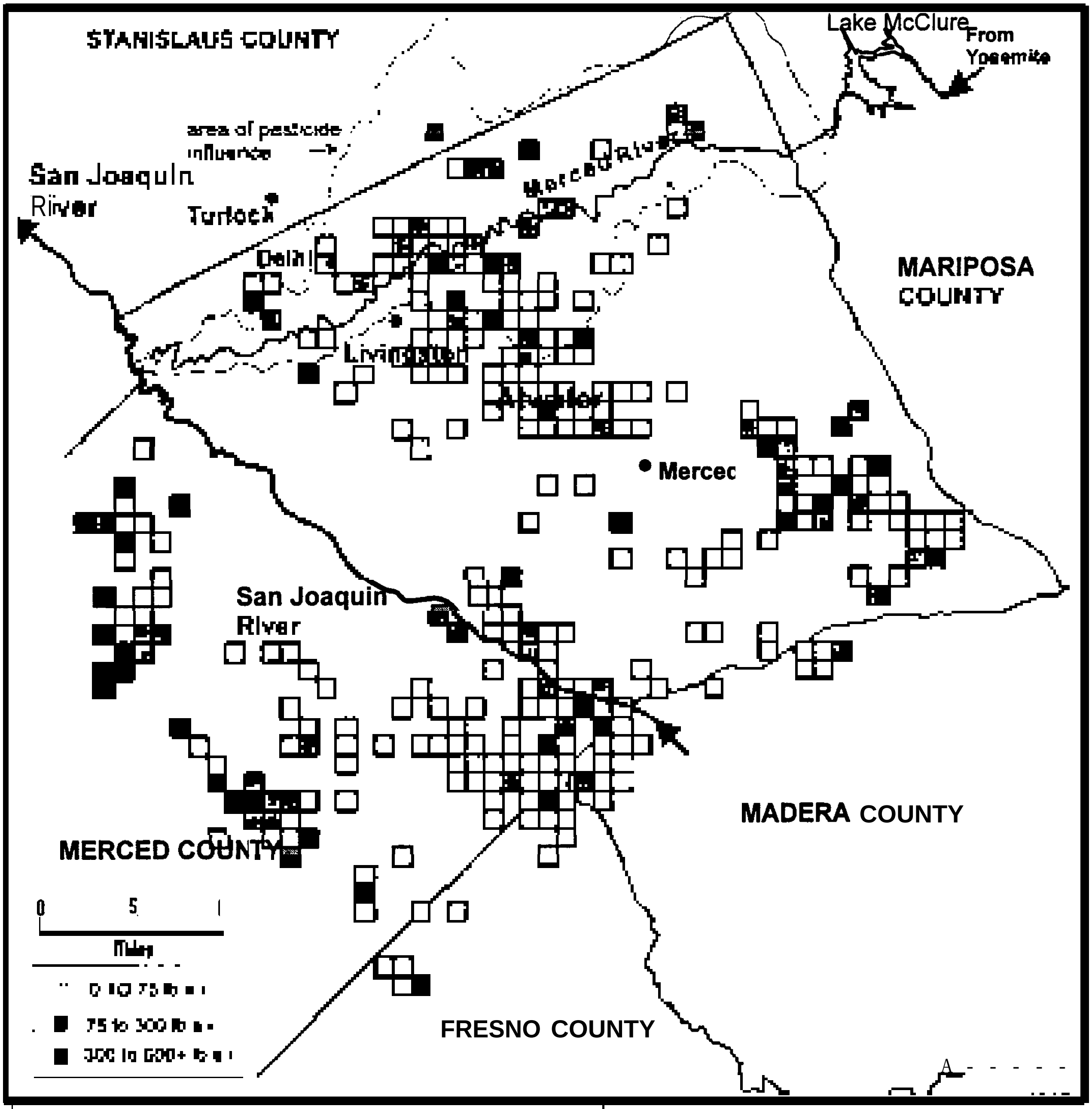
Diazinon was detected in several samples collected during the periods ending January 9, 30, and February 2, 1995 at concentrations of 0.11, 0.077 and 0.17 ppb, respectively (Table 6). These levels may exceed the CDFG recommended chronic freshwater criteria (4-day) for diazinon (Table 4). However, our samples were collected over 2 or 3-days.

Diazinon is used throughout the year with most use occurring during the dormant period, December through February (Figure 21). During this time, diazinon, as well as chlorpyrifos and methidathion, are applied with an oil on nut and stone fruit trees to control peach twig borer, San Jose scale, European red mite and brown mite pests. The applications are generally made during rain-free periods with enough time to apply the pesticide. Since most rain falls during the dormant period, the chance of transport of spray residues via runoff to streams and rivers is greatly increased. In the Merced River watershed, almost 4,000 lb a.i. of diazinon were applied on almond orchards and to a lesser degree on peach and plum orchards. The diazinon detections in the Merced River occurred during the rainy season and during peak pesticide use in the watershed. From December to the end of February more than 2,400 lb a.i. of diazinon were applied (Figure 22).

Rainfall in December was light, totalling about 0.40 inches prior to the diazinon applications which began the week ending December 24, 1994 (Figure 22). A small amount of rain fell on December 24 and 28 but there was no increase in the Merced River discharge to indicate that runoff occurred. According to discharge data below Merced Falls Dam, near Snelling, CA, dam releases were held steady below 250 cfs from November 1994 through March 10, 1995 (USGS, 1995). Therefore, increases in flow in January, February and the first half of March were due to rain runoff. The elevated flow after March 10 to the end of this study was due to dam releases.

Rainfall began again on January 3 and continued through January 17, 1995 (Figure 17). During this period there were no applications of diazinon (DPR, 1995). Diazinon

DIAZINON USE IN THE MERCED RIVER WATERSHED



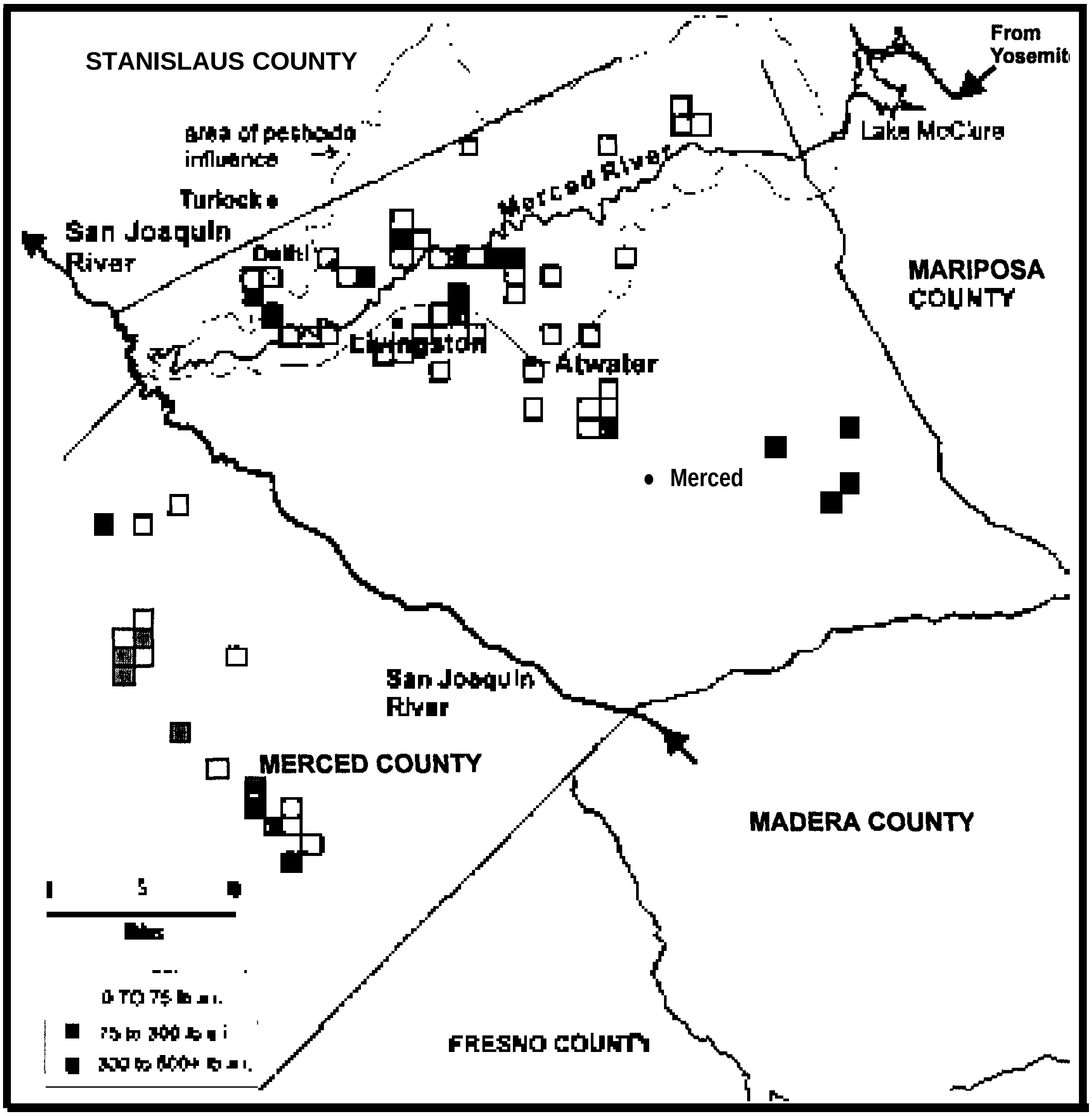
☆ Sampling site

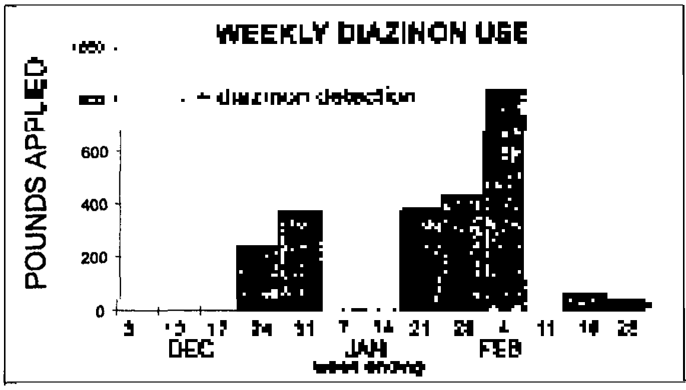
■ Each square represents one or more applications within a one square mile section

Primary Crops	Pounds
1. Almond	2,733
2. Peach	841
3. Plum	141
Total pounds applied during sampling year:	3,989

Figure 21. Applications and pounds of diazinon used in the Merced River watershed, June 1994 through May 1995.

DIAZINON USE IN THE MERCED RIVER WATERSHEC
DECEMBER 1994-FEBRUARY 1996





Sampling site

☐ Each square represents one or more applications within a one square mile section

Primary Crops	Pounds
1. Almond Orchards	1,682
2. Peach Orchards	708

Total pounds applied during the sampling period: 2,424

Figure 22. Applications and pounds of diazinon used in the Merced River watershed prior to the detections December 1994 through February 1995

was detected in the sample collected January 6-9, the 3-day sampling period which coincided with the peak and subsequent declining discharge. The river's discharge had increased 69% from January 2 to the peak on January 7. Since there were no diazinon applications in early January (Figure 22), this first detection was most likely the result of applications made during late December. The average half-life of diazinon is reported at 14 days (Kollman and Segawa, 1995) and 6.4 days (Ross et al., 1997); thus, diazinon was applied one or more half-lives before the detection.

There were no detections in the next two samples collected January 13-16 and 20-23, despite the fact that diazinon applications and rainfall both occured during the sampling periods. Rainfall occurred daily January 20 through 28 and discharge in the river increased to a level greater than 388% of the level prior to the storm. Diazinon was applied during this period, mainly on the days when only a trace of rainfall was recorded. During each of the weeks ending January 21 and January 28, the weeks preceding the next two detections, about 400 lb a.i. of diazinon were applied (Figure 22). The detections occurred on January 28-30 and January 31-February 2 during the week when the greatest quantity of diazinon was used, about 800 lb a.i., and when discharge was declining after peak discharge on January 28.

Due to these detections, a decision was made to more closely examine runoff of dormant spray residues; thus, sampling was increased to twice weekly, collecting sub-samples over two 2-day periods per week with the automatic sampler beginning on January 31 and ending on March 6. However, after the January 31-February 2 sample, diazinon was not detected again in subsequent sampling probably due to a decrease in the number of applications after the first week in February and an absence of significant rain in February (Figure 17).

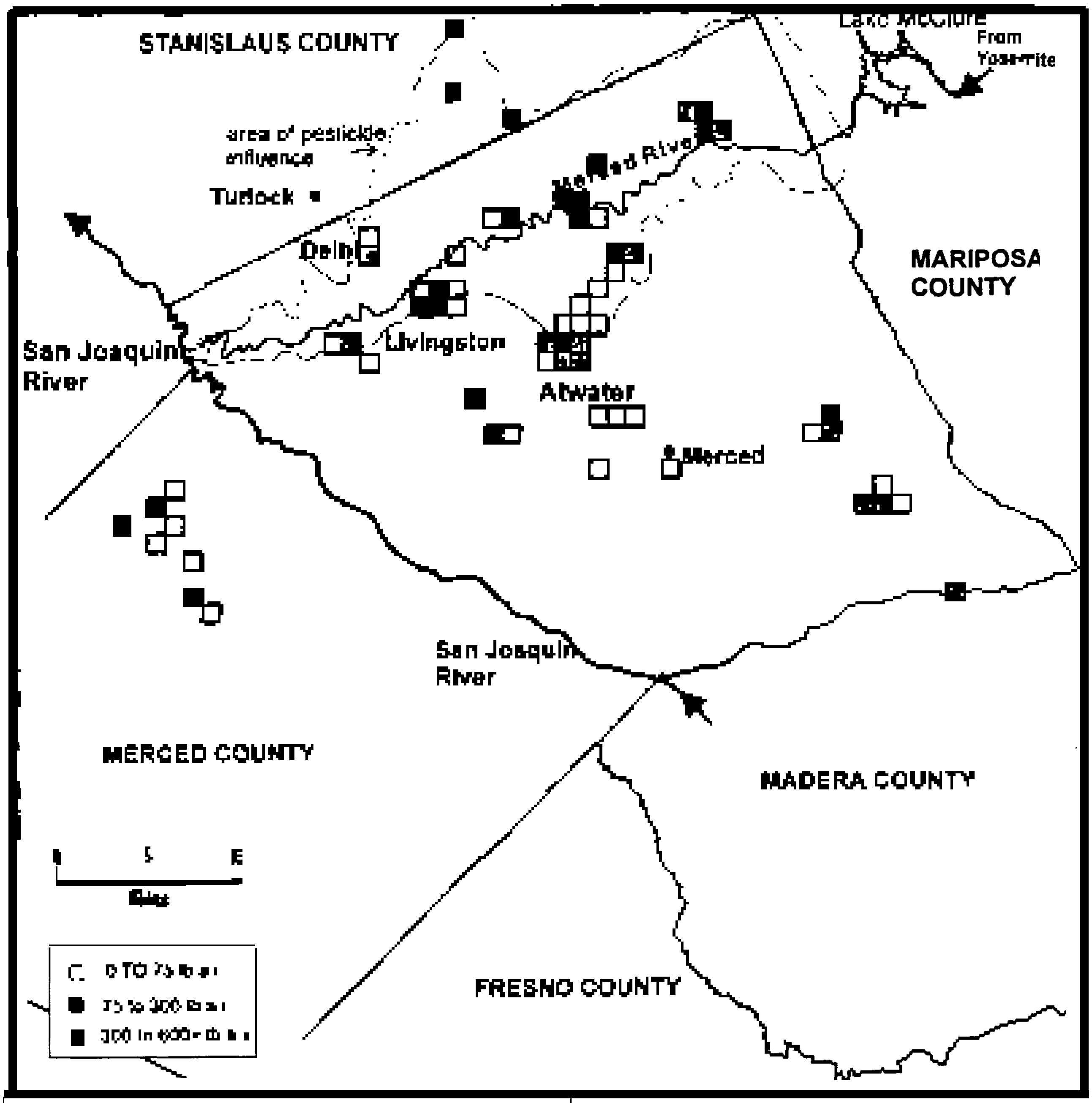
The detections of diazinon are consistent with previous data collected in the Merced River watershed which indicated that diazinon is present during winter months. In a study conducted during the winters of 1992 and 1993, samples collected during storms at several sites in the Merced River Watershed contained diazinon concentrations ranging from 0.07 to 2.54 ppb (Ross et al., 1996). During 1992 the CVRWQCB detected diazinon in the Merced River, four times from January through April at concentrations of 0.01 to 0.32 ppb (CVRWQCB, 1995). A USGS study conducted on the Merced River indicated that diazinon levels in the river increased as discharge increased and peak diazinon levels coincided with the highest flows (Domagalski, 1995). During a storm in February 1993, USGS detected diazinon in the five samples collected during part of a hydrograph of the Merced River. The levels detected ranged from 0.12 ppb prior to an increase in flow to 2.5 ppb during the decline after peak discharge (Domagalski, 1995). Our data also indicated that diazinon detections coincide with higher flows.

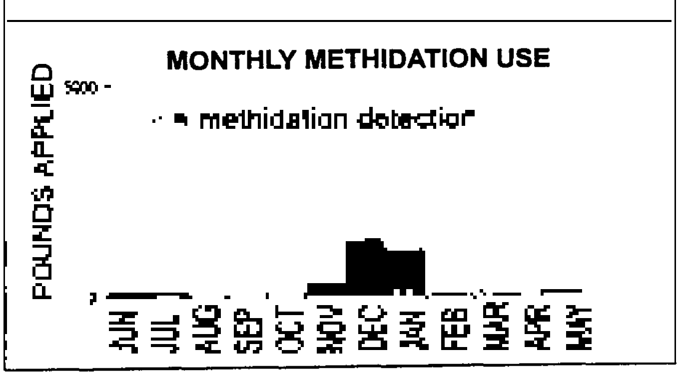
Methidathion was detected at concentrations of 0.22, 0.11, 0.13 and 0.061 ppb in samples collected during sampling periods ending on January 9 and 16, February 2, and March 13, 1995, respectively. Currently, there are no water quality criteria for methidathion for the protection of freshwater aquatic organisms (Table 4). Water quality criteria for methidathion have not yet been developed due to a lack of available information (Menconi and Seipmann, 1996). However, when compared with known toxicity data, CDFG noted that methidathion levels detected in previous studies of the Sacramento and San Joaquin River systems indicated methidathion may be a hazard to aquatic organisms, especially sensitive aquatic invertebrates.

Detections of methidathion coincided with peak use, rainfall and consequent peak discharges (Figures 17 and 23). About 2,500 lb a.i. of methidathion were applied in the watershed primarily on almond, walnut, apricot and prune orchards during the one-year study period (Figure 23). Most use occurred from November through January with the greatest amount applied applied in December (1,900 lb a.i.). There was little rainfall or runoff in December and there were no detections of methidathion in the samples collected. In January less methidathion was used (1,062 lb a.i.), but there was rainfall, followed by increased runoff and the first methidathion detections. The first two weeks of January, weeks ending on January 7 and 14, there were few applications of methidathion due to rainfall. Methidathion was dectected in the sample collected January 6-9, the same sample in which diazinon was detected. This sample period coincided with a minor peak in river flow followed by declining flow after a storm. The residues detected in the January 6-9 sample must have been from applications in December or the one 35 pound application January 2 on a peach orchard near Atwater (DPR, 1995).

Methidathion was not used from January 3 until after the January 13-16 sample collection period, when methidathion was detected again. The sampling period came between two peak discharges, January 12, a day prior to the sampling period and January 16, the last day of the sampling period. There was a 375% increase in flow from January 9 to January 12 and from the lull on January 14 to peak discharge on January 16 there was a 200% increase in flow.

METHIDATHION USE IN THE MERCED RIVER WATERSHED





☆ Sampling site

▪ Each square represents one or more applications within a one square mile section

Primary Crops	Pounds
1. Peach orchards	1,313
2. Almond orchards	1,003
3. Walnut orchards	215
4. Apricot orchards	149
Total pounds applied during sampling year.	2,846

Figure 23. Applications and pounds of methidation used in the Merced River watershed June 1994 through May 1995

During the next two weeks methidathion use increased compared to early January. There were 240 lb a.i. and 108 lb a.i. of methidathion applied in the watershed during the weeks ending January 28 and February 4 (Figure 24). These applications were made in sections that were about 15 or more miles upstream from the sampling site (DPR, 1995). Methidathion was not detected in the sample collected January 28-30, collected during peak and declining discharge. However, methidathion was detected in the sample collected January 31-February 2, 1995, 3 to 5 days after rainfall and peak discharge.

There was little use of methidathion after the last week in January. However, methidathion was again detected in the sample collected on March 13, 1995, approximately 3 weeks after the last methidathion application (Figure 25) The level detected was much lower than the levels detected in the other samples probably due to the length of time since the last application. Also the sample was collected as the discharge was declining, after the flood. Less methidathion may have been detected due to dilution since discharge was up 1,155% at the peak on March 12, which was a higher percent increase in discharge than prior to the other detections. Much of this increase was due to heavy rain in the mountains.

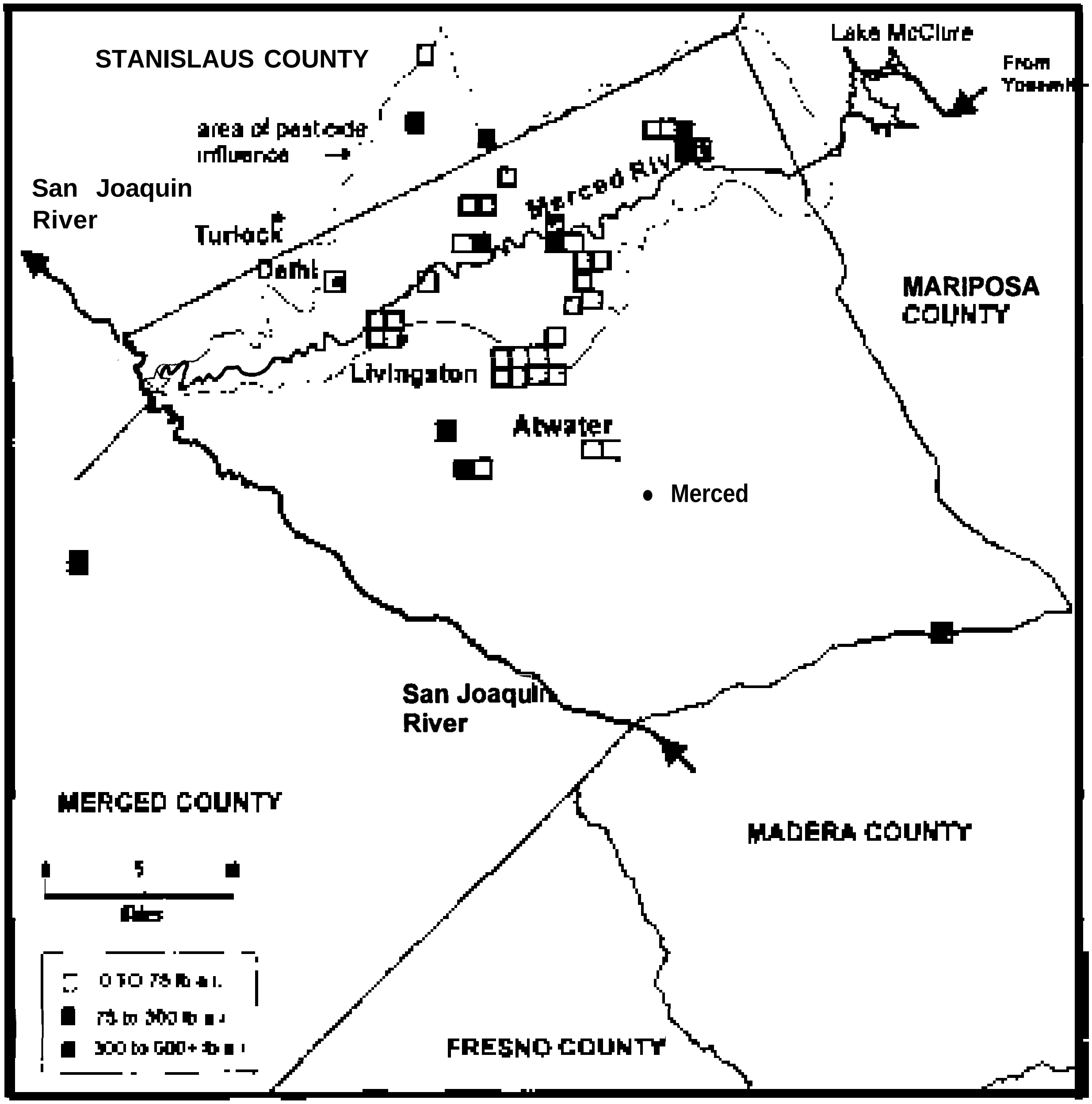
The heavy rainfall in the mountains in mid-March resulted in an increase in the Merced River flow through the remainder of the study due to releases from dams upstream. There were no further detections of any of the pesticides analyzed in this study due to declining use in the spring and possibly the increased flows diluting residues.

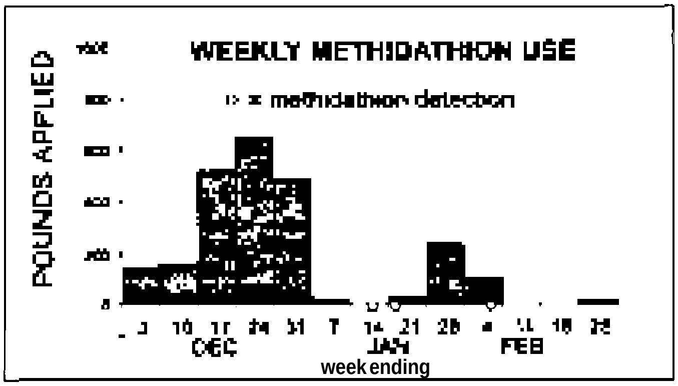
The detections of methidathion are consistent with previous data collected in the Merced River watershed which indicated that methidathion is present during winter months. In a study conducted during the winters of 1992 and 1993, two samples collected in the Merced River Watershed during storms contained methidathion at 0.14 and 0.18 ppb (Ross et al., 1996).

A degradation byproduct of carbofuran, 3-hydroxycarbofuran, was detected at 0.18 ppb in the January 28-30 sample. This sample was collected following peak discharge on January 28. There are no current water quality criteria established for the protection of freshwater aquatic organisms for carbofuran or its metabolites.

Approximately 1,760 lb a.i. of carbofuran were used during the study period on alfalfa in the Merced River watershed (DPR 1994 and 1995). It is typically applied during

METHIDATHION USE IN THE MERCED RIVER WATERSHED
DECEMBER 1994 -FEBRUARY 1995





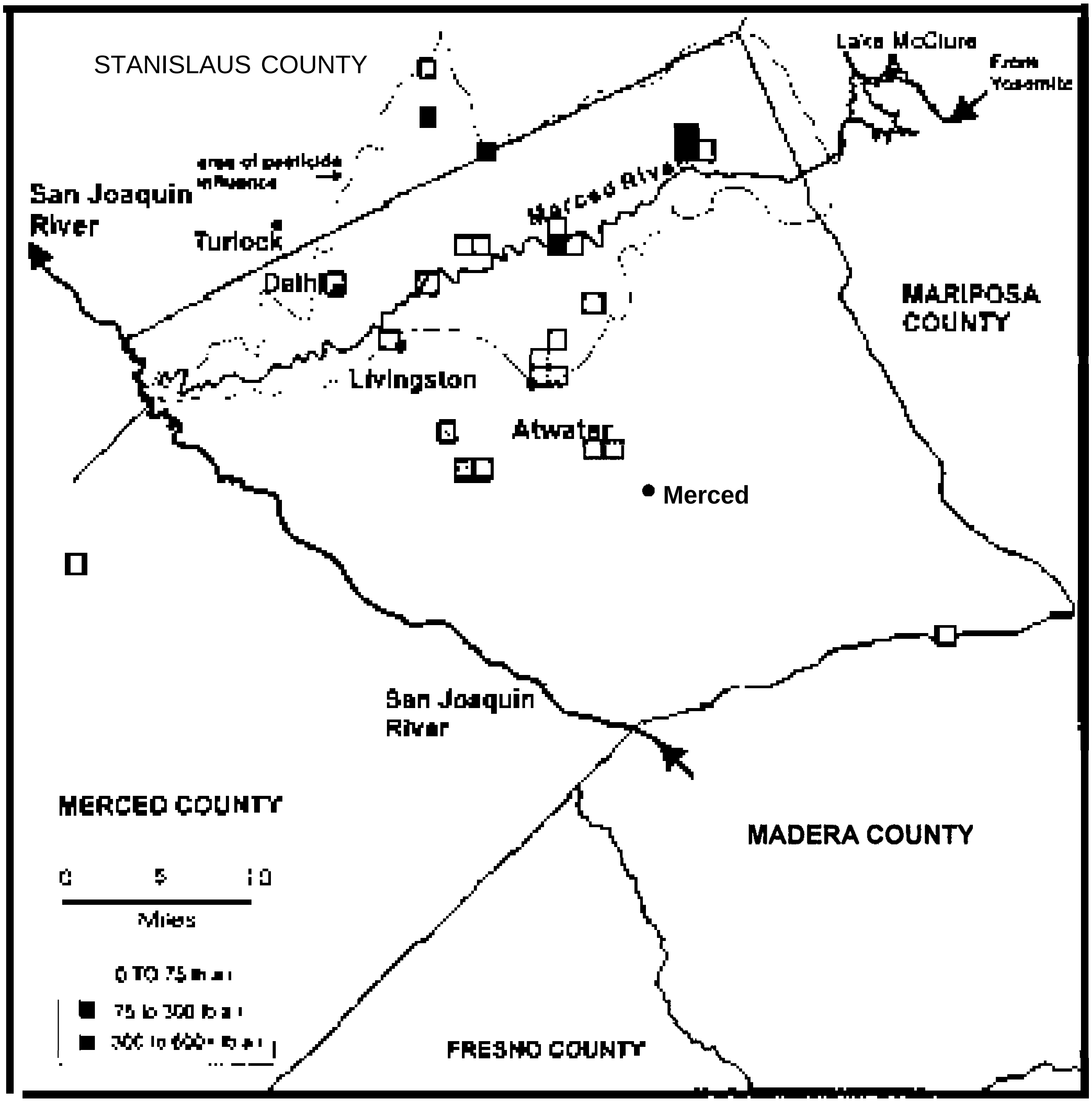
☆ Sampling site

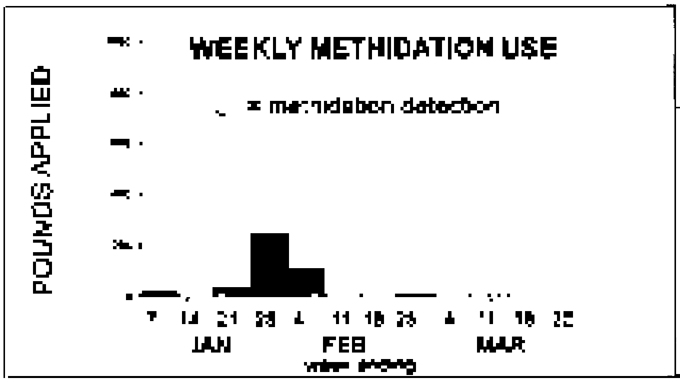
□ Each square represents one or more applications within a one square mile section

Primary Crops	Pounds
1. Peach Orchards	1,058
2. Almond Orchards	1,003
3. Apricot Orchards	149
4. Prune Orchards	84
Total pounds applied during sampling period:	2,294

Figure 24. Applications and pounds of methidathion used in the Merced River watershed, December 1994 through February 1995.

METHIDATION USE IN THE MERCED RIVER WATERSHED
JANUARY -MARCH 1995





☆ **Sampling site**

▨ Each square represents one or more applications within a one square mile section

Primary Crops	Pounds
1. Almond Orchards	210
2. Prune Orchards	84
3. Apple Orchards	66
4. Peach Orchards	47
Total pounds applied during sampling year:	390

Figure 25. Applications and pounds of methidation used in the Merced River watershed prior to the detections. January through March 1995.

February through April with highest use in March (DPR, 1992). The average field dissipation half-life listed by Kollman and Segawa (1995) is about 30 days. According to Howard (1991), carbofuran may leach significantly from soils with K_{oc} (sorption coefficient including organic content) values ranging from 14 to 160 (K_d is not reported in Kollman and Segawa, 1995). Carbofuran has been detected in water collected from the San Joaquin River during the months of March and April in 1991 and 1993 (MacCoy et al., 1995).

Toxicity Testing

Samples tested for toxicity by CDFG showed no significant mortality to cladocerans or fathead minnows in any of the 30 samples tested (Appendix V).

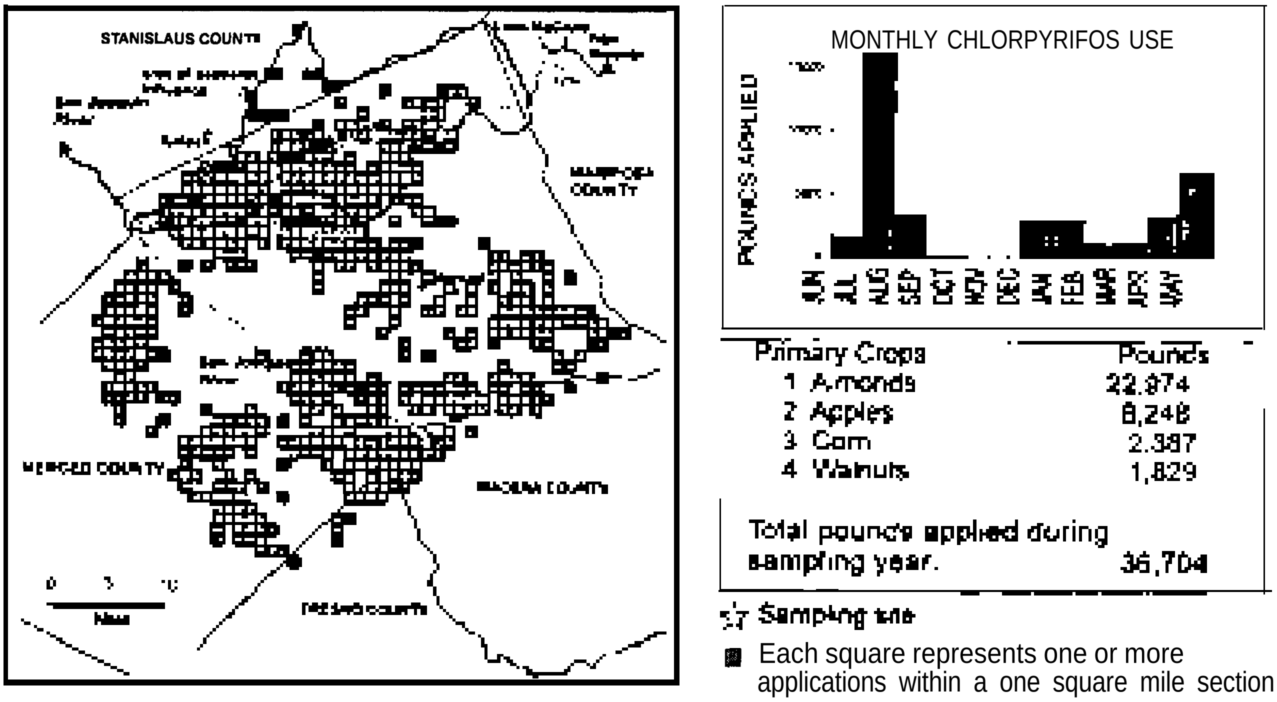
Other Pesticides Used in the Watershed

During this study, chlorpyrifos was not detected in the Merced River samples although it was used in the greatest quantity compared to the other organophosphate and carbamate pesticides analyzed in this study (Figure 26). It has previously been detected in the Merced River in other studies (Ross et al., 1996; CVRWQCB, 1995). Greater than 37,000 lb a.i. were applied in the watershed area during the study period (Figure 26). Chlorpyrifos was applied from December through August and most heavily applied in July. More chlorpyrifos was used than diazinon and methidathion combined during the dormant spray period (Figure 27). More than 6,000 lb a.i. were applied from December through February, mainly to almond and apple orchards and use was continued in March on alfalfa.

Chlorpyrifos has a longer half-life than diazinon or methidathion but a lower water solubility (Table 5). Chlorpyrifos may move offsite with soil errosion since it has a high soil absorptivity (Table 5). Pesticides that are tightly adsorbed to soil are held near the treatment site. Since chlorpyrifos is not very mobile in soil, residues may be transported off-site as residue bound soil particles that could be carried to surface water in runoff from agricultural fields. The amount of the pesticide in runoff depends on the extent of soil erosion, and the amount of sediment transported, and the amount and timing of applications.

Heavy amounts were applied prior to rainfall events and some was applied during small breaks in the rain. However, no chlorpyrifos was detected in the samples collected.

CHLORPYRIFOS USE IN THE MERCED RIVER WATERSHED



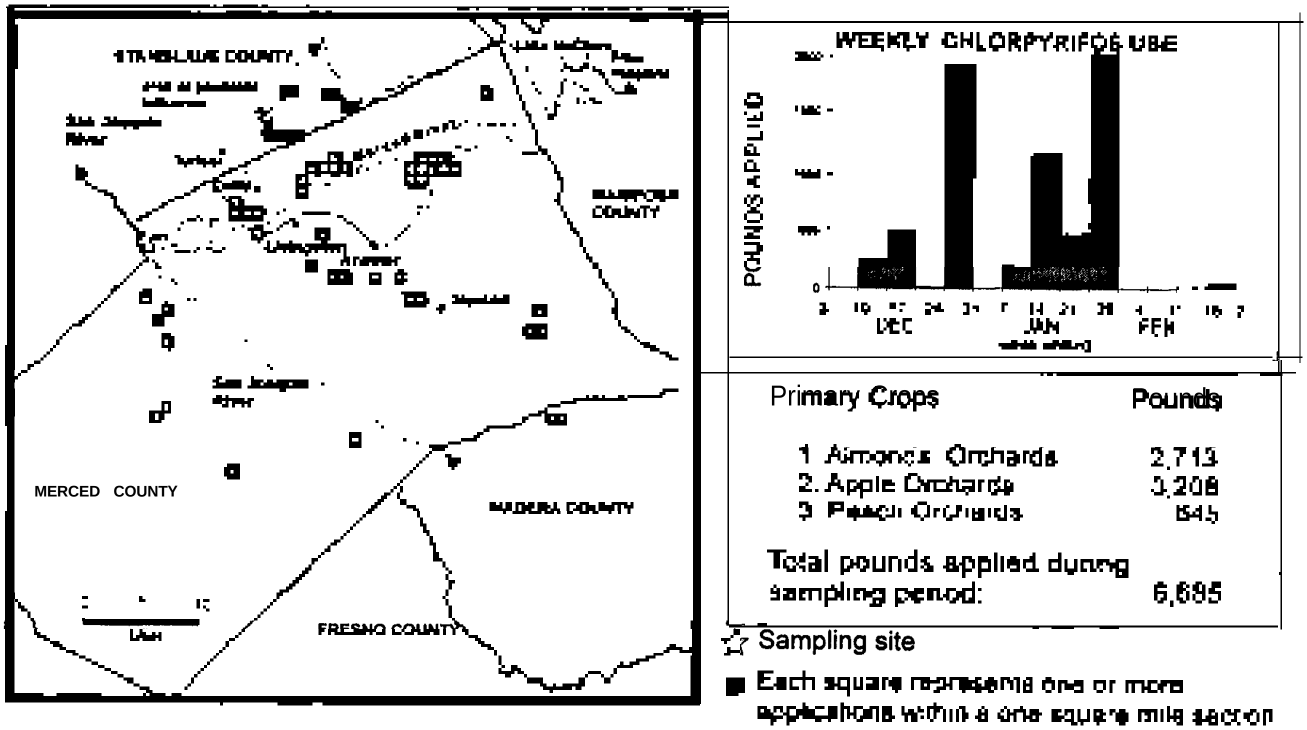
Primary Crops	Pounds
1 Almonds	22.874
2 Apples	8,248
3 Corn	2.387
4 Walnuts	1,829
Total pounds applied during sampling year.	36,704

☆ Sampling site

■ Each square represents one or more applications within a one square mile section

Figure 26 Applications and pounds of chlorpyrifos used in the Merced River watershed from June 1994 through May 1995 .

CHLORPYRIFOS USE IN THE MERCED RIVER WATERSHED, DECEMBER-FEBRUARY



Primary Crops	Pounds
1 Almonds Orchards	2.713
2. Apple Orchards	3,208
3 Peach Orchards	645
Total pounds applied during sampling period:	6,695

☆ Sampling site

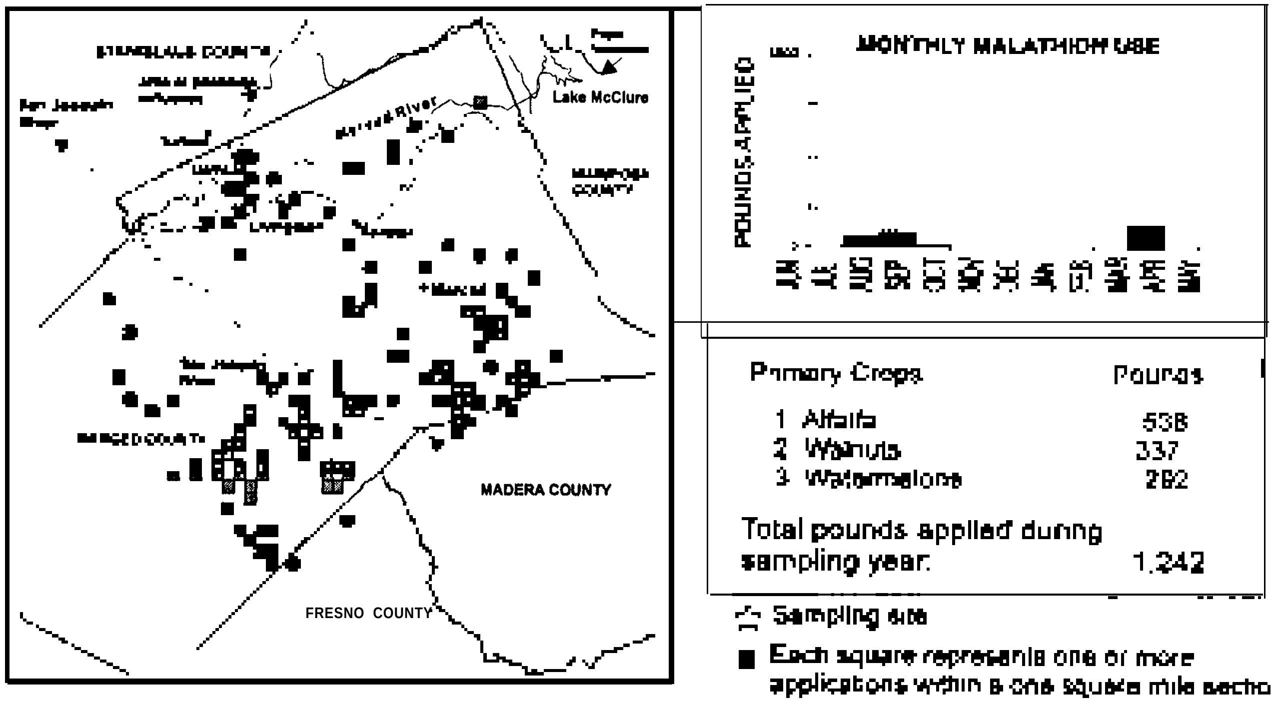
■ Each square represents one or more applications within a one square mile section

Figure 27 Applications and pounds of chlorpyrifos used in the Merced River watershed from December 1994 through February 1995

Chlorpyrifos might have moved offsite into the river during periods of rainfall and runoff that were not sampled and might have been present below our reporting limit. The CVRWQCB found chlorpyrifos six times in the Merced River from January through May 1992, at concentrations ranging from 0.01 to 0.13 ppb (Foe, letter to Kevin Bennett 1/4/94). In February of 1993, it was detected in the Merced River by DPR three times at concentrations ranging from 0.07 to 0.10 ppb (Ross et al., 1995) and by the USGS a 0.045 to 0.26 ppb (Domagalski, 1995).

Some of the other **OPs** and **CBs** that were analyzed and not detected in this study were used less or used during the dry season when rain runoff did not occur. For example, only about 1,200 lb a.i. of malathion were used in the watershed (Figure 28). Applications occurred in July, August and in March, mainly on alfalfa, walnut orchards and watermelon crops. Azinphos-methyl was used on almonds and peaches during the dry season from May through August (Figure 29); the month of peak use is July. Phosmet was applied June through August (Figure 30). Applications were mainly made to almond and peach orchards. The carbamate pesticide carbaryl was used during the dry season, mainly in July, on peach orchards and grape vineyards (Figure 31).

MALATHION USE IN THE MERCED RIVER WATERSHED



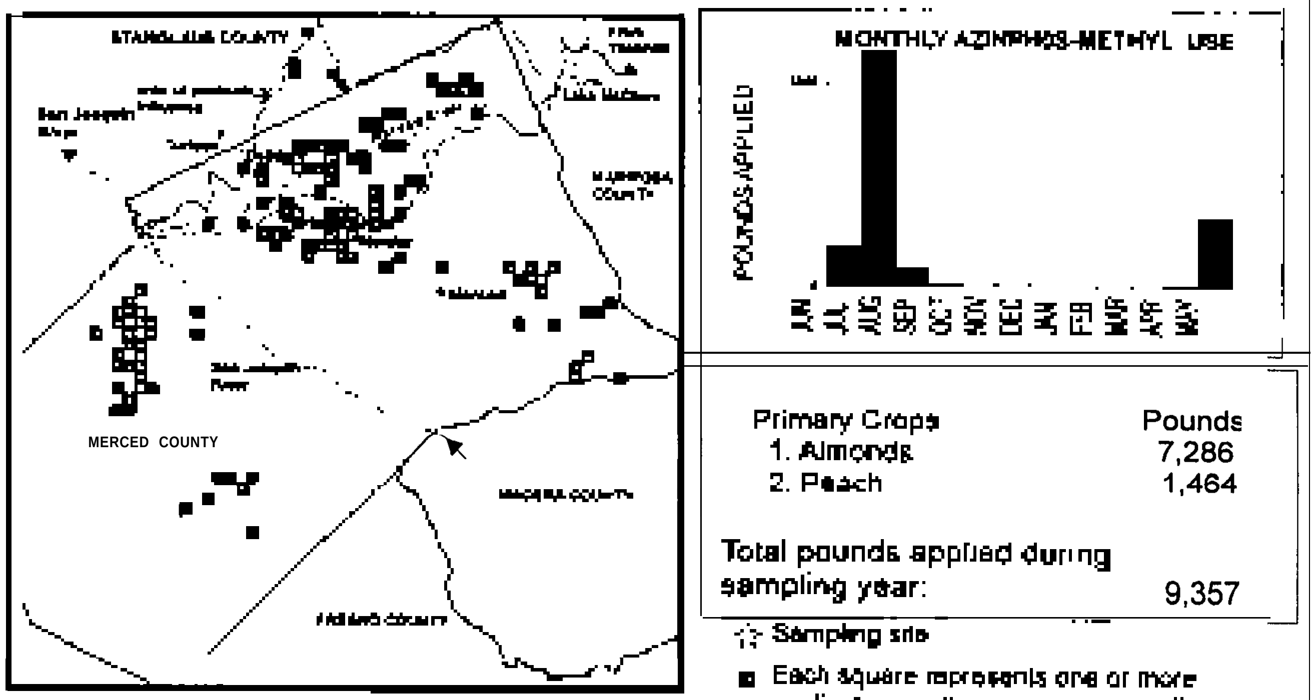
Primary Crops	Pounds
1 Alfalfa	538
2 Walnuts	337
3 Watermelons	282
Total pounds applied during sampling year:	1,242

☆ Sampling site

■ Each square represents one or more applications within a one square mile section

Figure 28. Applications and pounds of malathion used in the Merced River watershed from June 1994 through May 1995 .

AZINPHOS-METHYL USE IN THE MERCED RIVER WATERSHED



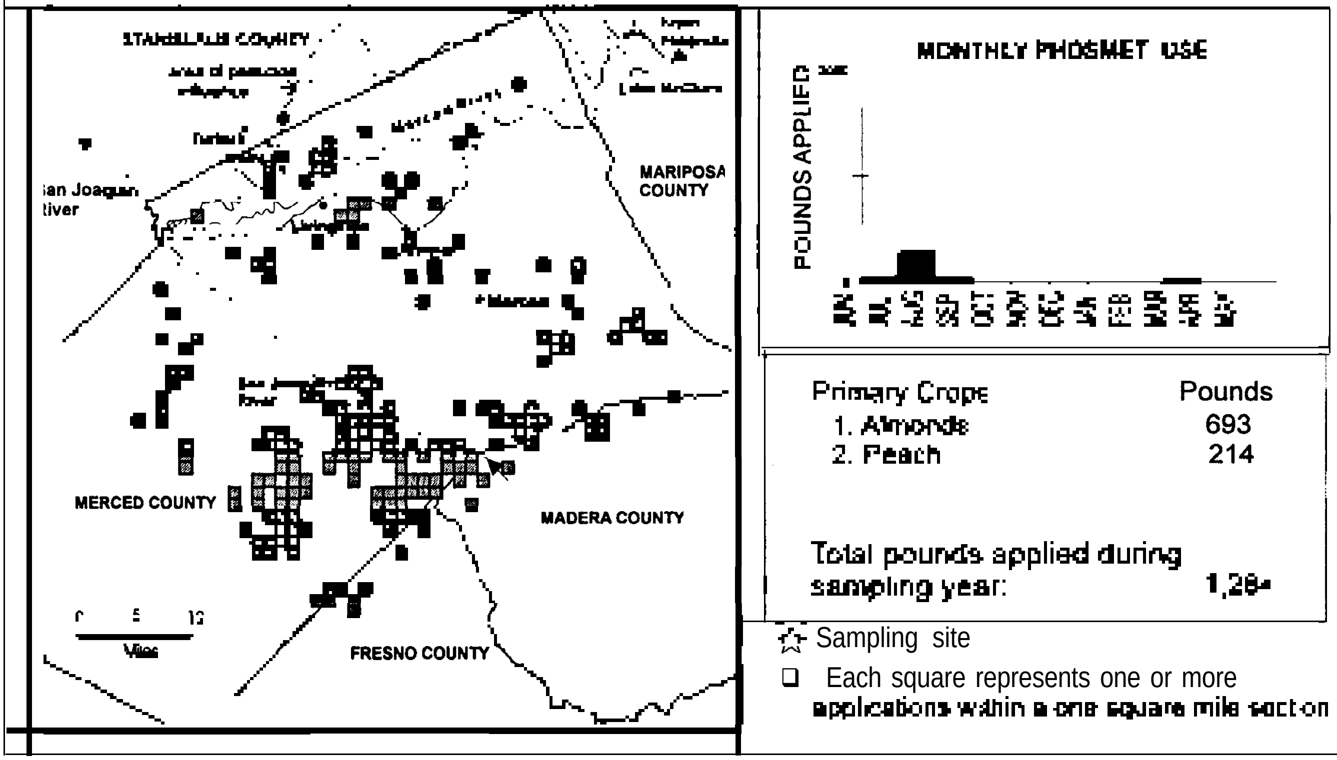
Primary Crops	Pounds
1. Almonds	7,286
2. Peach	1,464
Total pounds applied during sampling year:	9,357

☆ Sampling site

■ Each square represents one or more applications within a one square mile sectic

Figure 29. Applications and pounds of azinphos-methyl used in the Merced River watershed from June 1994 through May 1995 .

PHOSMET USE IN THE MERCED RIVER WATERSHED



Primary Crops	Pounds
1. Almonds	693
2. Peach	214

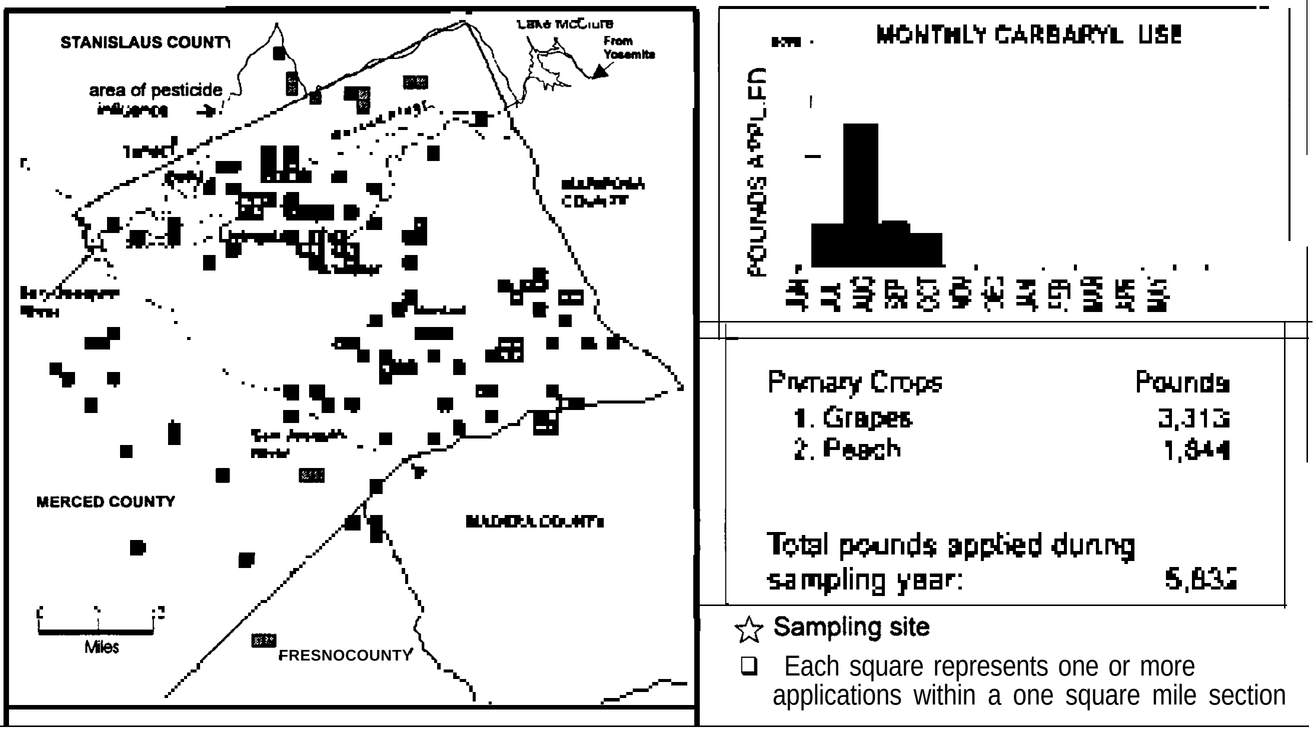
Total pounds applied during sampling year: 1,284

☆ Sampling site

❑ Each square represents one or more applications within a one square mile section

Figure 30. Applications and pounds of phosmet used in the Merced River watershed from June 1994 through May 1995.

CARBARYL USE IN THE MERCED RIVER WATERSHED



Primary Crops	Pounds
1. Grapes	3,313
2. Peach	1,844

Total pounds applied during sampling year: 5,832

☆ Sampling site

❑ Each square represents one or more applications within a one square mile section

Figure 31 Applications and pounds of carbaryl used in the Merced River watershed from June 1994 through May 1995.

Salinas River

Salinas River Watershed

The Salinas River watershed is situated between the Diablo mountain range in the east and the Santa Lucia Mountain range to the west (Figure 32). The watershed is about 150 miles long and about 20 to 30 miles wide (Salinas River Lagoon Management and Enhancement Plan, 1992). In this report, the Salinas River will be described as the upper, middle and lower portion. The upper reach of the river begins in the south at Santa Margarita Lake in San Luis Obispo County. The river flows northward to the middle reach where the flow increases due to releases from the reservoirs on the Nacimiento and San Antonio Rivers. Agricultural influences of the middle reach of the Salinas River begins at the confluence with the Nacimiento River since surface water flows upstream of Paso Robles are minimal during three quarters of the year (Palmer et al., 1994; Friebel et al., 1995). Below the confluence of the Nacimiento and San Antonio Rivers, flow occurs year round.

The Salinas River flow in the middle reach is dependent on releases from the Nacimiento and San Antonio Reservoirs. Water discharged from the reservoirs is primarily used in the middle portion of the river for groundwater recharge via the river channel and is also diverted for irrigation in the Salinas Valley. Information on agricultural drainage for the middle reach indicates that, although no major drains exist, significant agricultural runoff does occur through individual draining sites from farms located along the river.

During the dry-season, which last from approximately May through November, no rainfall-induced flow reaches the lower portion of the river (Salinas River Lagoon Management and Enhancement Plan, 1992). During this time, releases are regulated to flow down to Chualar, with no water reaching farther downstream. The geology of the river watershed has a significant effect on the amount and timing of the releases because flow is regulated to those areas that will allow drainage. For this reason, releases from the reservoirs are regulated to flow only into those areas where groundwater recharge may result. Consequently, flow from Chualar downstream to the Lagoon is intermittent throughout most of the year and consists mainly of agricultural return water, which enters the river channel from several agricultural drains. However, during the rainy season, flow throughout the river is increased as a result of rain runoff, agricultural return water, and periodic releases from the reservoirs.

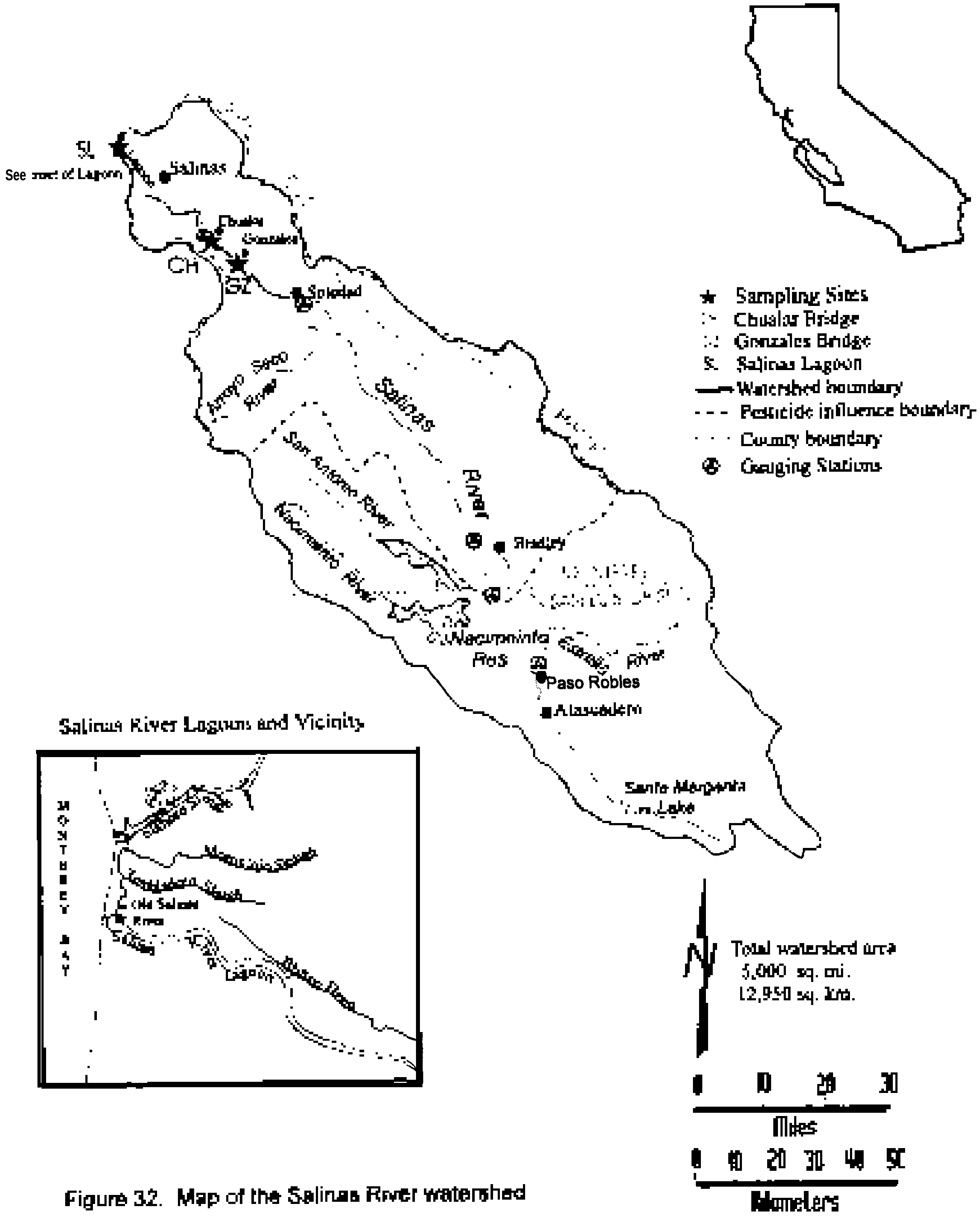


Figure 32. Map of the Salinas River watershed

The middle and lower reach of the Salinas River, situated in Monterey County, were sampled in this study. The sampling site chosen for the middle reach was located near the Gonzales River Road bridge, approximately 60-70 river miles downstream of the Nacimiento reservoir and 25 miles upstream from the mouth of the river. Information obtained through discussions with the Monterey County Water Resources Agency indicated that the flow at this site remains constant throughout the year. We determined that the area of pesticide influence at our sampling site begins at the confluence of the Nacimiento River and the Salinas River.

Rapid fluctuations in river stage height, and a lack of electrical power and security were several reasons why it was not feasible to use the autosampler on the Salinas River. Instead, samples were collected using the equal-width depth integration method (Guy and Norman, 1970). Since the discharge at Gonzales was different from the discharge 6 miles downstream at the gauging station at Chualar, discharge was measured using the six-tenths-depth method (Buchanan and Somers, 1969). Samples were collected weekly from the Gonzales site from August 1, 1994 to January 17, 1995. During January, February and March, regional flooding occurred and prevented access to the Gonzales site. On January 24 we began collecting water at the Chualar River Road Bridge, approximately 6 miles downstream of Gonzales. During the following 6-month period, water was collected at Chualar whenever river flow reached this site. Otherwise, samples were collected at Gonzales.

Since flows below Gonzales and Chualar were intermittent, the Salinas River Lagoon near Monterey Bay was sampled to survey the lower portion of the Salinas River for pesticide residues since water is present in the lagoon year-round. The lagoon is part of the Salinas River National Wildlife Refuge designated by the U.S. Fish and Wildlife Service and is a valuable resource for a variety of species.

The areas that drain into the Salinas River Lagoon and the outflow from the lagoon change throughout the year. During the dry season, from about May through October or November, flow consists of some irrigation return flow from the Blanco Drain, which drains about 6,000 acres of farmland, and from local agricultural drains along the lower portion of the river. During the dry season the lagoon is about 6 miles long (Salinas River Lagoon Management and Enhancement Plan, 1992).

In the winter, rainfall runoff may cause flows from the upper portion of the river to reach the lagoon. If flows in the Salinas River Lagoon become great enough to flood nearby farmland, the sandbar between the Monterey Bay and the lagoon is breached by the Monterey County Water Resource Agency to allow water to drain into the bay. During this time the lagoon is subject to tidal inflow from the Bay. The length of time the lagoon remains open to the bay is variable, dependent on both outflow from the lagoon and wave action. At times, the breach may only be open a few days. When the breach is closed, usually by spring if not earlier, the lagoon may contain a high percentage of seawater. During the summer this is diluted by the slightly brackish irrigation return water. The lagoon remains brackish due to seepage of bay water, and the evaporation of freshwater The Old Salinas River, which flows north to the Moss Landing Harbor receives periodic flows from the lagoon (Salinas River Lagoon Management and Enhancement Plan, 1992).

In addition to weekly samples collected from the Salinas River by DPR, staff from the Elkhorn Slough Foundation (ESF) collected monthly grab samples from the Salinas River Lagoon. As part of their conservation effort, the ESF monitors water quality in the lagoon area by collecting monthly samples analyzed for various water quality parameters. Samples collected by ESF for DPR were used to survey the lower portion of the Salinas River for pesticide residues. Water samples were collected by submersing 4-L amber glass bottles in the lagoon. Samples were treated the same as samples from the other four monitoring sites and were submitted to the CDFA Lab for OP and CB screens and endosulfan and diazinon analyses. CDFG however, did not conduct toxicity testing on the lagoon samples because the water typically has high salinity and nutrient (ammonia, nitrate, phosphate) content.

Environmental Measurements

Water samples collected during the year long study had pH values ranging from 7.4 to 8.9 and DO ranging from 6.3 to13.1mg/L (64% to 115% saturation, respectively) (Table 7). Generally the pH met the water quality objectives set by the CCRWQCB (Central Coast Regional Water Quality Control Board) in the Central Coast Basin Plan (CCRWQCB, 1994), only exceeding the maximum recommended level one time (Table 3). The samples were collected in a part of the Salinas River that supports both cold and warm freshwater habitats, thus the cold water criteria for DO should be considered since it is most protective. Measured DO levels were below the 7.0 mg/L minimum several times, primarily in February and March (Table 3 and 7). Water temperature on sample collection days varied from 8.7 to 22°C and air temperature ranged from 11 to 28°C.

Table 7. Salinas River Water Quality Data and Pesticide Detections

Date	Air Temperature	Water Temperature	Dissolved Oxygen (mg/L)	% Saturation	pH (in situ)	pH (in lab)	Detections (ppb)
Gonzales site							
8/9/94	18.1	20.1	NT	NT	NT	8.3	
8/15/94	25.2	20.2	NT	NT	NT	8.3	
8/23/94	15.5	18.4	NT	NT	NT	8.1	
8/30/94	18.5	19.2	NT	NT	NT	8.3	
9/6/94	20.4	20.6	8.8	97	NT	8.5	
9/13/94	20.8	20.6	9.2	103	NT	8.3	
9/20/94	22	20.2	9	100	NT	8.4	
9/27/94	27.8	22.2	9.2	106	NT	8.6	
10/4/94	20.4	17.8	9.2	97	NT	8.4	
10/11/94	19.8	19.1	9.2	100	NT	8.3	
10/18/94	23.5	14.9	12.3	122	NT	8.3	
10/25/94	16.5	15.8	9.5	96	NT	8.3	
11/1/94	19.5	16.5	9.8	101	7.9	8.4	
11/8/94	17.6	14.4	10	98	8.1	8.3	
11/15/94	19.8	8.7	11.3	97	8.3	8.3	
11/22/94	17.4	11.2	11.1	106	7.9	8.3	
11/29/94	15.1	9.6	11.6	103	8.5	8.3	
12/6/94	13.3	12.1	12.1	113	8.4	8.3	
12/13/94	11.2	10	10.2	90	8.3	8.3	
12/20/94	18.5	12.1	11.6	108	NT	8.5	
12/27/94	15.3	9.4	13.1	115	8.3	8.3	
1/3/95	17	12	11.3	105	8.8	8.4	
1/10/95	18	16.3	6.9	70	7.7	7.9	Chlorpyrifos (0.11)
1/17/95	12.7	12.1	8.6	90	7.9	8.1	
1/31/95	24.3	17.5	6.8	71	7.7	8.1	
Chualar site							
2/7/95	17.5	16.2	8.3	84	7.8	8.2	
2/14/95	17.4	16.2	8.9	90	7.8	8.4	
2/21/95	23.2	21.1	7	79	7.5	8.3	
2/27/95	NT	15.9	6.4	62	8.2	8.5	
3/7/95	NT	16.1	8.3	85	7.7	8.3	
3/14/95	21.1	17.5	8.5	89	7.7	7.8	
3/21/95	17.3	13	8.6	82	8.2	8.2	
3/28/95	23.4	19.8	7.3	79	7.7	8.8	
4/4/95	22.4	20.1	6.6	73	7.7	8.2	
4/11/95	22	17.8	6.8	72	8.1	8.4	
4/18/95	16.1	14.8	10	98	8.4	8.3	
4/25/95	18.3	20.5	7.3	81	8.1	8.3	
5/2/95	22	19.5	7.4	80	7.4	8.4	
5/9/95	22	20.2	7.6	84	8.2	8.6	
5/16/95	NT	NT	NT	NT	NT	8.6	
5/23/95	16.2	15.6	10	101	8.4	8.2	
5/30/95	22.9	19.8	11.4	121	8.1	8.3	
6/6/95	27.3	19.7	10.7	118	8.2	8.4	
6/13/95	23.3	23.4	10.6	125	8.2	8.4	
6/20/95	25.8	24	8.8	118	8.1	8.2	
6/27/95	24.5	27.1	5.3	67	7.9	8.3	
7/4/95	NT	20.5	9.4	103	8.3	8.2	
7/11/95	24.1	22	9.3	107	8.2	8.2	
7/18/95	25	22.6	9.4	109	8.2	8.3	
7/25/95	22.9	20.8	9.3	99	8.0	8.6	
8/1/95	NT	25	9.4	113	8.4	8.5	

NT = measurement not taken

NA = not applicable

Environmental Measurements were not collected by DPR at the Salinas River Lagoon

During the first quarter 0.37 inches of rain was recorded at the Salinas Municipal Airport and the Salinas River discharge rate fluctuated between 56 and 192 cfs at Gonzales, and 42 to 127 cfs at Chualar (Figure 33). Discharge rates were similar to those reported in 1993 (Palmer et.al., 1994), and 1992 (Markham et al., 1993) for the same time period. During the second quarter total rainfall was 12.0 inches at Salinas Municipal Airport and discharge ranged from 0 to 12,000 cfs at Chualar (Figure 34). In January, 1995, there was heavy rain and flooding throughout the Salinas River watershed. The stage height during January reached 13.85 feet, close to the record stage height of 14.92 feet in 1983.

During the third quarter 8.45 inches of rain were recorded at the Salinas Municipal Airport (figure 35). Rainfall that occurred on March 8 through 12 caused devastating flooding in the watershed. A record stage height at 19.70 feet and a record discharge of 92,000 cfs was set at Chualar on March II, 1995. In the fourth quarter (Figure 36), daily average discharge ranged from 814 cfs in May to the lowest recorded in early July at less than lcfs (Friebel et al., 1996). Total rainfall during the fourth quarter was 0.81 inches.

Pesticide Detections

During the year-long sampling period, only one of the 52 samples (1.9%) collected from the Salinas River had a pesticide concentration above the reporting limit (Table 4). Chlorpyrifos was detected in one sample collected along the middle reach in January. Diazinon and dimethoate were both detected in the monthly sample collected from the lagoon in June. There were no detections from the six equipment rinse samples or the six rinse samples of the DH-81 sampler bottle.

Chlorpyrifos was detected at a concentration of 0.12 ppb at Gonzales on January 10, 1995. This concentration exceeded the maximum (l-hour average) of 0.083 ppb established by the U.S. EPA as a criterion to protect freshwater aquatic life (U.S. EPA, 1986) (Table 4).

Greater than 52,000 lb a.i. of chlorpyrifos were applied to the Salinas River watershed within Monterey County (area of pesticide influence along the middle reach) during the study period (Figure 37). Chlorpyrifos was used primarily on broccoli and cauliflower fields with over 34,000 lb a.i. used to treat broccoli alone. Chlorpyrifos was used steadily throughout most of the year with the greatest amount used from August

Salinas River

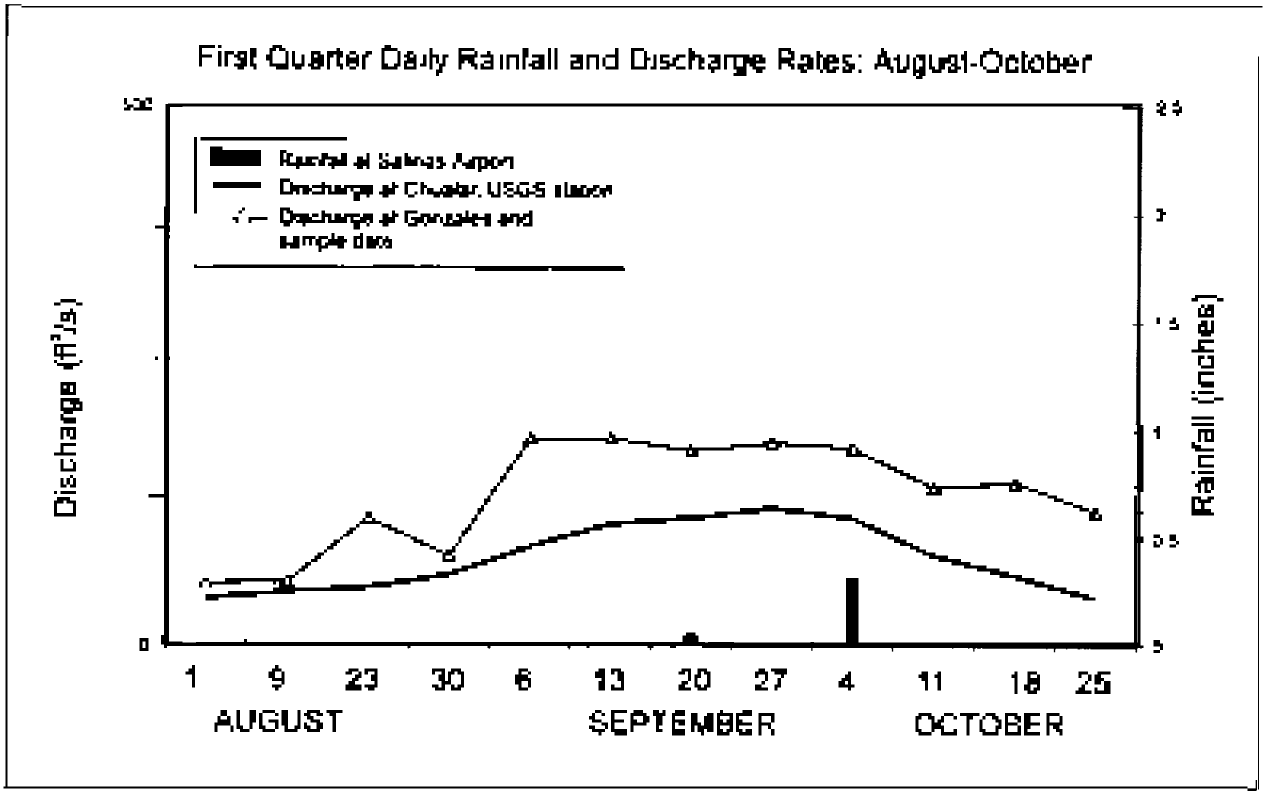


Figure 33. Daily rainfall and Salinas River discharge (river flow) from August 1 through October 25, 1994. River discharge at Gonzales were measured weekly by DPR staff at the time of sampling. Discharge at Chualar was recorded daily at the USGS gauging station.

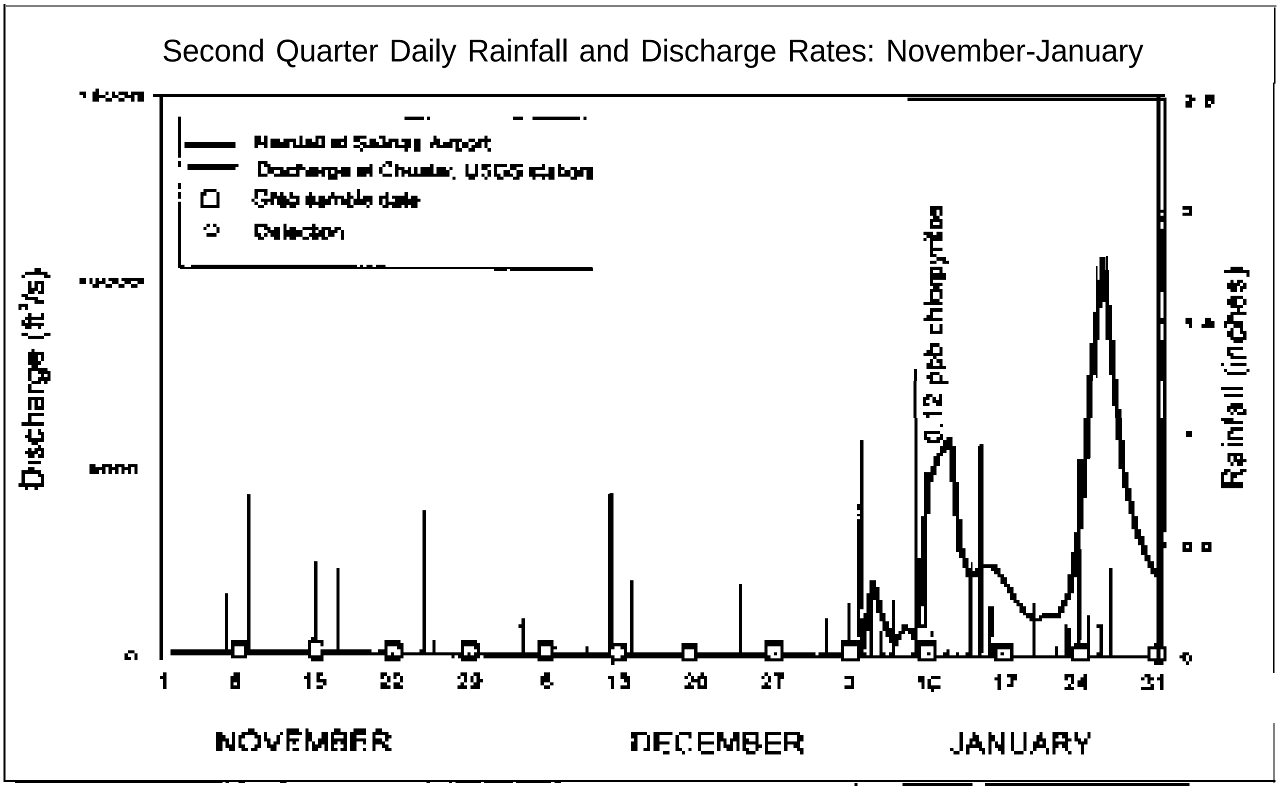


Figure 34. Daily rainfall and Salinas River discharge from November 1, 1994 through January 31, 1995

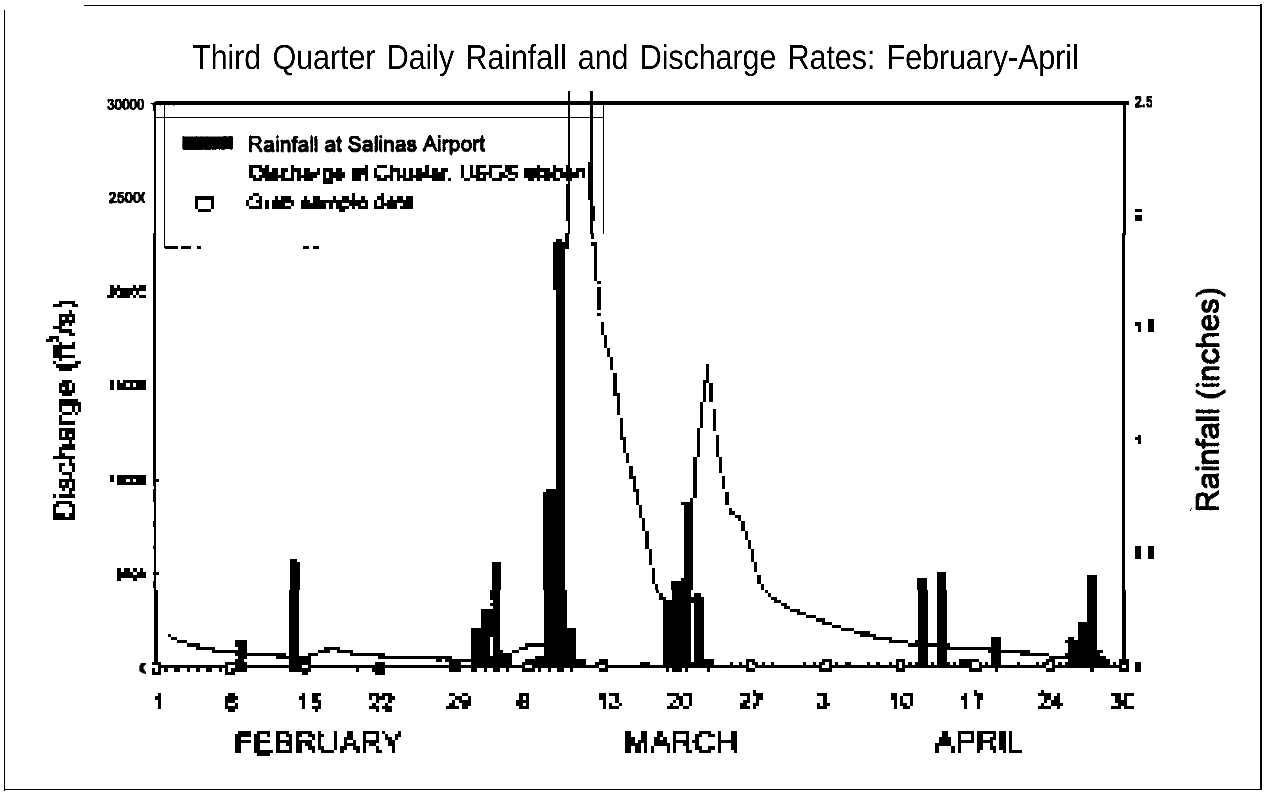

Third Quarter Daily Rainfall and Discharge Rates: February-April

Figure 35. Daily rainfall and Salinas River discharge from February 1 through April 30, 1994

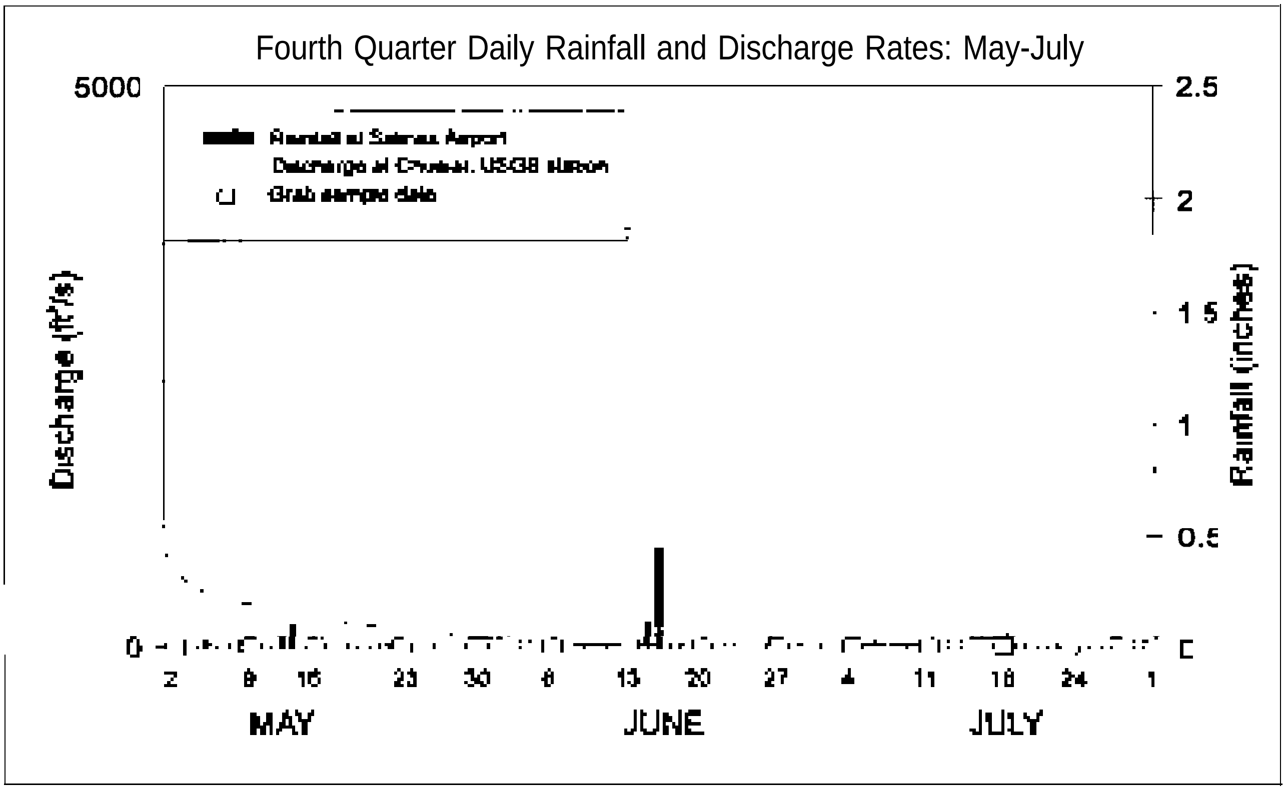
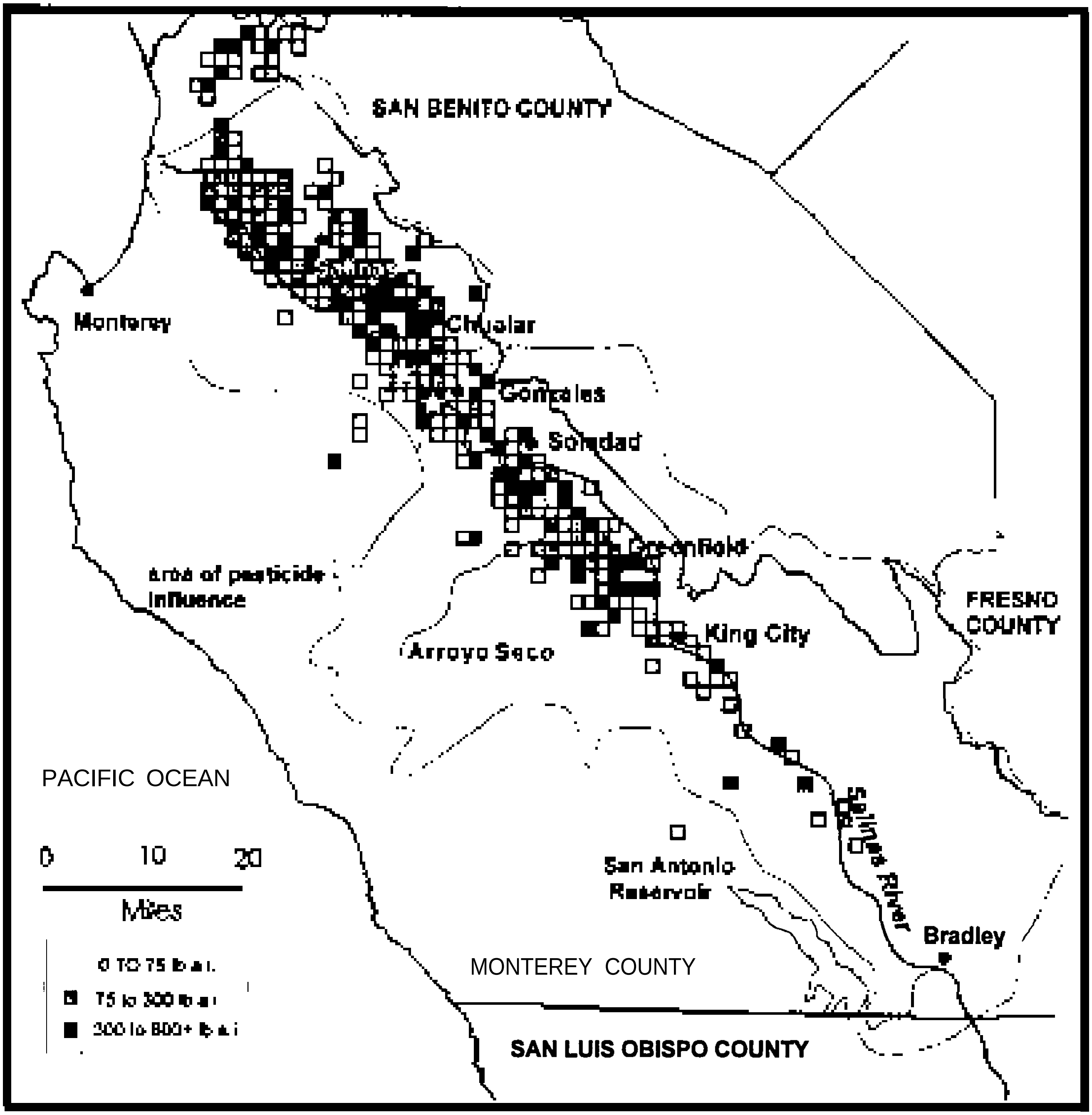
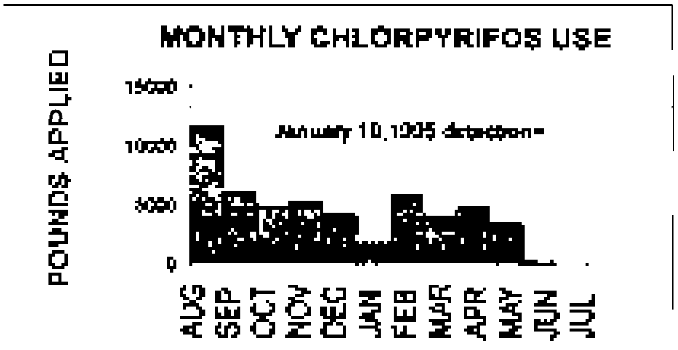

Fourth Quarter Daily Rainfall and Discharge Rates: May-July

Figure 36. Daily rainfall and Salinas River discharge from May 1 through July 31, 1995

CHLORPYRIFOS USE IN THE SALINAS RIVER WATERSHED





☆ Sampling site

☐ Each square represents one or more applications within a one square mile section

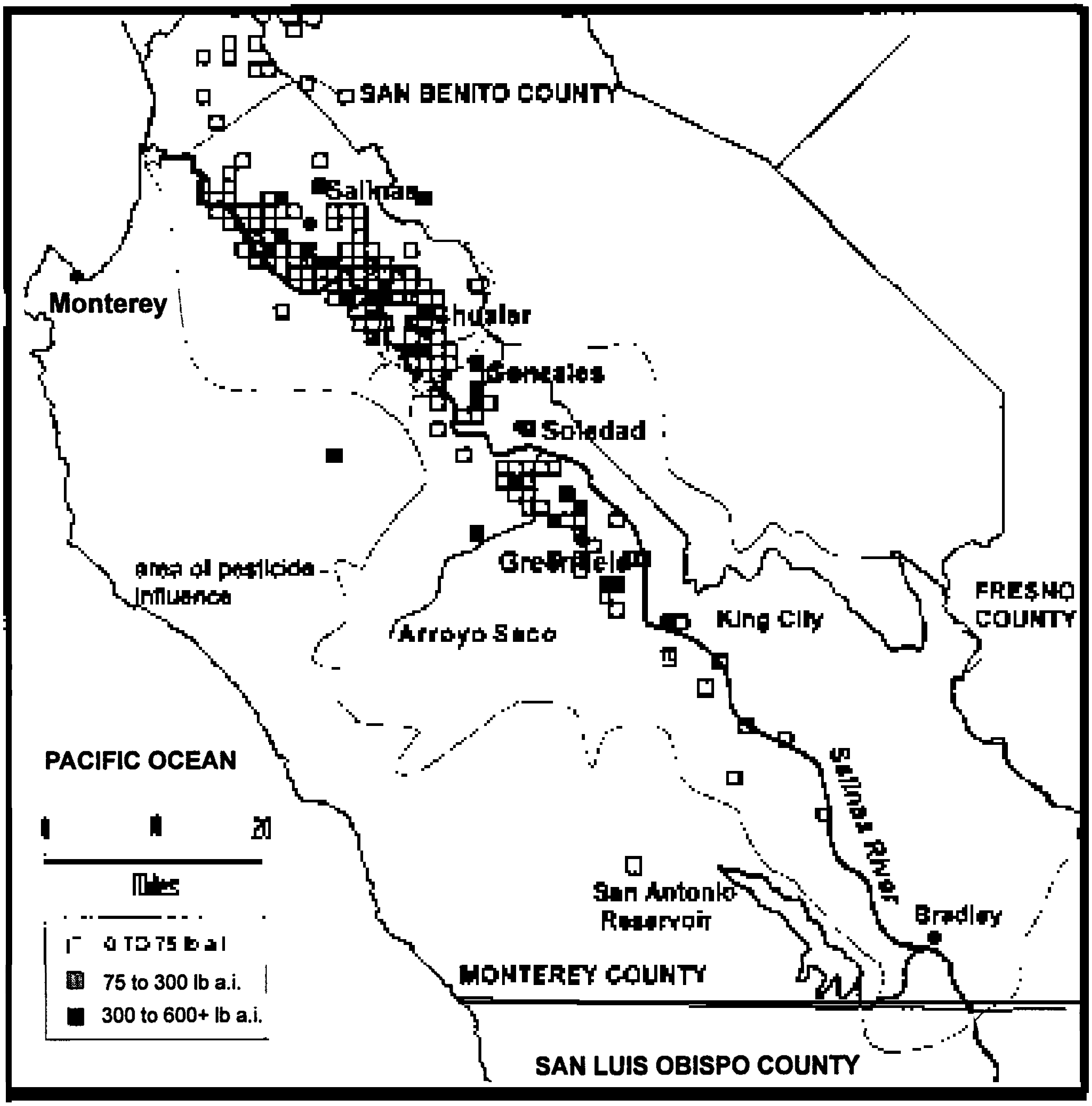
Primary Crops	Pounds
1 Broccoli	34,087
2. Cauliflower	12,682
3 Cabbage	1,657
4. Kale	1,113
Total pounds applied during sampling year:	52,095

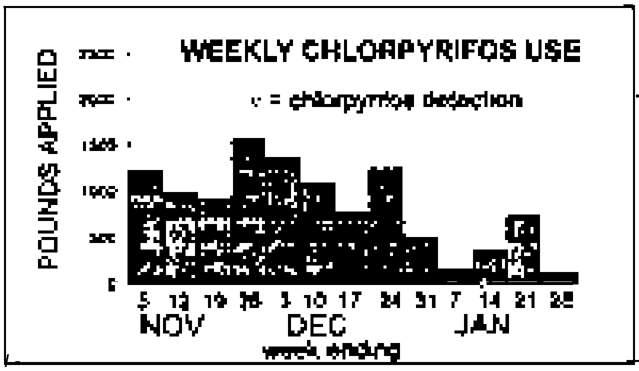
Figure 37. Applications and pounds of chlorpyrifos used in the middle and lower Salinas River watershed August 1994 through July 1995

through November. After November, use began to fall off, but there were still 170 applications between December 10 and December 31(DPR, 1994). More of these applications were situated upstream from the sampling site than the applications made in January. Ten days before the January 10, 1995 detection, 14 applications of chlorpyrifos were made, but most occurred downstream of the sampling site (DPR, 1995) (Figure 38). There was little rainfall before January, during the fall application period, and since the discharge of the Salinas River remained less than 200 cfs, little surface runoff occurred. During January, rainfall increased in duration and discharge increased significantly. In fact, the lone detection of chlorpyrifos was found in a sample collected during the first major storm of the year, when the discharge in the Salinas River was increasing. At the Chualar gauging station the daily average flow increased 11,000% from the low on January 3, to the day the sample was collected. At peak discharge on January 12, the flow had increased greater than 14,000%. Due to low solubility and a high soil sorption coefficient chlorpyrifos tends to bind tightly to soil (Table 5). The enormous increase in rainfall and runoff may have washed chlorpyrifos-bound soil particles from fields into the river. Due to the fairly long field dissipation half-life of chlorpyrifos, ranging from 33 to 56 days (Kollman and Segawa, 1995) and greater than 200 days (Racke,1993), and timing and distribution of the applications, it is likely that this first storm washed off chlorpyrifos residues from the applications made as early as fall.

Prior to the detection of chlorpyrifos, flows began to increase upstream in San Louis Obispo County as well as in Monterey County. According to the discharge data collected for 1994-95, the Salinas River flowed from San Luis Obispo County into Monterey County during January, February, and March (Friebel et al., 1996). At the time of the detection, flow was just beginning to increase in both counties. It is likely that the flow at the sampling site on January 10 was only from Monterey County and that flow during subsequent days was from both counties. During December and January, 1,141 and 25 lb a.i. of chlorpyrifos were applied respectively, in San Luis Obispo County. Although there were no further detections at the sampling site on the middle reach, past or future contribution of pesticide residues from San Luis Obispo County cannot be ruled out during the short duration that water flows from San Luis Obispo County into Monterey County. Since the two sampling sites are about 75 miles downstream of the county line, it is expected that this would probably only occur during high flows, when travel times are short since pesticides will continue to undergo degradation in river water.

CHLORPYRIFOS USE IN THE SALINAS RIVER WATERSHED NOVEMBER 1994-JANUARY 1995





☆ **Sampling site**

▢ Each square represents one or more applications within a one square mile section

Primary Crops	Pounds
1. Broccoli	9,054
2. Cauliflower	1,932
Total pounds applied during sampling period.	11,25'

Figure 38. Applications and pounds of chlorpyrifos used in the middle and lower Salinas River watershed, November 1994 through January 1995.

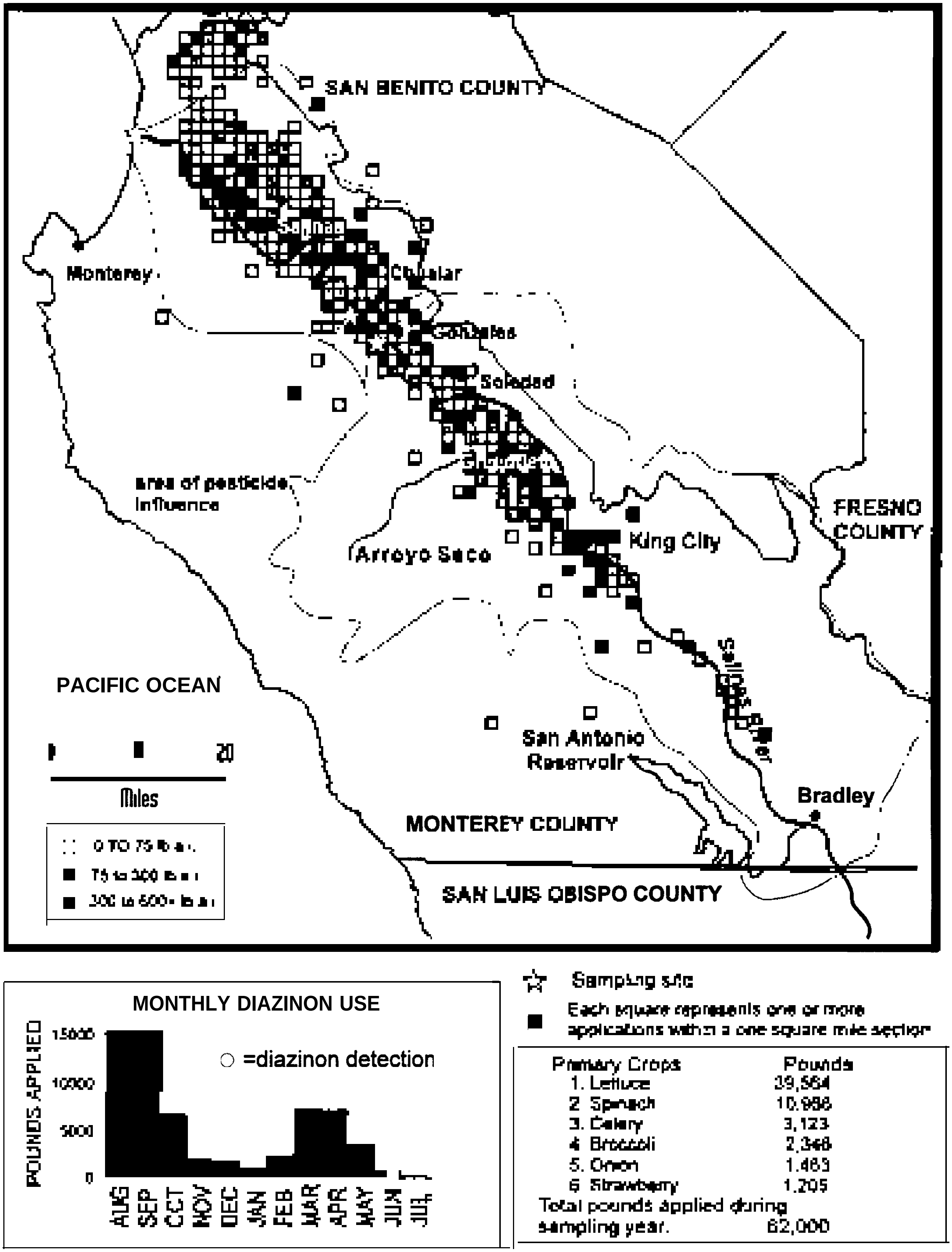
Despite an increase in chlorpyrifos applications in February, March and April, additional rainfall events and some sampling periods coinciding with increased discharge, there were no further detections of any pesticides in samples collected along the middle reach.

Chlorpyrifos has been found previously in clam, fish and sediment samples from the Salinas River Watershed. The SWRCB and DFG have monitored the river periodically with the State Mussel Watch Program (SMWP) and the Toxic Substance Monitoring Program (TSMP). The SMWP was developed to monitor trace metals, chemicals and a selected number of registered and non-registered pesticides chosen based on their potential to bioaccumulate. Chlorpyrifos was one of the registered pesticides analyzed from clam tissue and sediment. Resident clams were sampled or fresh water clams were transplanted into the river watershed for 1 to 3 months and then were collected for tissue analysis. In March 1995, monitoring results from 1987 to 1993 were published. Of the eight clam samples analyzed from the Salinas River and tributaries, seven had detectable residues of chlorpyrifos ranging from 3.1 to 288.0 ppb wet weight. Of the four sediment samples collected, chlorpyrifos was detected twice at 1.1 and 4.1 ppb wet weight (Rasmussen, 1995a). The TSMP is similar to the SMWP. Instead of mussel or clam tissue, tissue samples are collected from resident fish and turtles collected from surface waters and analyzed for the same analytes. In 1992 one sample from the watershed was collected at the Salinas River at Blanco Drain. The fish sample contained 61.0 ppb wet weight of chlorpyrifos (Rasmussen, 1995b).

Diazinon was detected at a concentration of 0.20 ppb in the monthly sample collected from the Salinas River Lagoon during the week of June 26. U.S. EPA has not yet determined a water quality criterion for the protection of freshwater aquatic organisms. However, the detection exceeded the CDFG acute freshwater criterion for diazinon of 0.08 ppb (Menconi and Cox, 1994) (Table 4).

Diazinon is used throughout the Salinas Valley and close to 62,000 lb a.i. were applied during the study period (Figure 39). The greatest amounts of diazinon were applied to lettuce and spinach. The peak in applications occurred in August and September, followed by decreased applications. The number of applications increased again in March and April before declining in May. One hundred thirty-two applications of diazinon were made in the middle and lower reach of the watershed during the month before the June 26 detection of diazinon in the Lagoon (Figure 40). The applications closest to the Lagoon were made primarily on lettuce (DPR, 1995).

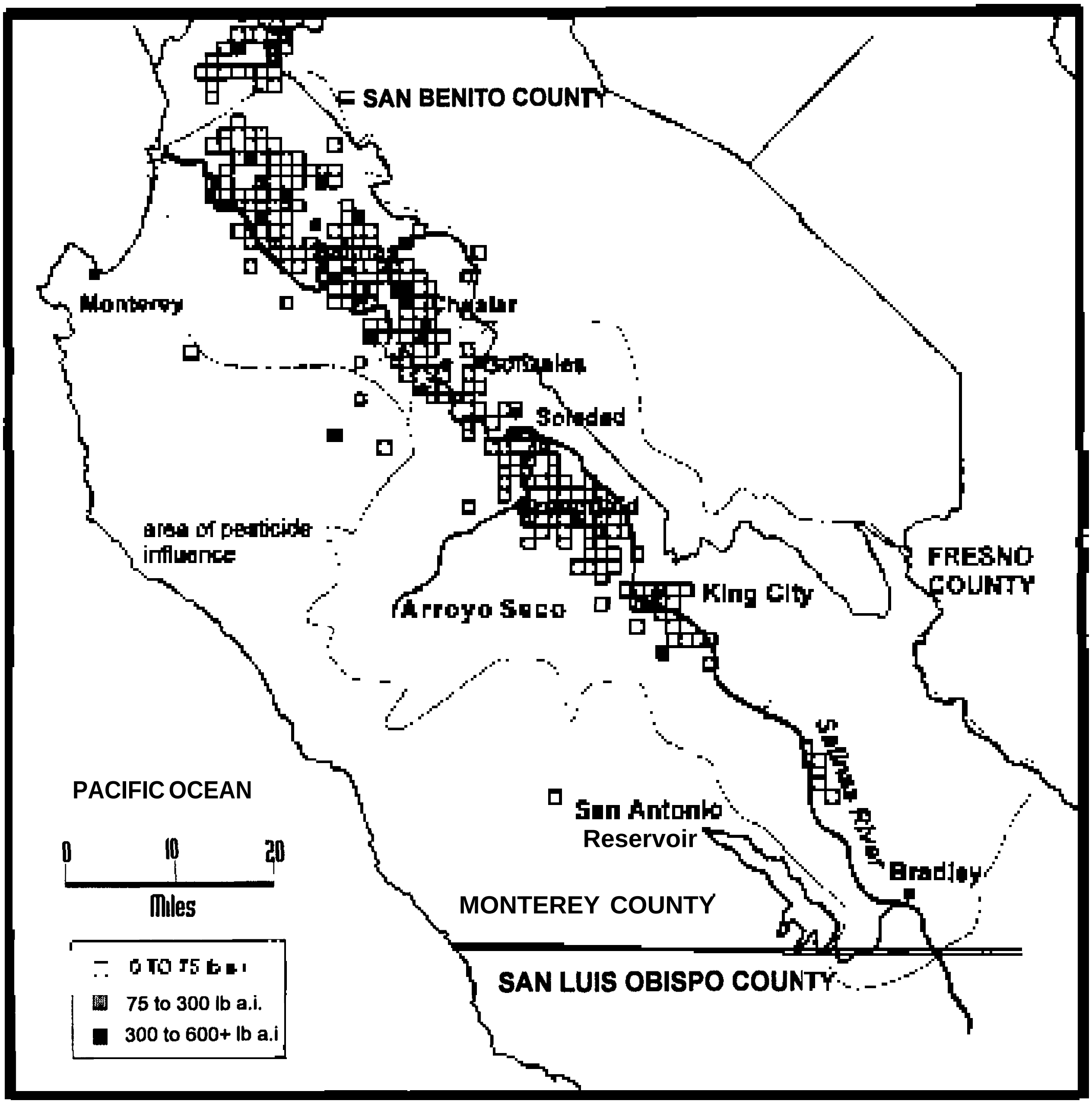
DIAZINON USE IN THE SALINAS RIVER WATERSHED

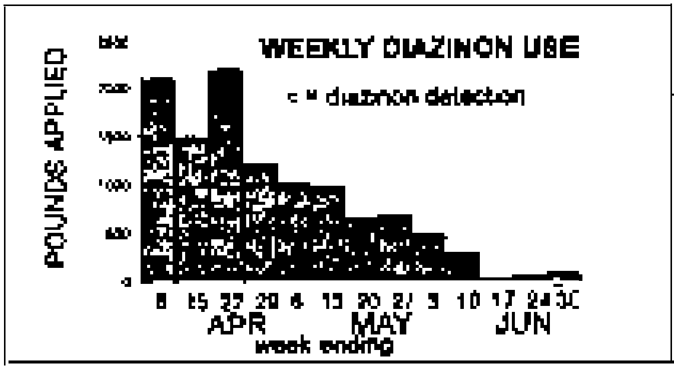


Primary Crops	Pounds
1. Lettuce	39,564
2 Spinach	10.988
3. Celery	3,123
4 Broccoli	2,348
5. Onion	1.483
6 Strawberry	1.205
Total pounds applied during sampling year.	62,000

Figure 39. Applications and pounds of diazinon used in the middle and lower Salinas River watershed August 1994 through July 1995.

DIAZINON USE IN THE SALINAS RIVER WATERSHED
APRIL-JUNE 1995





☆ Sampling site

▣ Each square represents one or more applications within a one square mile sector

Primary Crops	Pounds
1. Lettuce	7,558
2. Spinach	1,450
3. Strawberry	612

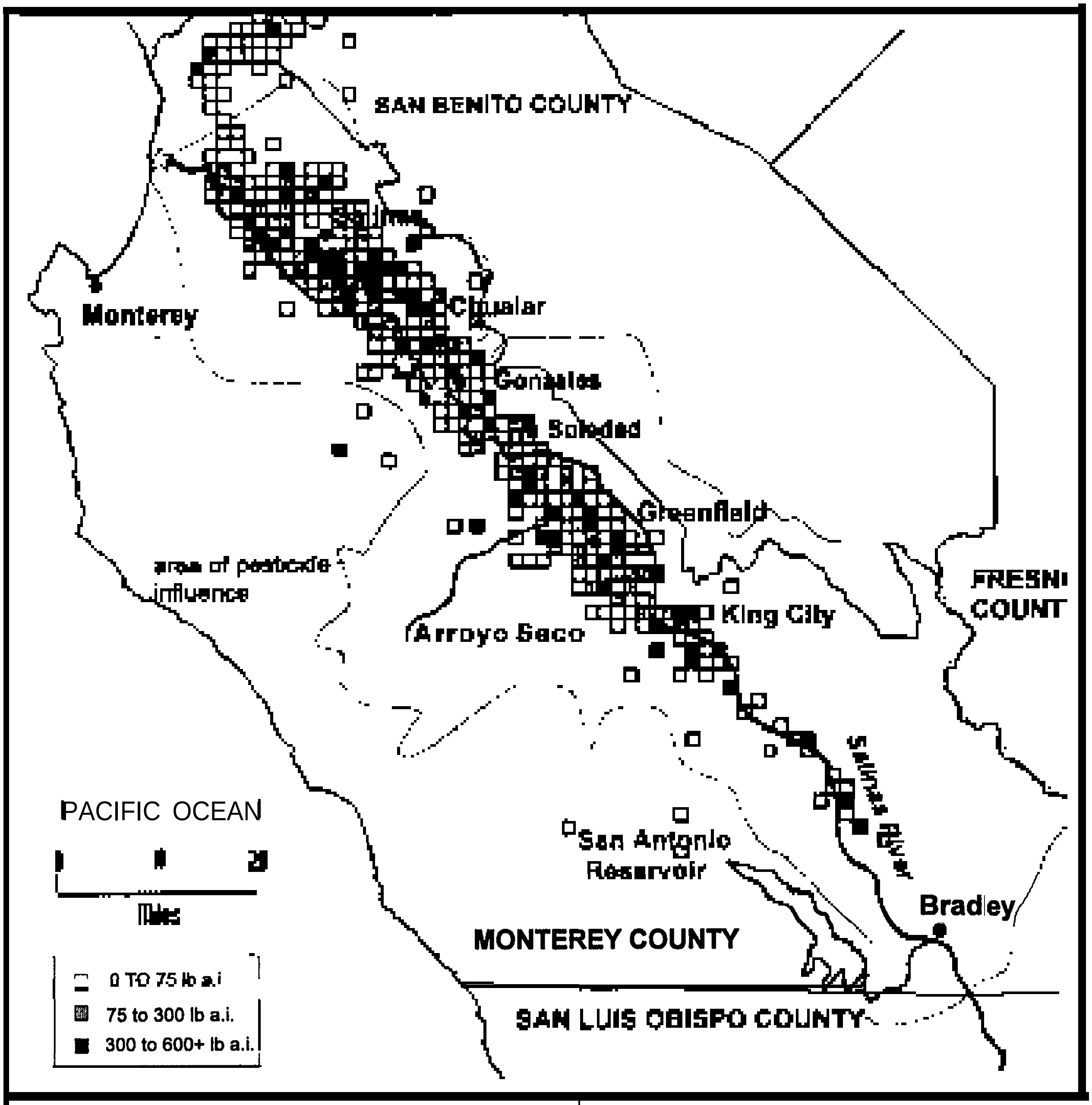
Total pounds applied during sampling period. 11,042

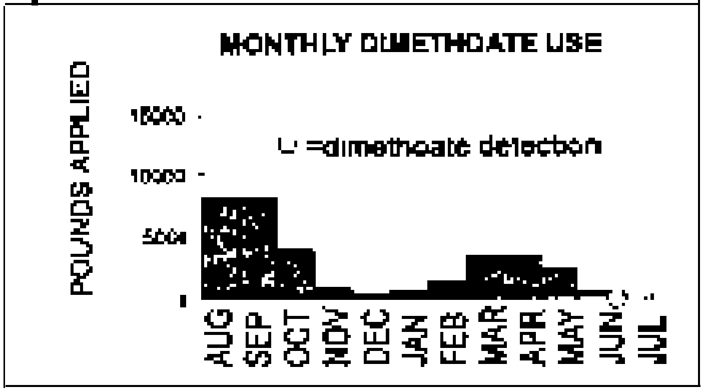
Figure 40. Applications and pounds of diazinon used in the middle and lower reach of Salinas River watershed April through June 1995.

According to the DPR pesticide use report, within 6-days of the detection, diazinon was applied in a section along the Lagoon and two applications were made along the Blanco Drain, which drains into the lagoon. Diazinon was also applied several more times near the lagoon in June, 20 days or more prior the detection. Since no rain had occurred before the detection, rain runoff was not the mode of transport. Therefore, the diazinon detection in the lagoon was likely due to drift during (or after) application and/or irrigation runoff from fields where recent applications were made. A study conducted on organophosphate pesticides including diazinon in Monterey and Fresno Counties showed that regional aerial movement and deposition of organophospate pesticides occurred in these counties during the summer months (Stein and White, 1993). The inflow into the lagoon during the low-flow season is largely agricultural. In the past, treated sewage was released into the lagoon (Salinas River Lagoon Management and Enhancement Plan, 1992). However, this flow has been diverted. The lagoon is surrounded by agriculture and rangeland, with the exception of the closed Army base, and therefore home and garden use is probably not the cause of the detection.

On June 26, 1995, 0.11 ppb of dimethoate was detected in the same sample in which diazinon was detected. Currently, there are no water quality criteria for the protection of fresh or salt water organisms.

A total of 33,000 lb a.i. of dimethoate were applied in Monterey County during the year-long study (Figure 41). The monthly total dimethoate use followed a pattern similar to diazinon; most was applied in August and September, and then a smaller peak in use came in March and April. Again, like diazinon, use decreased in May and the least was used in June and July (Figure 42). One hundred thirty-eight applications were made on lettuce, broccoli, cabbage and cauliflower in the month preceding the June 26 detection. Dimethoate does not adsorb well to soil and has potential to leach (Howard, 1991), but it has a short field dissipation half-life, about 8 days (Table 5). Eight days prior to the detection there were six applications of dimethoate to lettuce in one section along the Blanco Drain totaling about 25 lb a.i. and one 2-pound application to lettuce in a section along the lagoon (DPR, 1995). Another application was made to broccoli 15 days before the detection near the lagoon, and there were several applications made in the area early in June. Since there was no rain before the detection, dimethoate transport could have occurred either in agricultural runoff or drift from these applications.





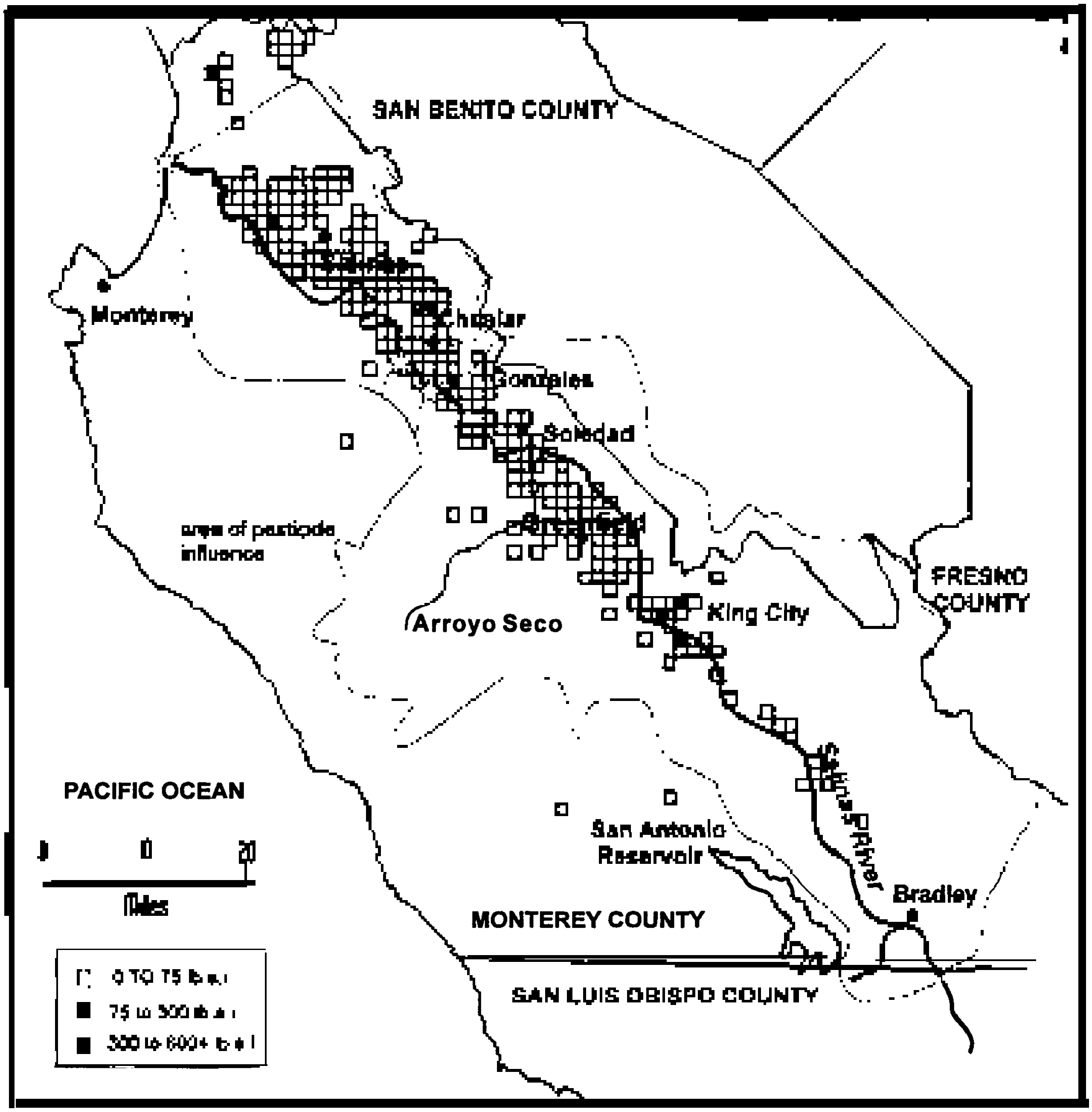
☆ Sampling site

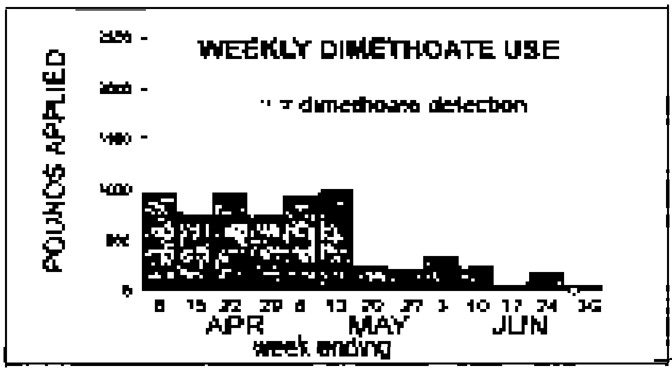
□ Each square represents one or more applications within a one square mile sector

Primary Crops	Pounds
1. Lettuce	14,954
2. Broccoli	10,442
3. Cauliflower	3,719
4. Spinach	1,647
Total pounds applied during sampling year:	33,024

Figure 41. Applications and pounds of dimethoate used in the middle and lower Salinas River watershed August 1994 through July 1995.

DIMETHOATE USE IN THE SALINAS RIVER WATERSHED
APRILJUNE 1995





☆ Sampling site

▫ Each square represents one or more applications within a one square mile section

Primary Crops	Pounds
1. Lettuce	3,497
2. Broccoli	1,479
3. Spinach	768
4 Cauliflower	506
Total pounds applied during sampling period	6,713

Figure 42. Applications and pounds of dimethoate used in the middle and lower reach of the Salinas River watershed. April through June 1995.

Toxicity Results

Split samples tested for toxicity by DFG showed no significant mortality to cladocerans or fathead minnows in the 27 samples tested (Appendix V).

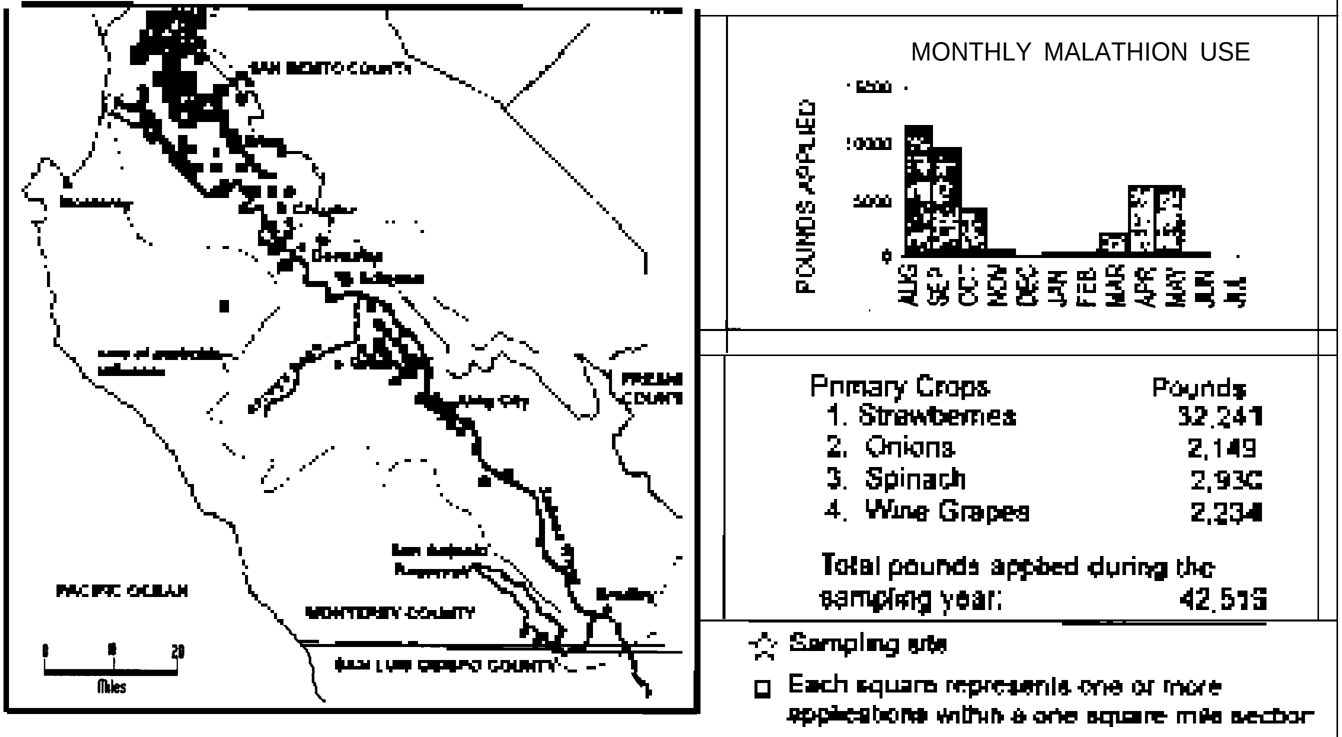
Other Pesticides Used in the Watershed

Approximately 42,000 lb a.i. of malathion were applied in the Salinas River watershed within Monterey County during the study period primarily to strawberry fields (Figure 43). Most use occurred in August and September and again in April and May. Malathion does not persist in soil and has a short half-life. The hydrolysis half-life is about 6 days at a neutral pH and it is even shorter lived when the pH is more alkaline as is the Salinas River (Table 5). Malathion is moderately soluble and has a low to moderate adsorptivity (Table 5). The physical-chemical properties of malathion make transport to surface water less likely.

Approximately the same amount of methomyl (63,149 lb a.i.) was used in the county as diazinon (Figure 44). Methomyl is a carbamate pesticide used as a broad-spectrum control for insects, primarily on lettuce (>33,000 lb a.i.) and to a lesser extent on broccoli, celery, strawberries, wine grapes and cauliflower. Methomyl use was greatest in August and September when more than 13,000 lb a.i. were used each month. The least was applied during the months of highest rainfall, November through February. Methomyl was applied in March, but there were abnormally high flows in the river that month. Despite being among the pesticides with the greatest quantities applied throughout the county, methomyl was never detected. It has been detected in California rivers in other studies (Ross, 1992 a and b; Foe and Sheipline, 1993). Methomyl is prone to leaching (Howard, 1991) and has a low average soil adsorptivity (Table 5). It has a fairly long half-life; less than chlorpyrifos but greater than diazinon (Table 5).

About 20,000 lb a.i. of carbofuran were applied in the county during the study period (Figure 45). Carbofuran is an insecticide, nematicide and miticide used mainly on grapes. Carbofuran is very mobile in soil and has a tendency to leach (Howard, 1991). The average field dissipation half-life is about the same as for methomyl (Table 5). Despite applications being made during some months when rain runoff occurred, carbofuran was not detected in the river.

MALATHION USE IN THE SALINAS RIVER WATERSHED



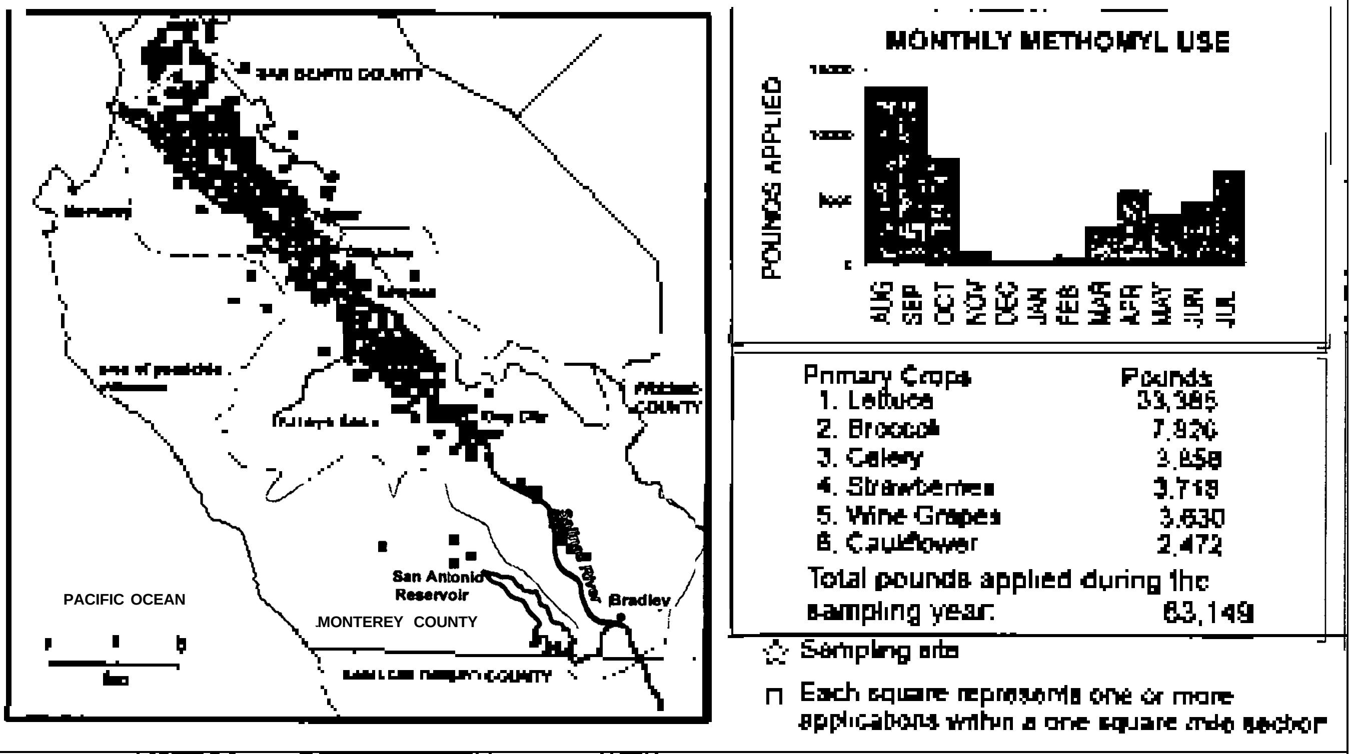
Primary Crops	Pounds
1. Strawberries	32,241
2. Onions	2,149
3. Spinach	2,93C
4. Wine Grapes	2,234
Total pounds applied during the sampling year:	42,513

☆ Sampling site

□ Each square represents one or more applications within a one square mile sector

Figure 43 Applications and pounds of malathion used in the middle and lower Salinas River watershed from August 1994 through July 1995 .

METHOMYL USE IN THE SALINAS RIVER WATERSHED



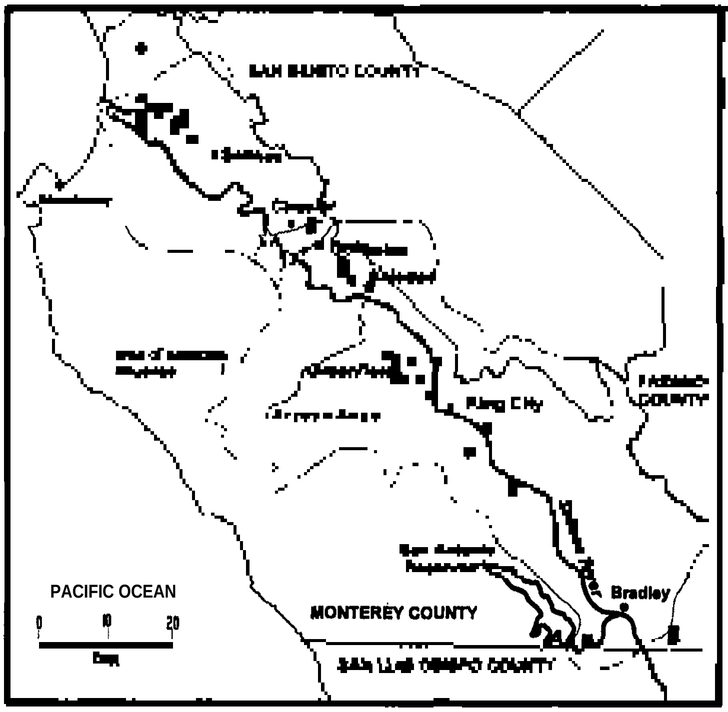
Primary Crops	Pounds
1. Lettuce	33,385
2. Broccoli	7,926
3. Celery	3,858
4. Strawberries	3,718
5. Wine Grapes	3,630
6. Cauliflower	2,472
Total pounds applied during the sampling year:	63,149

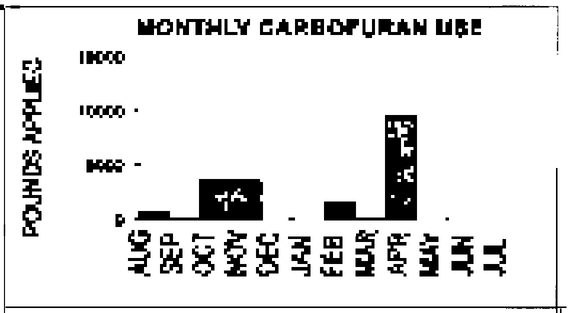
☆ Sampling site

□ Each square represents one or more applications within a one square mile sector

Figure 44. Applications and pounds of methomyl used in the middle and lower Salinas River watershed from August 1994 through July 1995 .

CARBOFURAN USE IN THE SALINAS RIVER WATERSHEC





Primary Crops	Pounds
1. Wine grapes	11,372
2. Table grapes	7,364
3. Artichokes	990
4. Alfalfa	311
Total pounds applied during sampling year.	19,983

☆ Sampling site

■ Each square represents one or more applications within a one square mile section

Figure 45. Applications and pounds of carbofuran used in the middle and lower Salinas River watershed from August 1994 through July 1995 .

Endosulfan residues (along with chlorthal-dimethyl) in soil and sediment was studied in Monterey County in 1986 (Fleck et al., 1988). Eight percent of the soil samples collected in the Salinas and Carmel Valleys contained endosulfan I, while 9 and 27% contained endosulfan II and endosulfan sulfate, respectively. Other studies conducted in the area also found endosulfan residues in drainages (Oakden and Oliver, 1988). Endosulfan is fairly persistent and exhibits high adsorptivity (Table 5). Endosulfan I, II and sulfate were analyzed in eight clam tissue samples for the SMWP. At least one or more of the three (when added together it is reported as total endosulfan) were detected in the clam samples every time ranging from 19.0 to 300.0 ppb wet weight of total endosulfan. Total endosulfan was detected two of the four sediment samples collected for the SMWP. Use of endosulfan has been reduced in recent years. In 1994, only 1,731 lb a.i. of endosulfan were used in Monterey County.

Russian River

Russian River Watershed

The Russian River watershed resides mostly in Sonoma and Mendocino Counties (Figure 46). The river's head waters are in Lake County, but less than 1% of the watershed lies in that county. The watershed is about 80 miles long and from 10 to 30 miles wide. The drainage area of the watershed upstream of the sampling site located near Guerneville, is about 1,202 mi^2. The river is about 110 miles long and flows primarily south, running parallel to the coastline. The last section of the river flows westward for almost 20 miles through the coastal hills to the Pacific Ocean. The Russian River has many beneficial uses including wildlife habitat, recreation, and municipal and domestic water supplies (NCRWQCB, 1993).

Generally, the highest flow of the Russian River occurs from October to May. Flow is continuous throughout the year and is controlled by releases from Coyote Dam at Lake Mendocino, and Warm Springs Dam at Lake Sonoma (Figure 46) (NCRWQCB, 1993). In addition, there is a hydropower project that diverts water from the Eel River into the Russian River above Lake Mendocino at an average annual rate of 330 cfs (SWRCB, 1994). Most of the tributaries flow during the wet-weather season, but flows dwindle by mid to late summer. There are greater than 40 tributaries to the mainstem of the Russian River. Most of the tributaries are intermittent and some are perennial (Goodwin, NCRWQCB). The principal tributaries are Big Sulphur Creek, Dry Creek, Mark West Creek and Austin creeks (NCRWQCB, 1993). The tributary farthest downstream that contributes agricultural runoff to the Russian River is Green Valley Creek (Klamt, NCRWQCB) which flows from south of Sebastopol to the Russian River near Rio Dell. Most tributaries entering the river upstream of Green Valley Creek carry some crop runoff while those downstream contribute less runoff from crops. Practically all insecticide use occurs upstream from the sampling site chosen (Figure 51 through 58). The major crops grown in the watershed include wine grapes, alfalfa, pears, hay, walnuts, apples and a variety of row crops.

The Russian River sampling site was located at a private residence on the Russian River approximately 1 mile upstream of the Highway 116 Bridge, in Guerneville (Figure 46). The site is 5 miles downstream of Green Valley Creek and about 17 miles upstream of the mouth of the river. Discharge data were obtained from the DWR

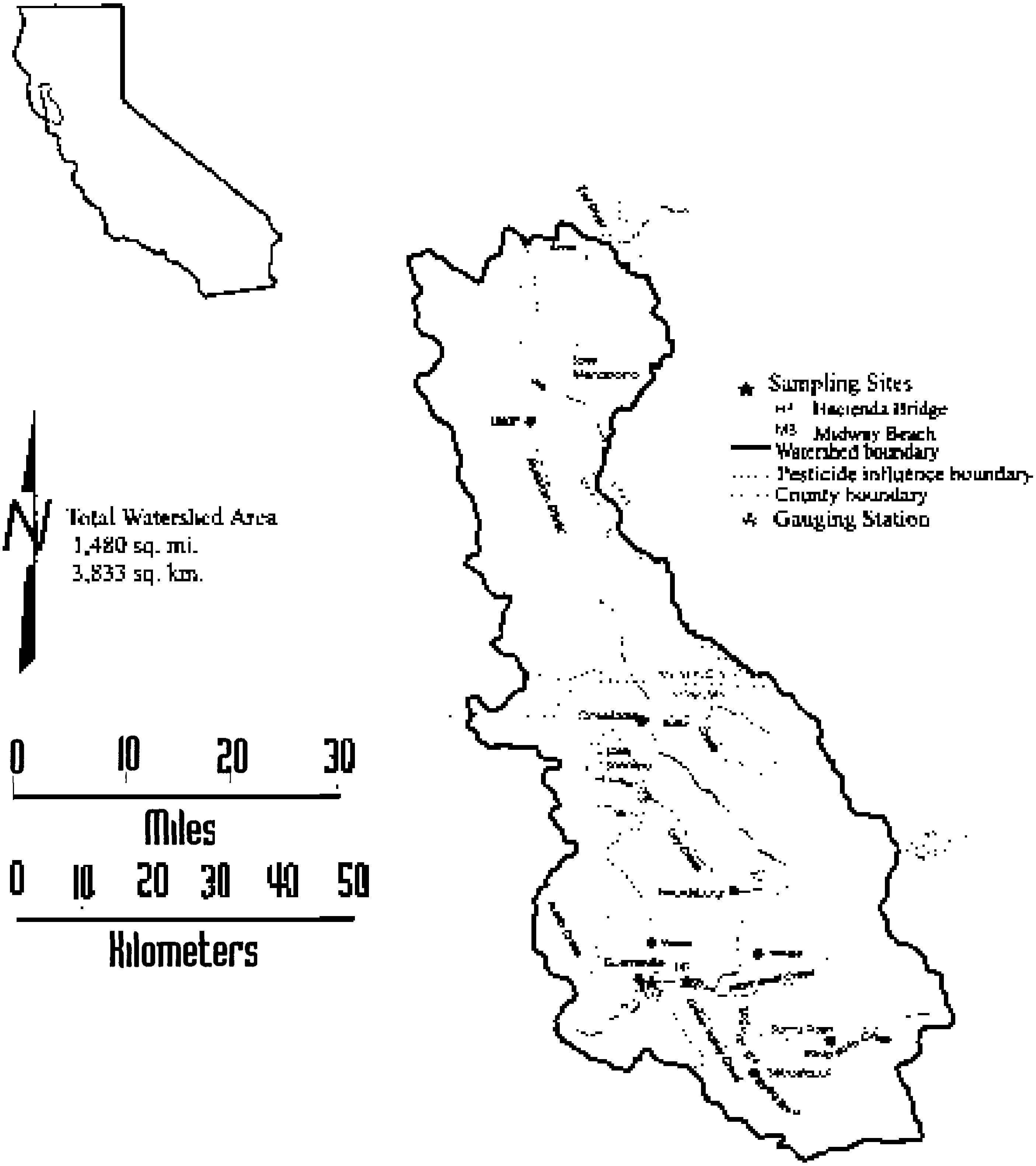


Figure 46. Map of the Russian River watershed.

gauging station located 4 miles upstream of the sampling site at Hacienda Bridge. At this location the river is impounded for recreational purposes during the summer months. During this period there is a chance that the river at this site may not be mixed adequately. Pesticides that tend to adhere to sediment have potential to settle and pesticides entering the river locally, within the impounded area, may not be completely mixed across the cross section. The environmental measurements would be affected the most during this period, and would be more accurate if taken across the river's cross section.

Weekly sample collection began on August 8, 1994, using the automatic sampler. Due to heavy rains that resulted in regional flooding in the sampling area, the automatic sampler was removed from its location on January 5. Subsequent samples were collected weekly from January 17 through May 1 from the Hacienda Bridge located 4 miles upstream of the original sampling site using two methods; a grab sample collected with a bucket at center-stream and the equal-width depth-integration method (Guy and Norman, 1970). From May 8 to August 8, samples were again to be collected using the automatic sampler that was returned to the site near Guerneville.

Environmental Measurements

Water samples taken during the year-long study had pH values ranging from 7.1 to 8.3 and DO ranging from 6.1 to 13 mg/L (72% to109% saturation, respectively. Table 8). The pH met the objectives set by the NCRWQCB in the Water Quality Control Plan for the North Coast Region (1994)(Table 3). The Water Quality Control Plan lists the pH objectives as a minimum of 6.5 and a maximum of 8.5. The DO values met the water quality minimum objective set specifically for the Russian River of 7.0 mg/L for all but one sample collected July 17, 1995. However, the DO values were at or above the 90% lower limit 88.6% of the time and at or above the 50% lower limit only 15.9% of the time. Water temperature on sample pick up days varied from 8 to 30°C and the air temperatures ranged from 7 to 37°C.

Besides parameters measured by DPR, discharge data were obtained from the DWR gauging station at Hacienda Bridge. Daily rainfall measurements were obtained from the DWR weather station at Venado, 6 miles north of the sampling site. During the first quarter there were 1.6 inches of rain recorded at the Venado weather station and the Russian River discharge rate fluctuated between 91 and 285 cfs (Figure 47). August

Table 8. Russian River Water Quality Data and Pesticide Detections

Start Sample Date	End Sample Date	Air Temperature	Water Temperature	Dissolved Oxygen (mg/L)	% saturation	pH (in situ)	pH (lab)	Detections
Midway Beach								
8/17/94	8/15/94	NT	30	NT	NT	NT	7.8	
8/16/94	8/22/94	31	24	8.0	95	NT	7.6	
8/26/94	8/29/94	33	22	8.0	92	NT	7.6	
9/2/94	9/6/94	24	21	7.6	85	NT	7.7	
9/9/94	9/12/94	22	23	7.6	84	NT	7.6	
9/15/94	9/19/94	NT	21	NT	NT	NT	7.8	
9/23/94	9/26/94	NT	21	7.9	89	NT	7.8	
9/30/94	10/3/94	32	22	NT	NT	NT	8.1	
10/6/94	10/11/94	35	17	8.9	85	NT	7.6	
10/15/94	10/18/94	NT	15	9.0	89	NT	7.8	
10/22/94	10/25/94	NT	18	9.0	91	NT	7.8	
10/29/94	11/1/94	21	14	8.8	85	NT	7.8	
11/4/94	11/8/94	32	13	7.3	88	NT	7.7	Diazinon 0.076
11/12/94	11/15/94	11	11	8.4	78	NT	7.8	
11/19/94	11/22/94	8	8	9.8	81	NT	7.8	
11/26/94	11/29/94	10	15	9.4	85	7.7	8.0	
12/2/94	12/5/94	7	8	9.7	83	7.1	7.1	
12/9/94	12/12/94	9	8	10.8	82	NT	8.8	
12/17/94	12/25/94	11	9	8.7	87	7.3	7.7	
12/23/94	12/26/94	12	15	9.3	85	7.5	8.1	
12/31/94	1/2/95	11	10	10.1	89	7.3	7.7	
skipped due to flooding in Guerneville								
Hacienda Bridge								
1/17/95	Grab sample	NT	11	13.4	92	7.4	7.8	
1/23/95	Grab sample	NT	11	10.9	99	7.6	7.7	
1/30/95	Grab sample	18	13	9.4	89	7.6	7.9	
2/6/95	Grab sample	18	12	9.8	89	7.5	7.8	
2/14/95	Grab sample	14	12	10.4	98	7.3	7.3	
2/21/95	Grab sample	23	13	8.4	75	7.8	7.8	
2/27/95	Grab sample	14	17	7.4	78	7.9	7.8	
3/6/95	Grab sample	18	9	12.8	109	7.8	7.8	
3/13/95	Grab sample	13	18	NT	NT	7.5	7.3	
3/20/95	Grab sample	15	NT	NT	NT	7.6	7.3	Dimethoate 0.15
3/27/95	Grab sample	12	18	NT	NT	7.4	7.5	
4/3/95	Grab sample	25	14	10.4	91	7.9	NT	
4/10/95	Grab sample	13	18	9.3	88	7.8	7.7	
4/17/95	Grab sample	14	13	9.4	85	7.8	7.5	
4/24/95	Grab sample		18	9.3	87	7.8	7.8	
5/1/95	Grab sample	14	18	9.2	82	7.6	7.5	
Midway Beach								
5/8/95	Grab sample	NT	18	9.8	96	8.5	7.4	
5/12/95	15-May	NT	15	9.4	93	7.8	7.6	
5/16/95	5/22/95	14	19	9.9	87	7.8	7.1	
5/27/95	5/30/95	8	23	8.5	93	7.9	7.6	
6/2/95	6/5/95	20	27	8.4	135	8.7	7.8	
6/9/95	6/12/95	35	23	8.3	105	8.2	7.8	
6/14/95	6/19/95	23	18	8.1	88	8.0	7.9	
6/26/95	Grab sample	27	28	7.4	89	7.8	7.9	
6/30/95	7/3/95	18	21	NT	NT	7.9	7.8	
7/7/95	7/10/95	NT	23	7.8	89	8.1	8.0	
7/14/95	7/17/95	29	24	6.1	73	8.3	7.6	
7/21/95	7/24/95	27	23	8.6	100	7.8		
7/28/95	7/31/95	31	26	7.6	92	7.7	7.6	
8/5/95	8/8/95	24	24	7.1	88	7.8	7.8	

NT=measurement not taken

Russian River

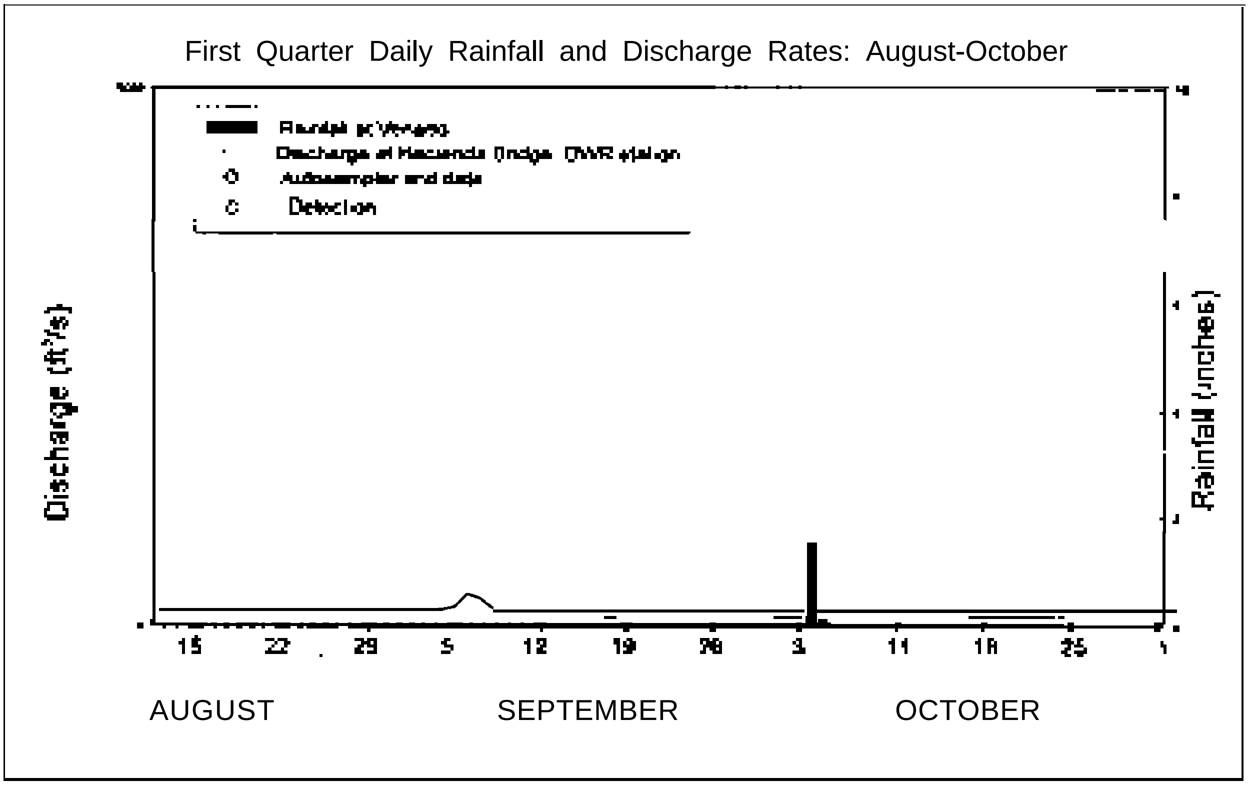


Figure 47. Daily rainfall and Russian River discharge (river flow) for August 12, 1994 through November 1,1994.

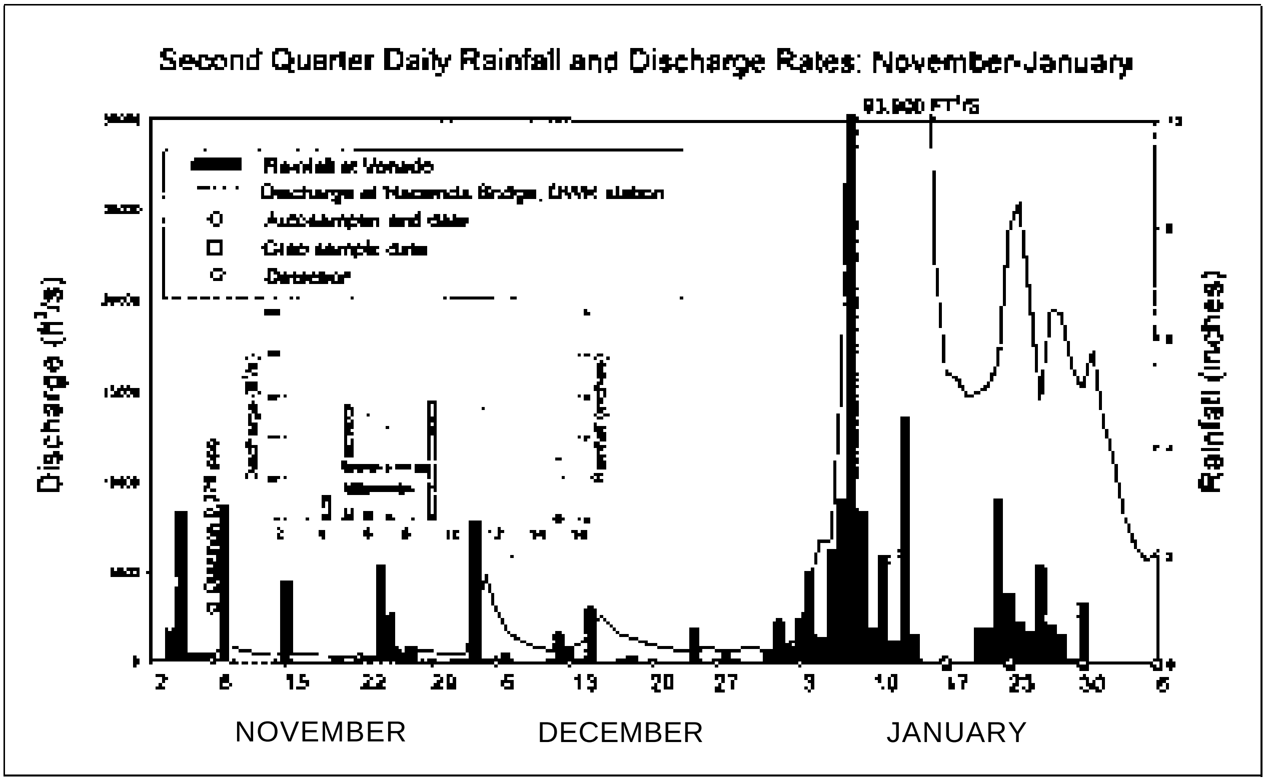


Figure 48. Daily rainfall and Russian River discharge for November 2, 1994 through February 6,1995

through December discharges were lower than the historical monthly averages (Ayers et al., 1995; Friebel et al.,1996). However, during the second quarter rainfall totaled 59.8 inches at Venado and the discharge ranged from 107 to 93,900 cfs (Figure 48). In mid-January heavy rain and flooding occurred in the watershed. The river gage height during January reached 48.0 feet, close to the record stage height of 48.6 feet during the 1986 flood (Friebel et al., 1996). Total annual runoff for the 1995 water year was greater than 200% of the historical average.

During the third quarter 38.1 inches of rain were recorded at the Venado weather station and the Russian River discharge rate fluctuated between 1,241 and 61,274 cfs (Figure 49). The highest discharge during the third quarter came in March, coinciding with heavy rain and flooding in the watershed for the second time that year. The stage height during the March flood reached 42.0 feet, 6 feet less than the flood in January. During the fourth quarter, rainfall totaled 2.08 inches at Venado and the discharge ranged from 188 to approximately 9,000 cfs (Figure 50).

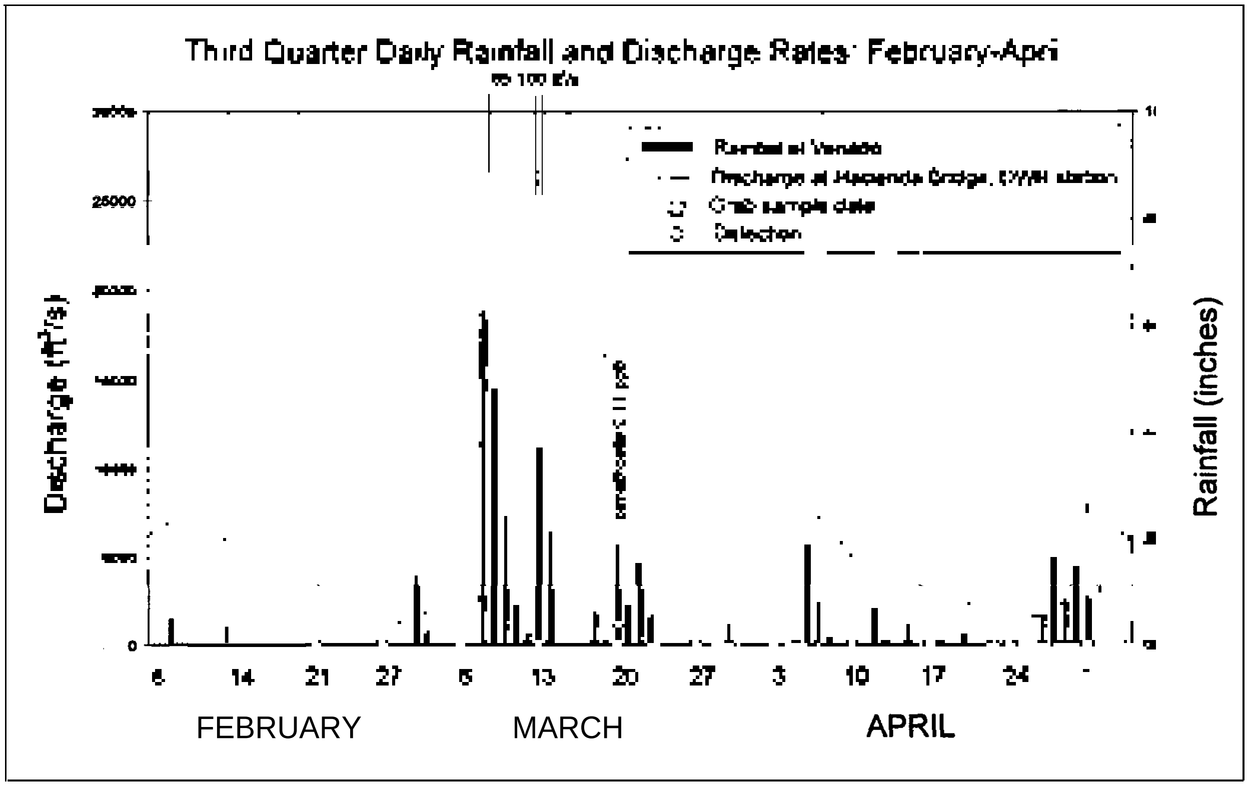
Pesticide detections

During the 12-month sampling period, two of the 52 samples (3.8%) had a pesticide concentration above the reporting limits (Table 8). Diazinon was detected in a sample collected in November 1994, and dimethoate was detected in a equal-width increment depth integrated sample collected in March 1995. There were no detections reported from the six quality control rinse blanks of the splitting equipment.

Diazinon was detected at a concentration of 0.076 ppb in the sample collected November 5-8, 1994. According to CDFG, freshwater organisms should not be affected unacceptably if the average concentration of diazinon does not exceed 0.04 ppb in a 4-day period more than once every 3-years (Menconi and Cox, 1994; Stephan et al., 1985, Table 4). Our results are not directly comparable to these criteria since the duration of sampling does not match the exposure period for which the criteria were developed. However, the detection indicates that additional, more intensive sampling for diazinon may be warranted.

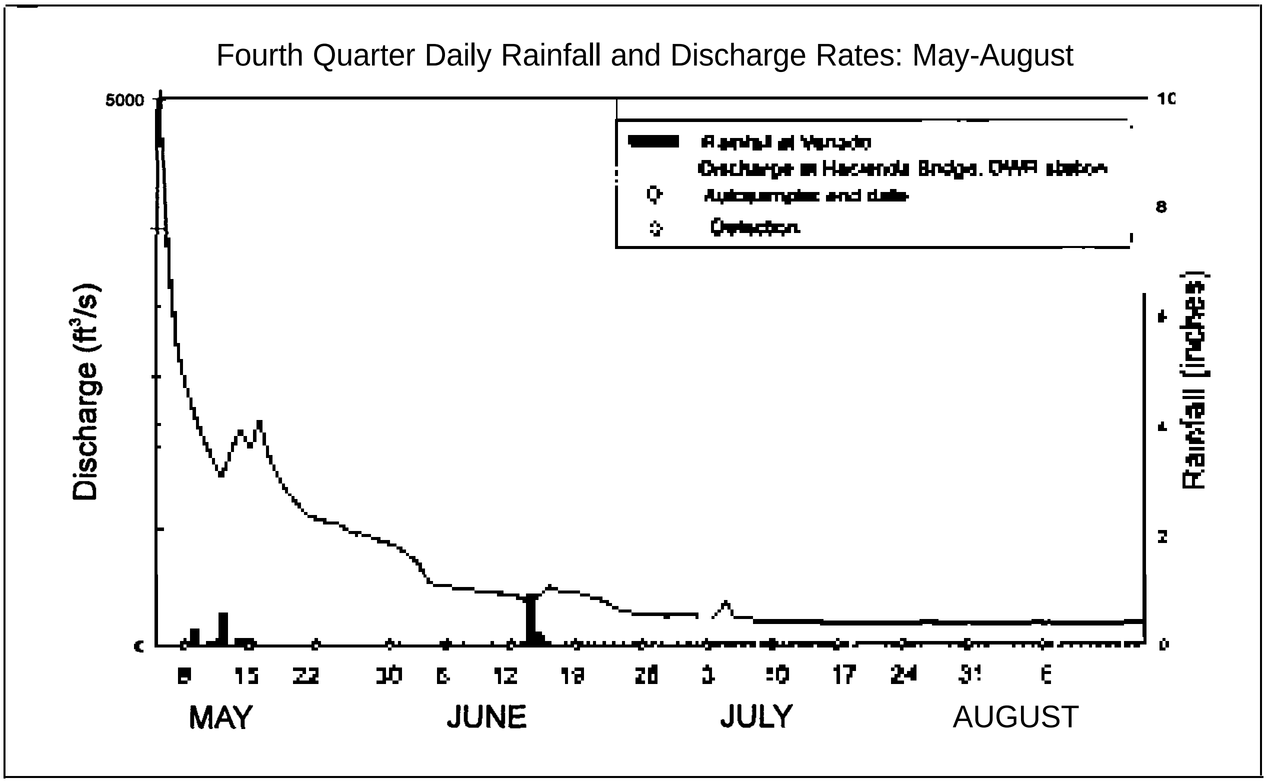
Diazinon was applied throughout the year in the Russian River Watershed with a peak in April. More than 2,200 lb a.i. of diazinon were used on a variety of crops and the use was scattered throughout the watershed (Figure 51). November was the month when the least diazinon was applied to crops, the same month in which diazinon was

Russian River



Third Quarter Daily Rainfall and Discharge Rates: February-April

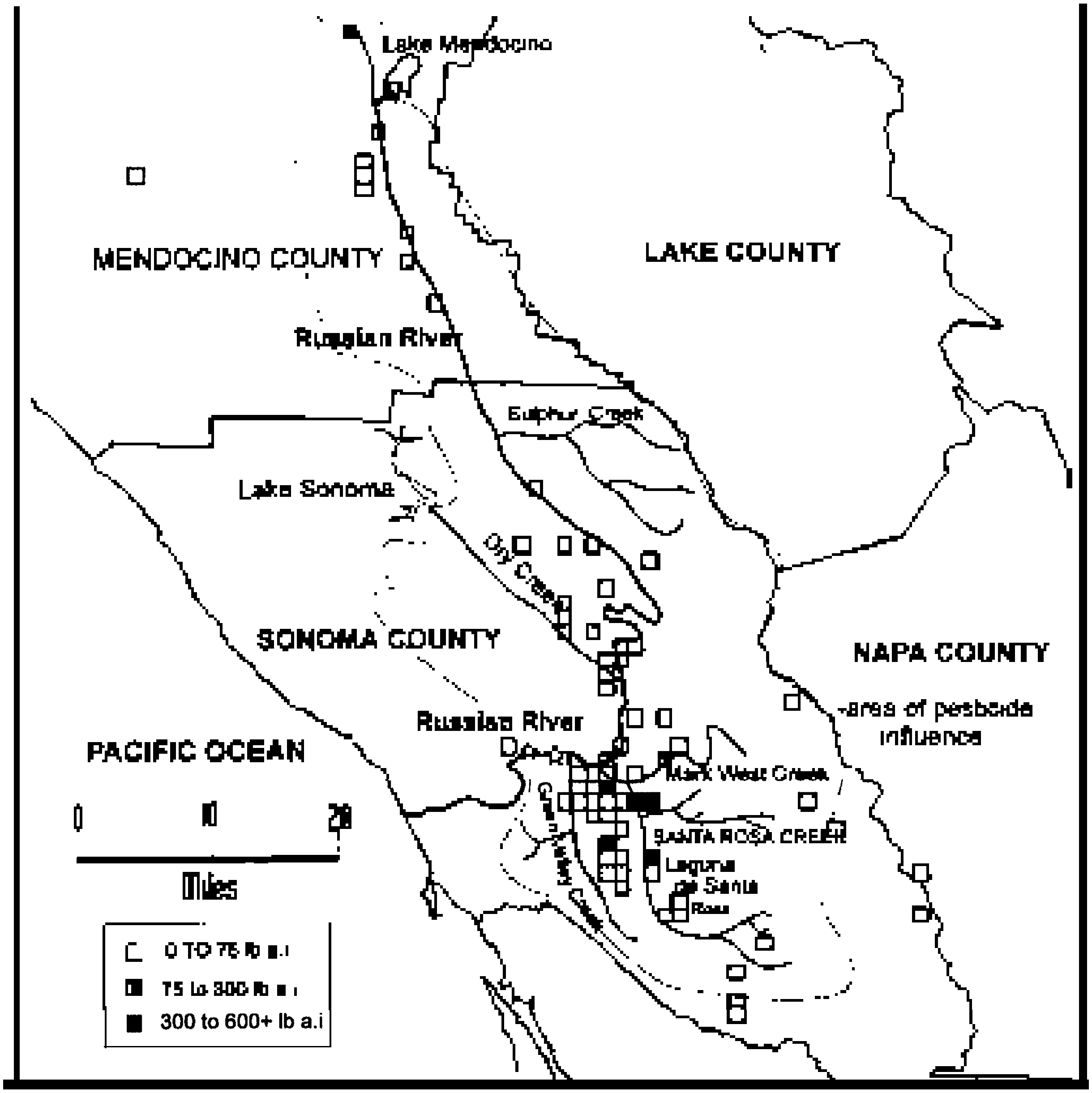
Figure 49. Daily rainfall and Russian River discharge for February 6, 1995 through May 5, 1995

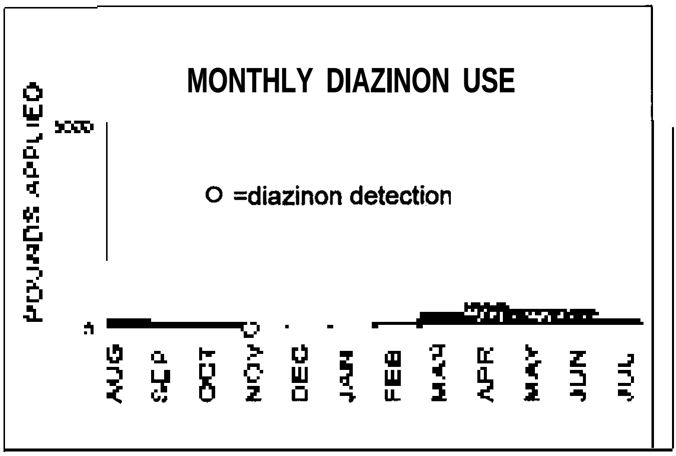


Fourth Quarter Daily Rainfall and Discharge Rates: May-August

Figure 50. Daily rainfall and Russian River discharge for May 5, 1995 through August 19, 1995

DIAZINON USE IN THE RUSSIAN RIVER WATERSHED





☆ Sampling sites

☐ Each square represents one or more applications within a one square mile sector

Primary Crops	Pounds
1. apples	500
2. squash	360
3. wine grapes	280
4. prune	170
5. lettuce	190
6 table grapes	160
7. pears	120
Total pounds applied during the sampling year	2,220

Figure 51. Applications and pounds of diazinon used in the Russian River watershed from August 1994 through July 1995.

detected in the river sample. During the 10 weeks before the November 8 diazinon detection, a total of 174 lb a.i. of diazinon was used in the watershed (Figure 52). The use was mostly in Sonoma County on row crops such as lettuce, mustard, broccoli, and Swiss chard at less than 20 lb a.i. per crop. Some was used on nursery plants. In the 3-weeks before the detection, only about 30 lb a.i. of diazinon were used for agriculture and no diazinon use was reported for the week prior to the detection. The application that was made closest to the sampling site in the highlighted section in figure 52, happened 58 days prior to the detection and was located downstream of the site.

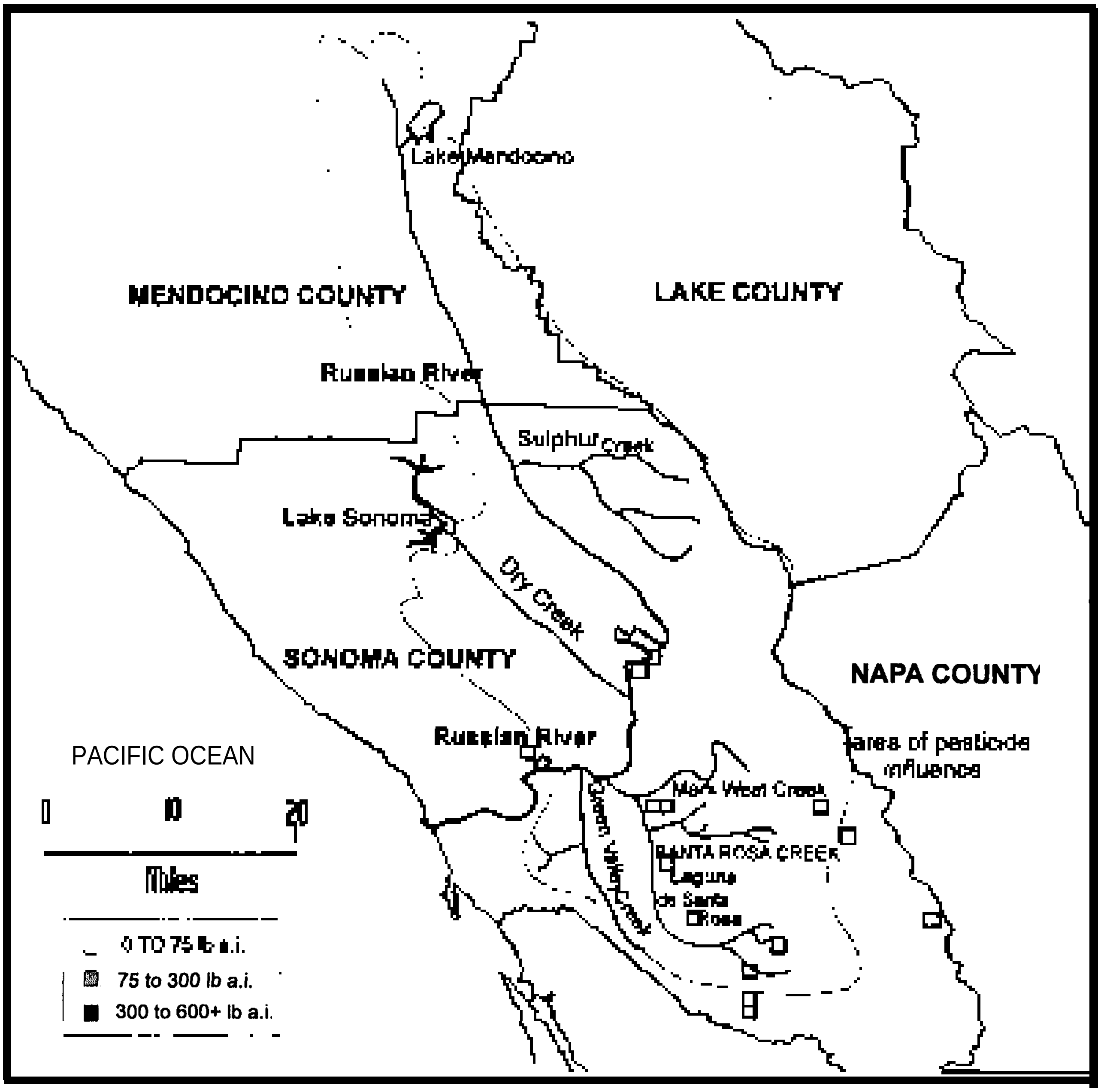
Due to the low agricultural use of diazinon in the watershed, there is a possibility that the detection resulted from landscape, structural or home and garden use. Diazinon is commonly used for home and garden applications to control pests such as ants, lawn grubs, and flies. Home and garden use is not reported to DPR and is not included in figures 51 and 52. In addition, diazinon has been detected in other parts of the United States and California in urban runoff (Schueler, 1995). Most of the urban runoff in Sonoma County is untreated. For instance, the Laguna de Santa Rosa receives discharges from street and stormwater drain systems which eventually flow to the Russian River (NCRWQCB, 1992). Typical of most diazinon detections in surface water, the detection came during rainfall and during a period of increased river discharge. The river flow increased about 309% by November 8 and greater than 700% at the peak 2 days later. This was the first storm of the season resulting in a significant increase in discharge.

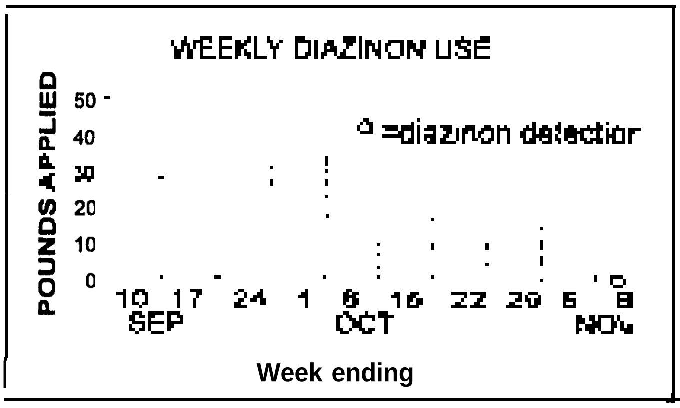
Diazinon has been detected in a previous study. Thirteen clam samples were collected and analyzed for Diazinon for the SMWP. Diazinon was detected once out of 13 samples collected from the Russian River and some of the tributaries, at 70 ppb at the Laguna de Santa Rosa (Rasmussen, 1995a).

Dimethoate was detected in the sample collected on March 20, 1995 at 0.11 ppb. There is no current U.S. EPA water quality criterion for the protection of freshwater aquatic organisms (Table 4).

Dimethoate was used throughout the watershed primarily from March through August with peak use in June and July (Figure 53). Dimethoate is a systemic insecticide and acaricide used mostly on wine grapes and some was used on table grapes and apples. About 6,200 lb a.i. were applied during the l-year study period. A total of 51 lb a.i. of dimethoate were applied on grapes and apples during the 3-week period prior to the

DIAZINON USE IN THE RUSSIAN RIVER WATERSHED
SEPTEMBER 4- NOVEMBER 8, 1994





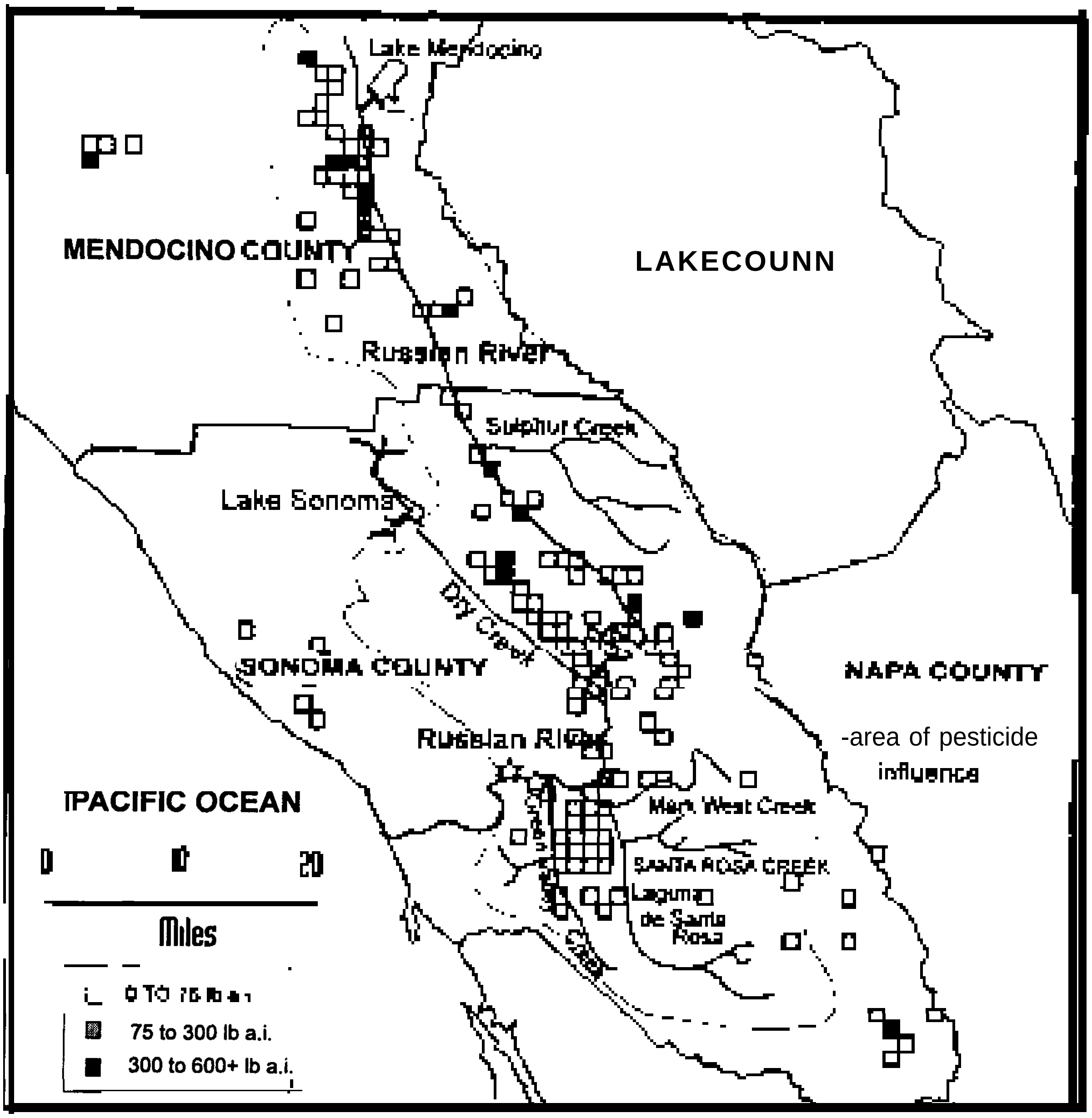
☆ Midway Beach sampling site

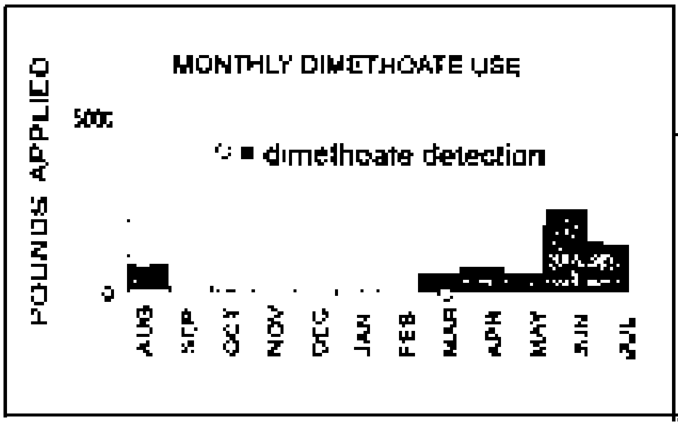
☐ Each square represents one or more applications within a one square mile sector

Primary Crops	Pounds
1. row crops combined	90
2. nursery plants	40
3. peas	20
Total pounds applied prior to detection:	170

Figure 52. Applications and pounds of diazinon used in the Russian River watershed from September 4 through November 8, 1994.

DIMETHOATE USE IN THE RUSSIAN RIVER WATERSHED





☆ Sampling sites

☐ Each square represents one or more applications within a one square mile section

Primary Crops	Pounds
1. wine grapes	5,280
2. table grapes	595
3. apples	250
Total pounds of applied during the sample year	6,280

Figure 53. Applications and pounds of dimethoate used in the Russian River watershed from August 1994 through July 1995.

March 20 detection, at a time when the season for dimethoate applications was just beginning (Figure 54). Applications were made on March 16, 18 and 19, which were days when there was no rain. Rain occurred every week during the month prior to the detection with flooding occurring March 9 though March 15. From March 7, before the storm to the peak discharge on March IO, there was greater than a 5000% increase in flow. The detection occurred as discharge was declining but during a minor increase due to another storm. Despite a short half-life, dimethoate can reach surface water due to its high solubility (Table 5). Therefore, it is likely that the dimethoate entered the Russian River in rain runoff from fields treated between the storms. The use of dimethoate increased significantly after March 20. However, despite applications in excess of 700 lb a.i. in April and with rainfall still occurring, dimethoate was not detected again. During February, March and April equal-width increment samples were collected instead of using the autosampler, and thus only a very small portion of the weekly discharge in the Russian River was examined.

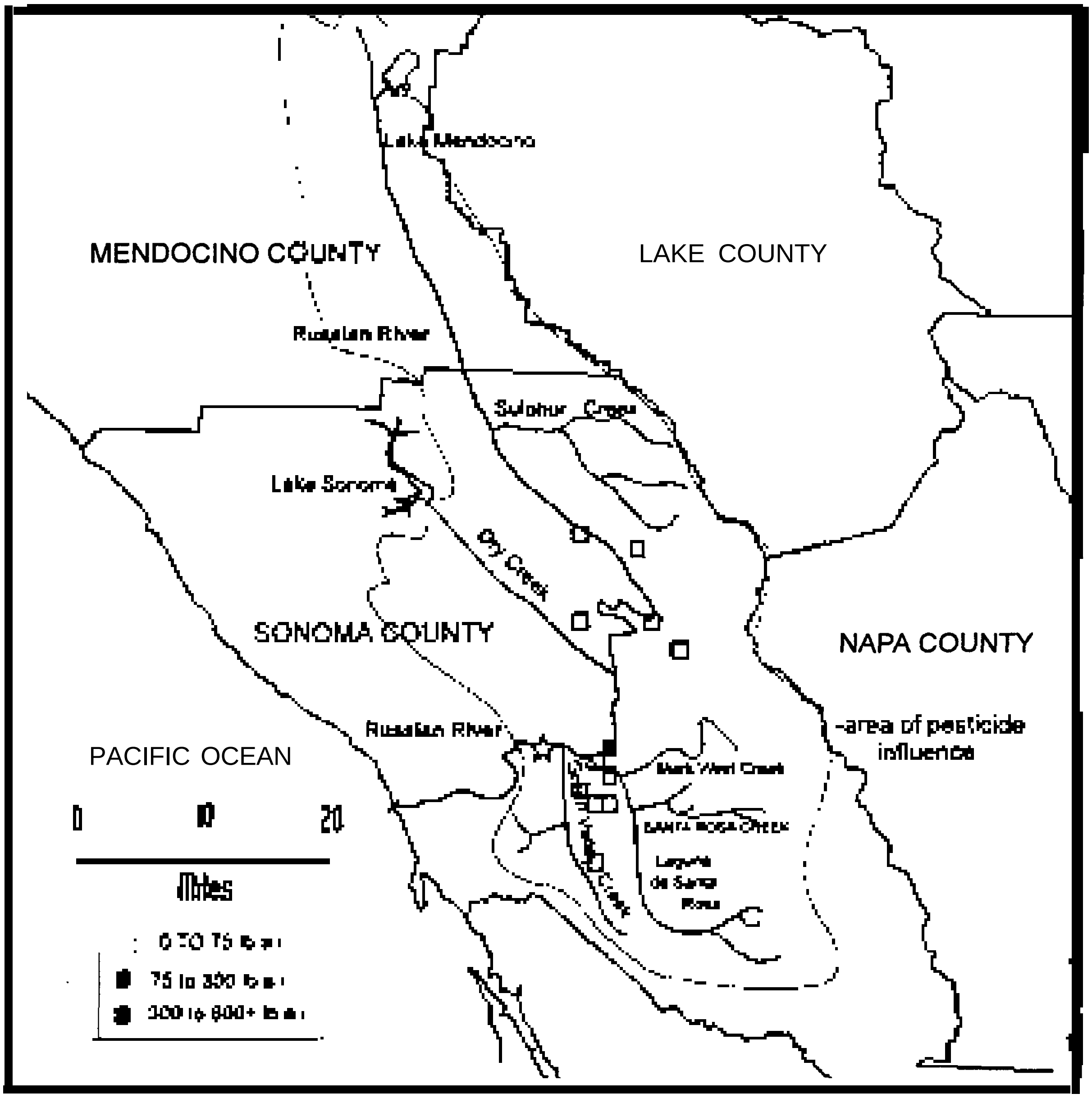
Toxicity Results

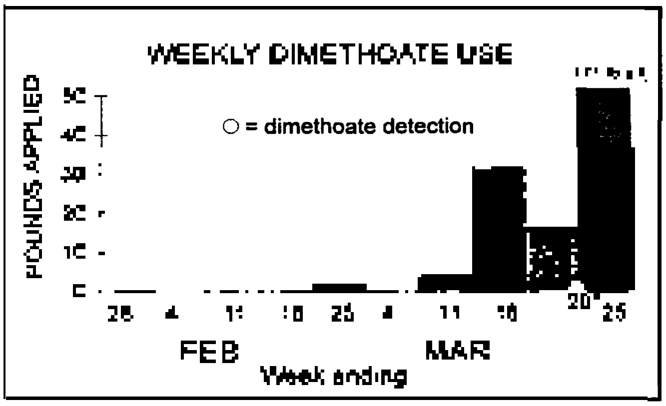
Only one of the 23 split samples analyzed by DFG for toxicity caused significant mortality to cladocerans. Mortality was not correlated with any pesticide detections. Tests showed no significant mortality to fathead minnows (Appendix V).

Other Pesticides Used in the Watershed

Chlorpyrifos was used primarily on apple orchards mainly in the area between Green Valley Creek and the Laguna de Santa Rosa from February through June at about 5,600 lb a.i. (Figure 55). Due to a longer half-life and a use period corresponding with the last half of the rainy period, chlorpyrifos had potential for being found in the river, but it was not detected. Since chlorpyrifos tends to bind with sediment and to move offsite with soil erosion, it may have moved offsite during periods of greatest rainfall, which may not have coincided with our sampling. Also these periods may have corresponded with flow discharges that diluted chlorpyrifos residue and made it undetectable. Chlorpyrifos was detected in the SMWP. Of the 21 clam samples taken at several locations in the watershed, IO had detectable levels of chlorpyrifos ranging from 4.4 to 290 ppb. The chlorpyrifos detection of 290 ppb was from mussels placed in Green Valley Creek in 1993 (Rasmussen, 1995a).

DIMETHOATE USE IN THE RUSSIAN RIVER WATERSHED
JANUARY 22 - MARCH 25.1995



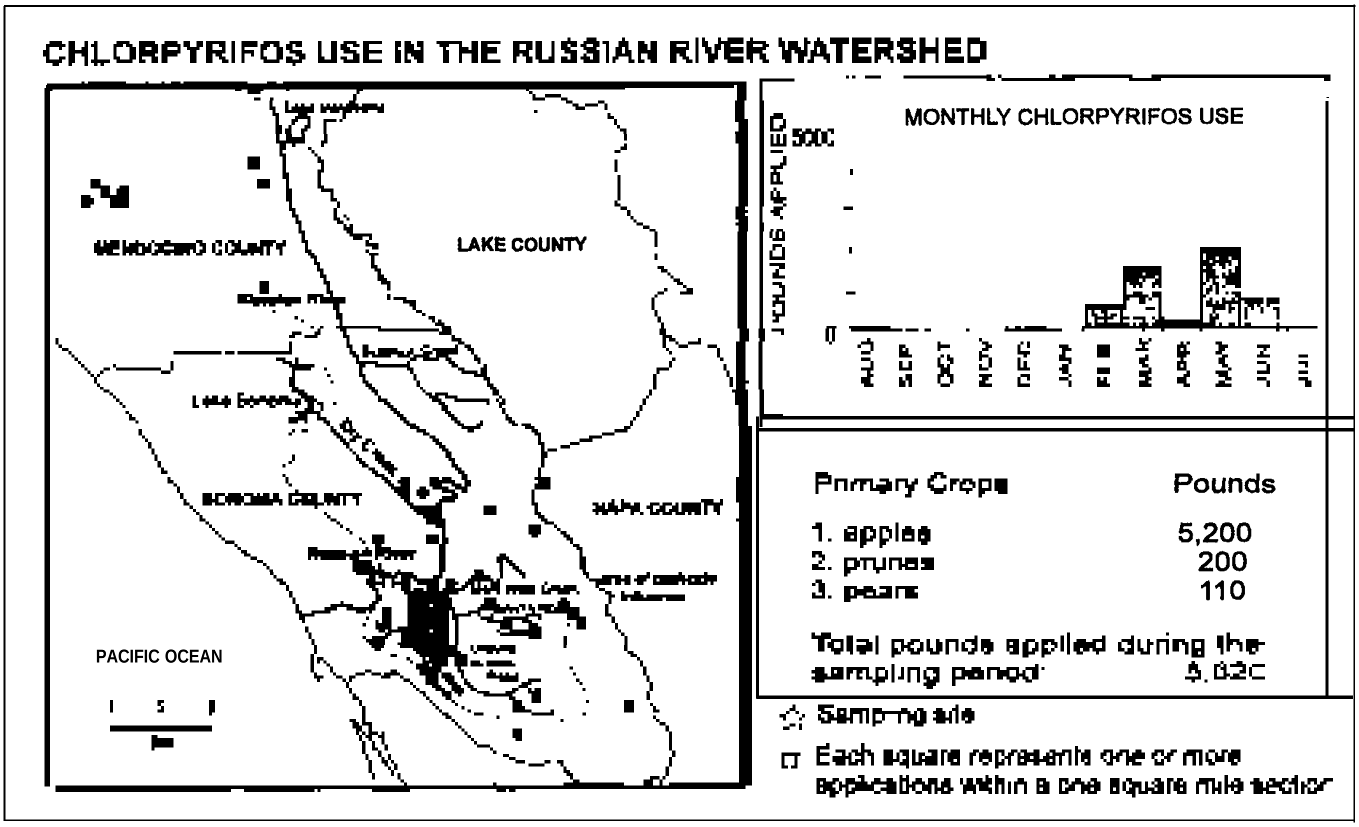


☆ Hacienda Bridge sampling site

■ Each square represents one or more applications within a one square mile section

Primary Crops	Pounds
1. Apple orchards	32
2. Wine grape vineyards	18
3. Pear orchard	2
Total pounds applied prior to detection:	52

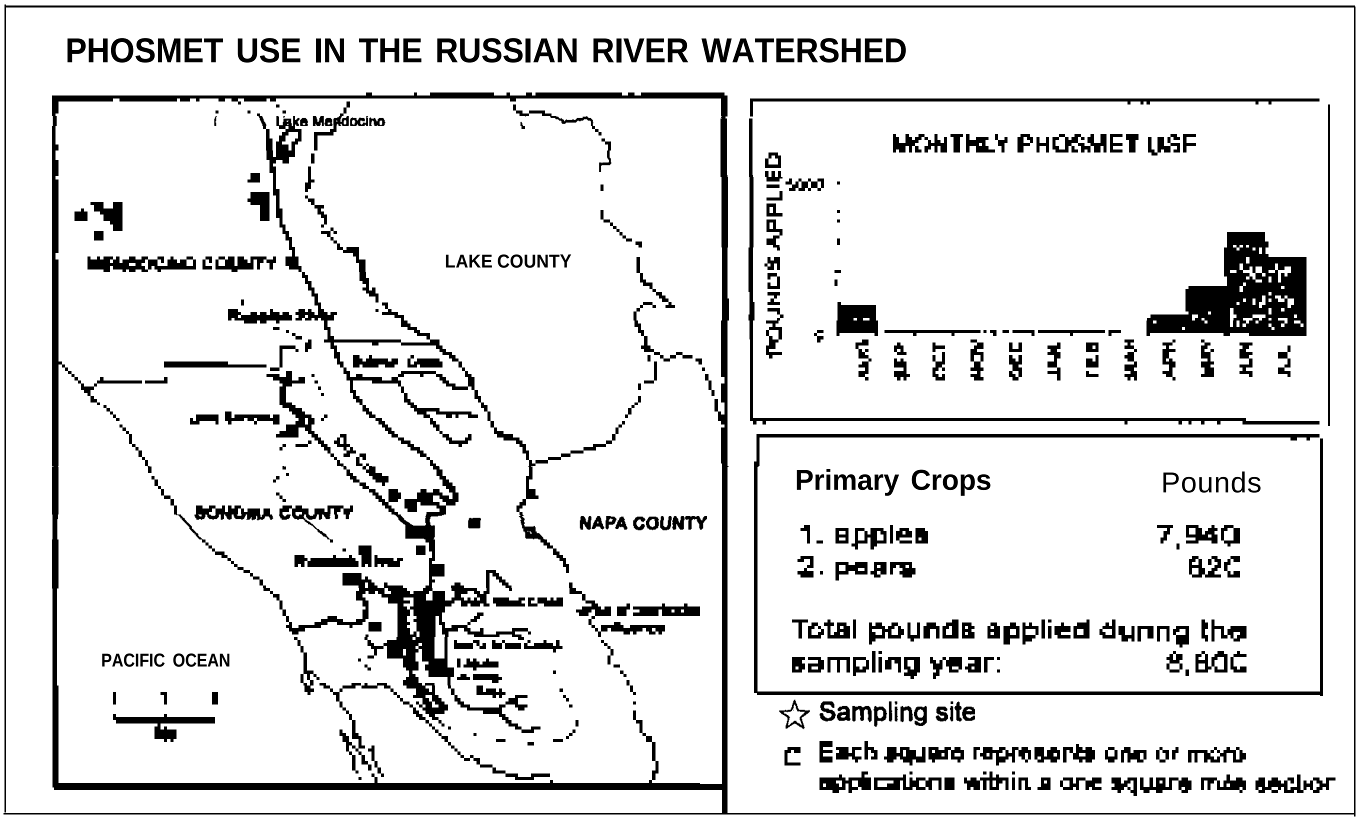
Figure 54. Applications and pounds of dimethoate used in the Russian River watershed from January 22 through March 25, 1995.



Primary Crops	Pounds
1. apples	5,200
2. prunes	200
3. pears	110

Total pounds applied during the sampling period: 5,02C

Figure 55 Applications and pounds of chlorpyrifos used in the Russian River watershed from August 1994 through July 1995 .



Primary Crops	Pounds
1. apples	7,940
2. pears	82C

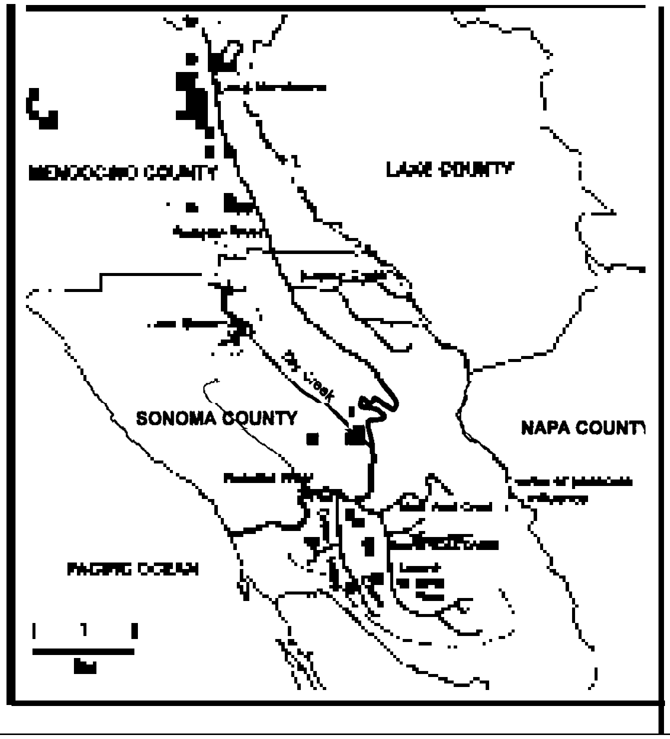
Total pounds applied during the sampling year: 8,80C

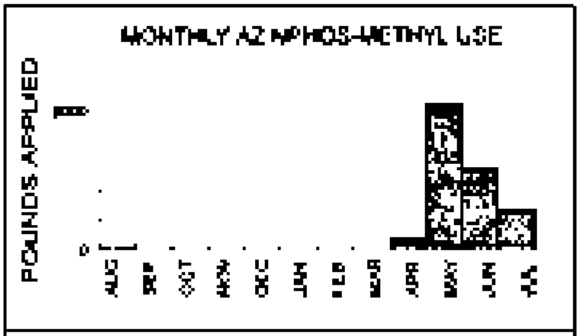
Figure 56. Applications and pounds of phosmet used in the Russian River watershed from August 1994 through July 1995 .

Phosmet was applied on apple orchards in many of the same sections where Chlorpyrifos was used (Figure 56). More than 8,800 lb a.i. of phosmet was applied during the study period but it was never detected in the samples collected. Phosmet was used from April through August, with the most use occuring in June and July. Azinphos-methyl was applied on pear orchards in Mendocino and Somoma Counties and apple orchards mainly in Sonoma County. It was used at greater than 9,800 lb a.i., primarily in May and through July (Figure 57). With the exception of the use in April, these OPs would be expected to have less potential to reach the Russian River because each were used during the early part of the dry season and have an average field-dissipation half-life of less than 2.5 weeks (Table 5). In April 560 and 322 lb a.i. of phosmet and azinphos-methyl were used, respectively. There was no reported use of phosmet or azinphos-methyl during September, October or November, the months prior to the first significant increase in discharge.

Carbaryl is the only carbamate applied in the watershed that was analyzed in our screen. Approximately 1,000 lb a.i. of carbaryl were applied within the watershed from February through September primarily on table grapes, apples, wine grapes and squash (Figure 58). Carbaryl may be found in February, March and April in surface water within this watershed since it is used during the rainy season. However, it is still unlikely carbaryl would end up in the Russian River from agricultural use due a short half-life of under 2 weeks (Table 5) and few applications.

AZINPHOS-METHYL USE IN THE RUSSIAN RIVER WATERSHED





Primary Crops	Pounds
1. Pears	9,120
2. Apples	660

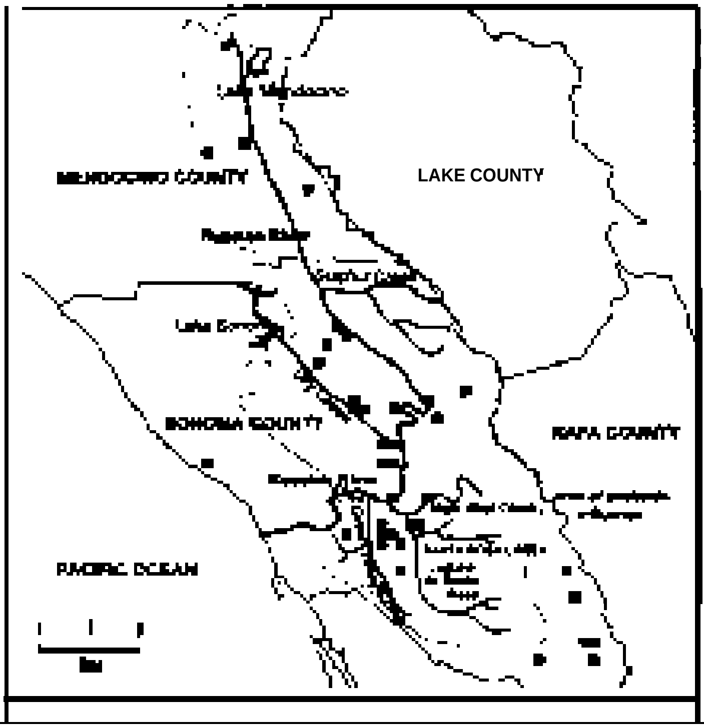
Total pounds applied during the sampling period: 9,860

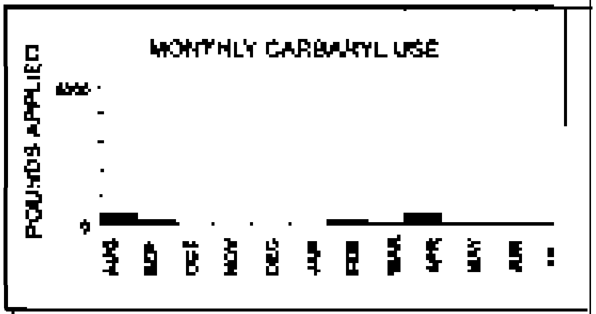
☆ Sampling site

❑ Each square represents one or more applications within a one square mile section

Figure 57. Applications and pounds of azinphos-methyl used in the Russian River watershed from August 1994 through July 1995 .

CARBARYL USE IN THE RUSSIAN RIVER WATERSHED





Primary Crops	Pounds
1. Apple Orchards	320
2. Table grape vineyards	290
3. Wine grape vineyards	290
4. Squash	110

Total pounds applied during the sampling year 1,020

☆ Sampling site

❑ Each square represents one or more applications within a one square mile section

Figure 58. Applications and pounds of carbaryl used in the Russian River watershed from August 1994 through July 1995 .

Conclusions

Overall, the DO levels and pH levels in all four rivers were good. The DO was below the minimum required levels (Regional Water Quality Control Boards) in 12 out of 157 measurements. However, the percent saturation never fell below 50% on any measurement. The pH readings taken primarily *in* ***situ*** with some taken in the lab, were below the regional board standards in only 4 of 212 measurements. Rainfall amounts during the winters included in the study were atypical. The winter of 1994 was fairly dry resulting in below normal discharge in the Sacramento River. In the winter of 1995, we experienced a tremendous amount of rainfall that produced flooding on the Merced, Russian and Salinas Rivers.

During the year-long sampling on the four rivers, the number of positive samples was 13 of 224 samples **(5.8%)**, and pesticides were detected 17 times in the 224 samples (7.6%) due to multiple detections in some samples. Five different pesticides were detected: diazinon was detected seven times, dimethoate was detected four times, methidathion was detected four times and chlorpyrifos and 3 OH-carbofuran were each detected once. Ten samples were positive during the rainy season while there were only three positive samples during the dry season. Diazinon, methidathion, dimethoate, 3 OH-carbofuran and chlorpyrifos were detected in the wet season, while dimethoate and diazinon were detected in the dry season. Most detections occurred just after or during rainfall, and all occurred with elevated discharge except in the Salinas River Lagoon, for which we have no flow data.

During the year-long sampling period, two of the 52 samples collected at the Sacramento River had a pesticide detection. Diazinon was detected twice at 0.11 and 0.07 ppb during January and February, respectively. Since the two detections came during periods of increased discharge due to rainfall, rain runoff from dormant spray applications to nut and stone fruit trees appears to be the principal means by which diazinon reached the Sacramento River.

The most detections were found in the Merced River samples (ten), primarily during the winter dormant spray period. The most types of pesticides were also found in the Merced River (4) including the only carbamate found, 3-OH-carbofuran. We began to sample the river twice a week on January 31 and the results suggest that more intense monitoring from December through March would be useful.

Chlorpyrifos was the only pesticide detected along the middle reach of the Salinas River. Chlorpyrifos was detected at 0.12 ppb in January, just after the first major storm of the year. The greatest number of detections per number of samples collected came from the Salinas Lagoon where only 12 monthly samples were collected. Diazinon and dimethoate were detected in the same sample collected in June, at 0.20 and 0.11 ppb, respectively. These two pesticides may have entered the lagoon via irrigation runoff or drift.

There were two detections in samples collected from the Russian River. Diazinon was detected at 0.076 ppb in November, after the first storm of the year producing significant runoff. Agricultural use of diazinon was low during the three months preceeding the detection. There is a possibility that the detection could be due to landscape, structural or home and garden use. Dimethoate was detected at 0.11 ppb in March, during a storm.

During the year-long study there were few detections in the Sacramento and Russian Rivers and the middle reach of the Salinas River for several possible reasons. First, there may not be much insecticide residue moving off-site into the rivers. Secondly, our sampling periods may have missed the residue pulses or diluted them. Third, the Salinas River had one and the Russian River had two flood events during sampling. As a result, residues may have been diluted in the abnormally high flows, at a time of the year when detections occurred in studies of other rivers. However, the heavier rainfalls that occur within the Russian River watershed can result in greater flow increases than in the other three rivers. These flows may render pesticides flowing into the Russian River during storms, when detections normally occur, undetectable due to dilution. Furthermore, along the Merced River, dam releases during the spring of 1995 may have diluted residues during the last three months of monitoring. And last, there may have been residues present in these rivers in localized areas, upstream or along the tributaries that were diluted at our sampling sites.

The 3-day composite method was chosen to sample more of the weekly discharge than collecting a one-hour-long equal-width increment sample. One disadvantage of using the 3-day sampling period is possible degradation of pesticide residues during the sample collection and during transport time. The results of a storage stability study conducted on carbamates and organophosphates showed that only five pesticides and seven breakdown products may begin to degrade during this length of time.

Another concern of using the 3-day composite method was the dilution of residues. The USGS's single-day sampling on the Sacramento River concurrently with our monitoring provided a comparison with our 3-day composite method. USGS's diazinon detections corresponded with two of our detections. When the USGS's daily concentrations of diazinon were averaged, the quantity of diazinon residues is the same as our 3-day composite method. In addition, DPR's negative 3-day sample periods (no detections) coincided with periods when either no detections were made by USGS or detections were below our RL. Peak levels of diazinon detected by USGS seemed to coincide with peak river discharges, which in some cases did not coincide with our 3-day sampling periods. USGS detections of methidation on the Sacramento River showed that levels were below our RL. According to the USGS data, our sample collection method was adequate in capturing the major pulses of diazinon.

Endosulfan was included in the analyses for this study since it is still detected in fish and clam tissues by the TSMP and SMWP. In addition, it was also included to see if changes in use permits, which are to prevent residues from moving offsite in drainage from fields beside waterways, have had an effect. Statewide use of endosulfan is declining; 475,743 Ibs. used in 1994 and 229,157 Ibs. in 1995. Use in Monterey County, where endosulfan has been detected in fish and clam tissues and in soil and sediment samples, was low compared with the other pesticides used, with 1,731 and 2,953 used in 1994 and 1995, respectively (PUR 1994, PUR 1995). Based on a lack of detections in this study, we have no evidence that the permits are not protecting these rivers.

The CDFG Aquatic Toxicology Laboratory tested 107 of the 212 samples collected at each of the four rivers for toxicity. The Salinas River Lagoon site was not included. DFG found no apparent relationship between the presence of pesticide residues and mortality observed in the samples tested for toxicity. Three samples caused significant mortality to either fathead minnows or cladocerans but those samples did not contain detectable concentrations of pesticides. The cause of the mortality is unknown at this time.

Recommendations

Since the rainfalls for both winters included in the study period were atypical, the fairly low number of pesticide detections from samples from the Sacramento and Russian Rivers and the middle reach of the Salinas River should not preclude further sampling on these rivers. There is potential, however, to increase the number of detections by optimizing the type of sampling and the timing. Monitoring during storms when the discharge is increasing, especially in periods after increased applications of these chemicals, may lead to more detections from all four rivers. Our sampling procedure was developed to survey each of these rivers for a whole year. Sampling dates were predetermined, and therefore may not have coincided with peak residue levels in these rivers. Also, pesticides might be detectable along the tributaries of all four rivers. Since we sampled at one site on each river (two on Salinas River), we have no knowledge of pesticide contamination along the tributaries that may have been diluted at the confluence of the rivers or at our sampling site.

The Merced River and Salinas River Lagoon stand out as needing further study based on the number of detections. The most detections were found in samples from the Merced River, primarily during the winter dormant spray periods. Also, the most types of pesticides, three **OPs** and the only CB found, 3-OH-carbofuran, were found there. Further sampling along the Merced River would be beneficial since the winter of 1995 was atypical and the dam releases in the spring were greater than normal. Since the lagoon is a recognized wildlife habitat area, more monitoring for pesticide residues there would be beneficial. Unlike the middle reach of the Salinas River, the stage height does not fluctuate greatly. Therefore, an autosampler and the 3-day composite method could be used at the lagoon.

The most frequently used pesticides in the Russian River Basin were herbicides and some fungicides which were not analyzed in this study. Since greater amounts of these pesticides were used in the basin rather than insecticides, those that have potential to move off-site and are toxic to aquatic organisms should be the focus of further study along with the pesticides we detected in this study. If further study is conducted on the Salinas River, chlorthal-dimethyl should be included due to the large quantity used and it has been detected numerous times in this watershed in other studies.

References

Anderson, S.W., T.C. Hunter, E.B. Hoffman, and J.R. Mullen. 1993. Water Resources Data, California Water Year 1992. Vol. 3. U.S. Geological Survey Water-Data Report . Report #CA-92-3. Sacramento, CA.

Ayers, W. and others. 1995. Water Resources Data, California, Water Year 1994. Vol. 2. U.S. Geological Survey Water-Data Report, CA-94-2. Sacramento, CA.

Buchanan, T.J. and W.P. Somers. 1969. Discharge measurements at gauging stations In; Techniques of Water-Resources Investigations of the United States Geological Survey. Book 3, Chap. A8. 65p

California Department of Food and Agriculture. 1994. 1993 County Agricultural Commissioner's Data. California Agricultural Statistics Service, California Department of Food and Agriculture joint report with The U.S. Department of Agriculture. Sacramento, California.

Central Coast Regional Water Quality Control Board. 1994. Water Quality Control Plan, Central Coast Region.

California Department of Health Services. 1990. Summary: Maximum contaminant levels (MCLs) and action levels (ALs). Office of Drinking Water. Berkeley, California.

California State Lands Commission. 1993. California's Rivers; A public trust report. Second Edition. Sacramento, CA. p. 130-I 33, 148-152.

Central Valley Regional Water Quality Control Board . 1989. Water diversion and discharge points along the Merced River: Cressey Bridge to San Joaquin River. Sacramento, CA.

Central Valley Regional Water Quality Control Board . 1995a. Insecticide concentrations and invertebrate bioassay mortality in agricultural return water from the San Joaquin Basin. Sacramento, CA.

Central Valley Regional Water Quality Control Board . 1995b. Water Quality Control Plan, Central Valley Region, Sacramento and San Joaquin Rivers. California Regional Water Quality Control Board, Central Valley Region and State Water Resources Control Board. Third Edition.

Domagalski, J.L. 1995. sources of pesticides in the San Joaquin River, California: input from Winter Storms, 1992-93. U.S. Geological Survey. Report # 95-165. Sacramento, CA.

Domagalski, J. and L.R. Brown. 1994. National Water Quality Assessment Program, Sacramento River Basin. U.S. Geological Survey. Sacramento, CA.

Department of Pesticide Regulation. 1991. Pesticide use report. Sacramento, CA.

Department of Pesticide Regulation. 1992. Pesticide use report. Sacramento, CA.

Department of Pesticide Regulation. 1993. Pesticide use report. Sacramento, CA.

Nonpoint

Department of Pesticide Regulation. 1993. Pesticide use report. Sacramento, CA.

Department of Pesticide Regulation. 1994. Pesticide use report. Sacramento, CA.

Department of Pesticide Regulation. 1995. Pesticide use report. Sacramento, CA.

Department of Water Resources. 1993. Quality Assurance Technical Document 3. Compilation of State Drinking Water Standards and Criteria. Division of Local Assistance. Department of Water Resources. Sacramento, CA. July 1993.

Fleck, J.E., L.J. Ross, and K. Hefner. 1988. Endosulfan and chlorthal-dimethyl residues in soil and sediment of Monterey County. Report # EH 88-06. Environmental Hazards Assessment Program. Dept. of Pesticide Regulation. Sacramento, CA.

Foe, C. 1994. Letter to K. Bennett regarding pesticide detections on the Merced River. Central Valley Regional Water Quality Control Board. Letter dated January 4, 1994. Sacramento, CA.

Foe, C. and R. Sheipline. 1993. Pesticides in surface water from applications on orchards and alfalfa during the winter and spring of 1991-92. California Regional Water Quality Control Board, Central Valley Region, Sacramento, CA.

Friebel, M.F., L. F. Trujillo and K.L. Markham. 1996. Water resources data, California, Water Year 1995. Vol. 2. U.S. Geological Survey Water-Data Report CA-95-2. Sacramento, CA.

Goodwin, C. 1994. Personal communication regarding Russian River watershed. North Coast Regional Water Quality Control Board. March 1994.

Goodwin, C. 1993. California Regional Water quality Control Board, North Coast Region. Letter to C. Ganapathy regarding Russian River tributaries and past monitoring of the Russian River. December 6, 1993.

Guy, H. P. and V.W. Norman. 1970. Field methods for measurement of fluvial sediment In:Techniques of water-resources investigations of the United States Geological Survey. Book 3. Chapter C2. U. S. Gov. Print. Office. Washington, D.C.

Howard, P. H. 1991. Handbook of environmental fate and exposure data for organic chemicals. Volume III, Pesticides. Lewis Publishers. Chelsea, Michigan.

Klamt, R. 1995. Personal communication regarding dissolved oxygen levels. North Coast Regional Water Quality Control Board. August 1995.

Klamt. R. 1994. Personal communication regarding Russian River watershed boundary. North Coast Regional Water Quality Control Board. April 1994.

Kollman, W., and R. Segawa, 1995. Interim report of the pesticide chemistry database. Envrionmental Hazards Assessment Program. Dept. of Pesticide Regulation. Sacramento, CA.

Kratzer, C. 1997. Personal communication in January 1997 regarding Merced River Basin. U.S. Geological Survey. Sacramento, CA.

Kuivila, K.M. and C.G. Foe. 1995. Concentrations, transport and biological effects of dormant spray pesticides in the San Francisco Esturary, California. Environ. Toxicol. Chem. 14(7):1141-1150.

Lee, J M , L J Ross and R G Wang 1993 Integrated environmental toxicology and monitoring in the development and maintenance of a water quality program: California's rice herbicide scenario In Effective and Safe Waste Management. Chapter 18 Lewis Publishers. p211-224.

MacCoy, D., K.L. Crepeau, and K.M.Kuivila. 1995. Dissolved pesticide data for the San Joaquin River at Vernalis and the Sacramento River at Sacramento, California, 1991-94. U.S. Geological Survey. Report# 95-l 10.

Markham, K.L., J.R. Palmer, M.F. Friebel, L. F. Trujillo. 1993. Water Resources Data, California, Water Year 1993. Vol. 2. U.S. Geological Survey Water-Data Report CA-92-2. Sacramento, CA.

Marshack, J. B. 1995. A compilation of water quality goals. Central Valley Regional Water Quality Control Board. Sacramento, CA.

Mayer, F.L. and M. R. Ellersieck. 1986. Manual of acute toxicity: Interpretation and data base for 410 chemicals and 66 species of freshwater animals. U.S. Fish and Wildlife Service, Washington, DC.

Menconi, M. and S. Seipmann, 1996. Hazard assessment of the insecticide methidation to aquatic organisms in the Sacramento-San Joaquin River system. California Dept. of Fish and Game, Rancho Cordova. Administrative Report# 96-l.

Menconi, M. and C. Cox. 1994. Hazard assessment of the insecticide diazinon to aquatic organisms in the Sacramento-San Joaquin River system. California Department of Fish and Game. Environmental Services Division. Administrative Report# 94-2.

Miller, J.C. and J.N. Miller. 1988. Statistics for analytical Chemistry. 2nd ed. Ellis Horwood Limited. Chichestier, West Sussex.

Mullen, J.R., M.F. Frieble, K.L. Markham and S.W. Anderson. 1994b. Water Resources Data, California, Water Year 1993. Vol. 4. U.S. Geological Survey. Water-Data Report CA-934 Sacramento, CA.

Mullen, J.R., S.W. Anderson, and P.D. Hayes. 1994a. Water Resources Data, California Water Year 1993. Vol. 3. U.S.Geological Survey. Water-Data Report CA-93-3. Sacramento, CA.

North Coast Regional Water Quality Control Board , 1992. Investigation for nonpoint source pollutants in the Laguna de Santa Rosa, Sonoma County. September 24, 1992.

North Coast Regional Water Quality Control Board . 1994. Water Quality Control Plan for the North Coast Region (Basin Plan). Revised 1997. Santa Rosa, CA.

North Coast Regional Water Quality Control Board . 1993. Interim staff report regarding Russian River water quality monitoring. Santa Rosa, CA.

Oakden, J.M. and J.S. Oliver.1988. Pesticide persistence in fields and drainages of the central Monterey Bay Area. Report prepared for the RWQCB, Central Coast Region by Moss Landing Marine Laboratories. Moss Landing, CA.

Palmer, J.R., M.F. Friebel, L. F. Trujillo and K.L. Markham. 1994. Water Resources Data, California, Water Year 1993. Vol. 2. U.S. Geological Survey Water-Data Report CA-93-2. Sacramento, CA.

Racke, K.D. 1993. Reviews of environmental contamination and toxicology. Vol. 131. Springer-Verlag. New York, NY.

Rasmussen, D. 1995b. Toxic Substances Monitoring Program, 1992-93. Report # 95-1WQ. California State Water Resources Control Board. Sacramento, CA.

Rasmussen, D. 1995a. State Mussel Watch Program,1987-1993 Data Report. Report # 94-l WQ. California State Water Resources Control Board. Sacramento, CA.

Rassmussen, D. 1994. Preliminary Summary of the 1994 Species Data. Toxic Substances Monitoring Program. California State Water Resources Control Board. Sacramento, CA.

Rassmussen, D. 1991 .Toxic Substances Monitoring Program, 1988-89. Report # 91-WQ. California State Water Resources Control Board. Sacramento, CA.

Rassmussen, D. 1993.Toxic Substances Monitoring Program, 1991. Report # 91 -WQ. California State Water Resources Control Board. Sacramento, CA.

Ross, L.J. 1992a. Preliminary results of the San Joaquin River study; Summer 1991. Memorandum to Kean Goh, Environmental Hazards Assessment Program. Department of Pesticide Regulation. May 21, 1992.

Ross, L.J. 1993a. Preliminary results of the San Joaquin River study; Summer 1992. Memorandum to Kean Goh, Environmental Hazards Assessment Program. Department of Pesticide Regulation. September 22, 1993.

Ross, L.J., R. Stein, J. Hsu, J. White, and K. Hefner. 1996. Distribution and mass loading of insecticides in the San Joaquin River, California; Winter 1991-92 and 1992-93. Report #EH 96-02. California Department of Pesticide Regulation. Sacramento.

Ross, L.J., K.D. Bennett, K.D. Kim, K. Hefner, J. Hernandez. 1996. Reducing dormant spray runoff from orchards. Environmental Hazards Assessment Program. Report # EH 97-03. Department of Pesticide Regulation. Sacramento, CA.

Salinas River Lagoon Management and Enhancement Plan. 1992. Prepared by Habitat Restoration Group for the Salinas River Lagoon Task Force. (Draft).

Schueler, T. 1995. Urban pesticides: From the lawn to the stream. Watershed Protection Techniques. Vol.2, No.1.

Seipman, S. and T. Yargeau. 1996. Hazard assessment of the insecticide dimethoate to aquatic organisms in the Sacramento-San Joaquin River system. California Dept. of Fish and Game, Rancho Cordova. Administrative Report# 96-4.

Shelton, L.R. and L.K. Miller.1988. Water quality data, San Joaquin valley, California. March 1985 to March 1987. U.S. Geological Survey. Open file Report 88-479. Sacramento, CA.

Stein, R.G. and J. H. White. 1993. Aerial movement and deposition of diazinon, chlorpyrifos, and Ethyl parathion. Report # EH 93-04. Dept. Pesticide Regulation. Sacramento, CA.

Stephan, C.E., D.I. Mount, D.J. Hansen, J.H. Gentile, G.A. Chapman, and W.A. Brungs. 1985. Guidelines for deriving numerical national water quality criteria for the protection of aquatic organisms and their uses. U. S. EPA. Office of Research and Development. Washington, D.C.

State Water Resources Contol Board. 1990. Sacramento River toxic chemical risk assessment project. Final Report. California State Water Resources Control Board, Division of Water Quality. Report# 90-I 1 WQ. Sacramento, CA

State Water Resources Contol Board. 1994. Notice of Public Workshop on January 4,1995. Information relating to water right issues on the Russian River. Notice date December 1, 1994. California State Water Resources Control Board. Sacramento, CA.

U.S. Environmental Protection Agency. 1986. Quality Criteria for Water. Office of Water Regulations and Standards, Washington, D.C. May 1, 1986.

U.S. Environmental Protection Agency. 1988. Health advisories for 50 pesticides. Part 1. U.S. Dept. of Commerce. National Technical Information Service. Washington D.C. p. 268-285.

U.S. Geological Survey. 1995. Water Resources Data, California, Water Year 1995. Region 3. Internet- http://wr.usgs.gov/data/index.html

Wauchope, R.D.1978. The pesticide content of surface water draining from agricultural fields-A review. J. Envrion. Qual., Vol. 7. no. 4.

Wofford, P.L. and P. Lee. 1995. Results of monitoring for the herbicide MCPA in surface water of the Sacramento River Basin. Environmental Hazards Assessment Program. Report # EH 95-l 1. Dept. of Pesticide Regulation. Sacramento, CA.