Occurrence of Aquatic Toxicity and Dormant-Spray Pesticide Detections in the San Joaquin River Watershed, Winter 1996-97

by

K.P. Bennett[1], C.E. Nordmark[1], J. Schuette[1], H. Feng[2], J. Hernandez[2], and P. Lee[2]

[1]Department of Pesticide Regulation
Environmental Monitoring and Pest Management Branch

[2]California Department of Food and Agriculture, Center for Analytical Chemistry

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STATE OF CALIFORNIA
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ABSTRACT

The presence of organophosphorus pesticides in surface waterways of the San Joaquin Valley is of continuing concern to those charged with the task of protecting quality of the region's waters. During the late 1980's and early 1990's, some waterways in the Valley were found to have contained some pesticide residues at levels high enough to be acutely toxic to aquatic organisms. Thus, the Department of Pesticide Regulation created the Dormant Spray Water Quality Program to prevent aquatic toxicity from organophosphate pesticide residues in the Sacramento and San Joaquin Rivers. The program promotes voluntary efforts such as improved orchard floor management and more careful application methods to prevent off-site movement of these materials. Additionally, an annual monitoring program was implemented in the winter of 1996-97 to measure the concentrations of pesticides and test for aquatic toxicity in these waterways. The organophosphorus insecticides – chlorpyrifos, diazinon, and methidathion – used as dormant sprays during the winter months are of greatest concern because they are used during the period of seasonal rainfall, have been detected most frequently in previous studies, and are acutely toxic to some aquatic invertebrates at relatively low concentrations.

Surface water samples were collected from two sites in the San Joaquin River watershed during the dormant spray application period (December to February). Orestimba Creek, a small creek with drainage from predominantly agricultural land uses, was tested for acute toxicity with *Ceriodaphnia dubia*. The other site, main stem San Joaquin River with multiple discharge inputs, was tested for chronic toxicity with *C. dubia*. Samples from both sites were analyzed for a suite of organophosphorus and carbamate pesticides.

The winter was characterized by unusually high rainfall amounts and resultant flooding which forced growers in the region to alter dormant spray application patterns. Dormant spray use in the study area was down approximately 60 percent from the previous year. During this year's monitoring, maximum pesticide concentrations measured in Orestimba Creek were 0.092 ug/L for diazinon, 0.082 ug/L for dimethoate, and 0.238 ug/L for carbofuran. In the San Joaquin River, the only pesticide detected was diazinon at a maximum concentration of 0.070 ug/L.

Background levels in these waterways, measured prior to the onset of dormant spray applications, indicated no detectable residues for all pesticides. The total estimated amount of diazinon, dimethoate, and carbofuran transported to the San Joaquin River from Orestimba Creek was 7.87, 2.93, and 6.68 lbs., respectively. 85.8 lbs was estimated to have been transported past the monitoring site on the San Joaquin River.

Samples collected from Orestimba Creek were acutely toxic to *C. dubia* on one of fourteen occasions. The source of toxicity was undetermined and did not appear related to the pesticides analyzed. There was no chronic toxicity observed in San Joaquin River samples. As dormant spray pesticide levels in the waterways of the San Joaquin Valley are dependent on numerous and dynamic variables (e.g. use patterns, orchard floor management, and weather), accurate prediction of those levels is difficult, and continued monitoring is recommended during future dormant spray seasons to verify compliance with water quality standards and to monitor the success of the Dormant Spray Water Quality Program.

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DISCLAIMER

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CONVERSION FACTORS AND ABBREVIATIONS

Note: Units used in this report are a mixture of metric and non-metric units designed to provide the reader with information in a familiar format.

Conversion Factors

Multiply	By	To obtain
hectare	2.471	acre
$kilometers^2$	0.3861	$miles^2$
cubic meters per second	35.31	cubic feet per second
meter	3.281	feet
kilometer	0.6214	mile
kilogram	2.204	pound

Temperature can be converted from degrees Celsius (°C) to degrees Fahrenheit (°F) with the following equation: °F = 1.8(°C) + 32

Abbreviations

g, gram	mg, milligram	kg, kilogram
L, liter	ml,milliliter	km, kilometer
ug/L, microgram per liter	mg/L, milligram per liter	ha, hectare
ppm, parts per million	ppb, parts per billion	cms, cubic meter per sec.

INTRODUCTION

The San Joaquin River (SJR) flows from the Sierra Nevada Mountain Range through the northern portion of the San Joaquin Valley to its terminus in the Sacramento-San Joaquin Bay Estuary. The river extends approximately 134 miles from Friant Dam to Stevinson where flows are intermittent, and from Stevinson to Vernalis (about 60 miles) where flows are perennial (Figure 1). The perennial portion of the SJR coincides with a region of intensive agriculture; in 1995, the counties with perennial SJR flow (Merced, San Joaquin, and Stanislaus), reported that over 350 pesticides were applied with a total usage of approximately 24 million pounds (DPR, 1995). Runoff from rain events occurring in the San Joaquin Valley provides short-term increases in river discharge and a mechanism for off-site movement of pesticides. Seasonal rains occur from October to March with little significant rain from June to September. River discharge during the summer is composed of dam releases of snow-melt water for agricultural, urban, recreational and wildlife purposes.

From 1988 to 1990, the Central Valley Regional Water Quality Control Board (CVRWQCB) conducted an aquatic toxicity survey in the San Joaquin Valley. Surface water samples collected from certain reaches of the SJR watershed during this survey were acutely toxic to the water flea, *Ceriodaphnia dubia* (Foe and Connor, 1991). The cause of toxicity was not determined but was attributed to pesticides in general. A further study was conducted in the Valley during the winter of 1991-92, and the resultant toxicity was attributed to the presence of chlorpyrifos and diazinon (Foe and Sheipline, 1993; Foe, 1995; Kuivila and Foe, 1995). Chlorpyrifos (phosphorothioic acid O,O-dietyl O-(3,5,6-tricholoro-2-pyridinyl) ester), diazinon (phosphorothioic acid O,O-diethyl O-[6-methyl-2-(1-methylethyl)-4-pyrimidinyl] ester), and methidathion (phosphorodithioic acid S-[(5-methoxy-2-oxo-1,3,4-thiadiazol-3(2H)-yl)methyl] O,O-dimethyl ester), along with weed oil are commonly used as dormant sprays to control peach twig borer, San Jose scale, European red mite, and brown mite pests on nut and stone fruit trees. The toxicity found in these studies was in violation of the CVRWQCB's narrative water quality objective (Foe, 1995) which states that, "All waters shall be maintained free of toxic substances in concentrations that produce detrimental physiological responses in human, plant, animal, or aquatic life" (CVRWQCB, 1994).

Department of Pesticide Regulation (DPR) staff monitored the SJR watershed during the winters of 1991-92, and 1992-93 and reported the detection of chlorpyrifos, diazinon, and methidathion in 10, 72, and 18 percent of the 108 water samples collected, respectively (Ross *et al.*, 1996). In addition, a study conducted in 1993 by Kuivila and Foe (1995) found diazinon detections in the SJR near Vernalis ranged from 0.148 to 1.07 ug/L[1], on 12 consecutive days. They concluded that chronic toxicity due to diazinon might be problematic at this site. Dormant spray insecticides, at levels acutely toxic to test organisms, also have been reported in Orestimba Creek, a tributary to the SJR, during the 1992-93 dormant spray period (Domagalski, 1995).

Research has shown that cover crops such as clover and oats can reduce the mass of dormant spray insecticides moving offsite in experimental plots (Ross *et al.*, 1997). Additionally, as part of its Dormant Spray Water Quality Program, DPR has established an outreach program that provides suggestions for reducing off-site movement of pesticides from orchards. Measures include the reduction of application rates, integrated pest management, better orchard floor management, and avoidance of mixing and loading near waterways.

This study was conducted to monitor the concentrations of dormant spray insecticides and the occurrence of aquatic toxicity, both acute and chronic, in portions of the SJR watershed. Additional organophosphate and carbamate insecticides were monitored (Table 1) as these chemicals are historically used in the region during the dormant spray season. Acute toxicity to *C. dubia* was examined in a relatively small drainage basin which does not contain major inputs from municipal or industrial sources. Chronic toxicity was examined in the SJR at a point where major agricultural sources contributed to the total flow of the river. Pesticide mass transport was also estimated at both monitoring sites for comparison with future DPR monitoring programs. This study was the first in a five-year-long program designed to investigate water

[1] 1 ug/L is equivalent to 1 part per billion (ppb).

quality in the SJR watershed. A report on a similar study, conducted concurrently in the Sacramento River watershed, is also available (Nordmark, 1997). Long-term monitoring of aquatic toxicity in these watersheds will help DPR scientists evaluate the effectiveness of programs designed to decrease the runoff of dormant spray insecticides.

MATERIALS AND METHODS

Study Area

One site each was selected for acute and chronic toxicity monitoring. Acute toxicity monitoring was conducted at Orestimba Creek, a western tributary to the SJR (Figure 1), where runoff was predominantly agricultural. Flow in this ephemeral stream consists of return irrigation and short-term rain runoff. Soils on the west side of the valley originate from marine shales of the Coastal Range and are generally fine textured and highly erodible (Domagalski, 1995). Monitoring for chronic toxicity was conducted on the SJR near Vernalis, where discharges are received from all of the River's major agricultural tributaries, including the Merced, Tuolumne, and Stanislaus Rivers. Soils on the east side of the valley originate from the Sierra Nevada batholith and are generally coarse textured and well drained (Domagalski, 1995). Discharge records for both monitoring sites were available from collocated gaging stations.

Sample Collection

Background sampling was conducted during the week of December 2, 1996, prior to the onset of the dormant spray season. Sampling was originally scheduled to resume on January 6, 1997 and continue through early March, 1997. However, due to flooding in the region in early January, sampling did not resume until January 20, 1997. Sampling continued until March 7, 1997, when no more dormant sprays were reported to be applied.

Chemical analyses were performed on each water sample collected for both acute and chronic tests. Selected organophosphate and carbamate insecticides were analyzed in two separate analyses with diazinon being analyzed in a third analysis (Table 1). Pesticides included in the analyses were chosen based on pesticide use reports indicating historical use during the dormant spray season in the Central Valley, previous detections in the watershed, established analytical methods, and to standardize analyses between the San Joaquin and Sacramento River studies.

Acute toxicity tests were performed twice per week, with samples collected on Monday and Wednesday. One chronic toxicity test was conducted weekly using water samples collected on Monday, Wednesday, and Friday. Water collected on Monday was used to commence chronic toxicity tests. Water collected on Wednesday and Friday was used to renew chronic test water (see "Pesticide Analysis and Toxicity Tests" section below).

From December 2, 1996 to February 12, 1997, a depth-integrated sampler (D-77), with a 3-liter Teflon® bottle and nozzle, was used to collect water samples from Orestimba Creek at River Road and the SJR near Vernalis. A center channel water sample was collected at the Orestimba Creek site. Three locations, spaced evenly across the SJR, were used to collect samples from the SJR near Vernalis site. This sampling technique has historically been used at this site by U.S. Geological Survey (USGS) personnel. Due to the unusually high flows at the SJR near Vernalis site, key components of the D-77 sampling equipment were lost on February 14. A 10-liter stainless steel bucket was used to collect subsequent samples from center channel for the remainder of the monitoring period. For both methods, sub-samples were composited in a larger 38-liter stainless steel container until 11 to 12 liters were collected. This composited sample was then stored on wet ice until it was delivered to the DPR sampling handling facility in West Sacramento later that day.

Immediately upon arrival at West Sacramento, the samples were split into ten 1-liter glass bottles using a Geotech® 10-port water splitter and sealed with Teflon®-lined lids. For the Orestimba site, 1 liter each was analyzed for organophosphate, diazinon, and carbamate pesticides, 2 liters each were tested for acute toxicity and its corresponding quality control (see Quality Control section below), and 3 liters were stored as backups (10 liters, total). For the SJR near Vernalis site, 1 liter each was analyzed for organophosphate, diazinon, and carbamate pesticides, 2 liters were tested for chronic toxicity, and 4 liters were stored as backups (9 liters, total). Additionally, split samples that would have normally been stored as backups, were provided to the CVRWQCB, for acute aquatic toxicity testing on February 3, and 26, 1997, and chronic testing on February 24, 26, and 28, 1997 to augment their continued research in the region.

Samples to be analyzed for organophosphate and carbamate pesticides were first acidified with 3N hydrochloric acid to a pH between 3.0 and 3.5 to preserve them during storage and transport. Diazinon readily degrades under acidic conditions (Ross *et al.*, 1996), therefore, it was analyzed for in a separate unacidified sample. All samples were delivered to the appropriate laboratory within 24 hours of collection and kept at 4°C until tested or analyzed.

Environmental Measurements

Dissolved oxygen (DO), electrical conductivity (EC), pH, and water temperature were measured on-site for each collection event. Dissolved oxygen content and water temperature were measured with an YSI (Yellow Springs Instruments) DO meter (model 58). Specific conductance or EC was measured with an Orion conductivity meter (model 142). pH was measured with a Sentron pH meter (model 1001). Additionally, alkalinity, hardness, and ammonia were measured by the California Department of Fish and Game's (DFG) Aquatic Toxicology Laboratory (ATL) upon delivery of the toxicity samples. Totals of alkalinity and hardness were measured with a Hach titration kit. Total ammonia was measured with an Orion multi-parameter meter (model 290A) fitted with an Orion ammonia ion selective electrode (model 95-12).

In addition to the above parameters, daily rainfall measurements were obtained from the Burns Creek Dam weather station located approximately 40 miles east of the Orestimba Creek site. Discharge data from two USGS gaging stations were collected. Orestimba Creek discharge was obtained from Orestimba Creek at River Road (station indentification # 11274538), and discharge for the SJR site was obtained from "San Joaquin River near Vernalis" (station identification # 11303500). This information will be used to follow annual changes in pesticide concentrations with respect to fluctuations in flow and will also be useful for modeling efforts, should they be undertaken.

Pesticide Analysis and Toxicity Tests

Chemical Analysis

Pesticide analyses were performed by the California Department of Food and Agriculture Center for Analytical Chemistry and consisted of organophosphate and carbamate screens and diazinon analysis (Table 1). Briefly, the organophosphate samples were extracted with methylene chloride. The extract was passed through sodium sulfate to remove residual water. The extract was evaporated to dryness on a rotary evaporator and brought to 1 mL final volume with acetone. The extract was then analyzed using gas chromatography (GC) with flame photometric detection (FPD). Carbamate samples were also extracted with methylene chloride. The extract was evaporated to a concentrate of 3-5 mL on a rotary evaporator. Sodium sulfate was added to remove residual water. The extract was then reduced to dryness, brought to a final volume of 0.2 mL with methanol, and separated by high performance liquid chromatography (HPLC). The eluant was derivatized with OPA by post column reaction and detected with a fluorescence detector. Comprehensive chemical analytical methods are provided in Appendix A. Method validation results are presented in Appendix B.

Quality control (QC) was conducted in accordance with Standard Operating Procedure QAQC001.00 (DPR, 1996). Data generated during method validation (Appendix B) were used to assess all subsequent study results. Specifically, the data were used to establish warning and control limits. A warning limit is the mean ±2s, where the mean is the average % recovery found in method validation and s, the standard deviation. A control limit is the mean ±3s. Continuing QC samples consisted of water samples spiked with an analyte at a given concentration, extracted and analyzed with each extraction set. An extraction set consists of 1 to 12 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 were compared back to the warning and control limits. If a continuing QC sample exceeded the warning limit, the chemist was notified. If the continuing QC sample exceeded the control limit, corrective measures were taken in the lab to bring conditions back under control. Only field samples potentially low in concentration – below the lower control limit for continuing QC – are noted in the report.

In addition to a continuing QC program, approximately 10 percent of the total number of primary analyses were submitted with field samples as blind spikes and equipment rinse blanks. 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 unknown by the chemist performing the analysis. Rinse blanks were prepared by pouring deionized water over and through the equipment used in sample preparation after a typical cleaning procedure. The resultant rinse water was then collected, processed, and submitted for chemical analysis as a normal field sample to check for any potential contamination.

<u>Toxicity Tests</u>

Two sample splits (1 primary and 1 QC) per collection event from Orestimba Creek were delivered to DFG's ATL for acute toxicity testing. Acute tests were performed in undiluted sample water using 96-hour, static-renewal bioassays with the cladoceran *Ceriodaphnia dubia* in accordance with current U.S. Environmental Protection Agency procedures (U.S. EPA, 1993). One sample per week from the SJR was delivered to DFG's ATL for chronic toxicity testing. Chronic tests were performed using a 7-day bioassay with *C. dubia* in accordance with current U.S. Environmental Protection Agency (1994) procedures. Test organisms used in chronic testing were placed in sample water on day one of the testing, with newly collected test water replenished on days three and five. All bioassays were commenced and renewal water used within 36 hours of sample collection. Data were reported as the percent survival for both acute and chronic tests and the average number of offspring per surviving female adult (fecundity) for the chronic tests.

Quality control for acute toxicity tests consisted of submission of a split sample to DFG's ATL for each sample collected from Orestimba Creek. Samples were labeled only with a sample number and were submitted along with samples from the companion Sacramento River study. The resultant data, collected over the 5-year program, will help DPR scientists better understand and characterize intralaboratory precision of acute toxicity tests performed on ambient water samples.

RESULTS AND DISCUSSION

The results of this monitoring program consist of the following sections: environmental measurements, pesticide use, concentrations, transport, and aquatic toxicity. Basic environmental parameters were measured on site and examined in an historical context. Pesticide loads (concentration x discharge volume) were estimated for those pesticides detected to establish a dormant spray season baseline. Finally, toxicity test results were examined with respect to pesticide residues present in these samples. It should be noted that the following results include data collected during an unusually wet season which included extensive flooding during the first half of winter followed by a dry second half. Any interpretation of the results by the reader should take into account the fact that conditions during this monitoring period were not necessarily characteristic of a typical winter season.

Environmental Measurements

Orestimba Creek

Dissolved oxygen measurements at the Orestimba Creek site ranged from 9.0 to 11.3 mg/L and water temperature there ranged between 8.6 and 12.8 °C (Figure 2). DO here met the CVRWQCB (1994) (Basin Plan) water quality objective of 5.0 mg/L for water bodies designated warm. EC measurements ranged from 348 to 784 uS/cm and pH ranged between 7.7 and 8.6 (Figure 2). There is currently no established State or Federal acute water quality objective for EC for Orestimba Creek or main stem SJR near its confluence with Orestimba Creek. pH measurements fell outside the Basin Plan's water quality objective range of 6.5 to 8.5 on only one occasion and did not appear to be problematic.

Alkalinity ranged from 84 to 178 mg/L and hardness ranged from 121 to 296 mg/L (Figure 2).

There are no established acute water quality objectives or criteria for these parameters. Ammonia concentrations ranged from below a detection limit of 50 ug/L to 237 ug/L (Figure 2). Total ammonia criteria are temperature and pH dependent and therefore, have a wide range of values. Maximum ammonia criteria for data collected at Orestimba Creek are expressed as one-hour average concentrations and range from 1,586 to 9,617 ug/L N (U.S. EPA, 1987). All water quality parameters measured at Orestimba Creek were consistent with values measured there in previous years (USGS, 1995 and 1994).

During the weekly monitoring period from January 20, 1997 to March 7, 1997, rainfall reported at Burns Dam totaled 1.06 inches. Discharge in Orestimba Creek ranged from no flow to 2,240 cfs (Figure 3). Flooding of the San Joaquin River resulted in periods of backwater moving upstream into Orestimba Creek, interrupting discharge measurements as indicated in Figure 3. Records outside those dates were considered reliable. Discharge for the 1996-97 monitoring period was 8.3 and 15.2 times that for equivalent 1995-96 and 1994-95 dormant spray periods, respectively. Rainfall and discharge data were collected from the California Department of Water Resources and USGS, respectively. These data are provisional and subject to change.

San Joaquin River near Vernalis

Dissolved oxygen measurements at the SJR site ranged from 8.9 to 11.1 mg/L and water temperature ranged between 8.8 and 12.1 °C (Figure 4). DO here met the Basin Plan water quality objective of 5.0 mg/L for warm waters. EC measurements ranged from 142 to 556 uS/cm and pH ranged between 6.7 and 8.2 (Figure 4). There is currently no established State or Federal water quality objective for EC for the SJR near Vernalis, and pH values met Basin Plan objectives.

Alkalinity ranged from 25 to 86 mg/L and hardness ranged from 37 to 133 mg/L (Figure 4). The freshwater chronic criterion for alkalinity is a minimum of 20 mg/L and measured values here met U.S. EPA (1987) criterion. There is no established water quality objective or chronic water quality criterion for hardness. Ammonia concentrations ranged from below the detection limit of 50 ug/L to 189 ug/L (Figure 4). Maximum ammonia criteria for data collected at the SJR are expressed as four-day average concentrations and range from 468 to 1,264 ug/L N (U.S. EPA, 1987). All water quality parameters measured at Vernalis were consistent with values measured there in previous years (USGS, 1995 and 1994).

During the weekly monitoring period from January 20, 1997 to March 7, 1997, discharge at the SJR site ranged from 23,000 to 37,500 cfs (Figure 3). Discharge for the 1996-97 monitoring period was 4.4 and 6.4 times that for equivalent 1995-96 and 1994-95 dormant spray periods, respectively. Flooding throughout the study area rendered many acres of nut and stone fruit orchards inaccessible, drastically altering the pesticide use patterns of the region's growers.

Pesticide Use

The San Joaquin Valley is an area of extensive agriculture with over 20 million total pounds of fungicides, herbicides, and insecticides used annually in the tri-county region of Merced, San Joaquin, and Stanislaus Counties (DPR, 1993-5). During the winter months, the organophosphorus insecticides chlorpyrifos, diazinon, and methidathion are used with a dormant oil on nut and stone fruit trees to control pests including peach twig borer (*Anarsia lineatella*) and San Jose scale (*Quadraspidiotus perniciousus*). The best time to achieve control of these pests is December through February, when trees are dormant and better pesticide coverage is possible (Zalom *et al.*, 1995).

During the 1996-97 dormant spray season, in the tri-county study area, there were totals of 7,299, 20,573, and 13,434 pounds of chlorpyrifos, diazinon, and methidathion applied, respectively (Table 2). These data are provisional and subject to change pending final error checks. This season's use represented a 63 percent decrease in the use of chlorpyrifos, 58 percent decrease in the use of diazinon, and 55 percent decrease in the use of methidathion compared to 1995-96. As dormant sprays are preferably applied by ground rigs in clear weather, this marked decrease in use was attributable to intense rainfall and subsequent flooding. These conditions prohibited growers from entering their orchards to manage overwintering pests. The geographical component of the spatial distribution of these chemicals during winter, however, remains consistent over the years as they are predominantly applied to orchard crops (Figures 5 - 7).

Pesticide Detections

Orestimba Creek

No detectable pesticide residues were found in background samples collected during the first week of December. Water samples from Orestimba Creek were found to have residues of diazinon, carbofuran, and dimethoate in 20, 13, and 7 percent of the samples collected, respectively (Table 3). No other pesticides were detected throughout the monitoring period. The maximum diazinon, carbofuran, and dimethoate concentrations detected were 0.092, 0.238, and 0.082 ug/L, respectively.

There is no established water quality standard for diazinon, however, CDFG has suggested that "freshwater aquatic organisms should not be affected unacceptably if the one-hour average concentration does not exceed 0.08 ug/L..." (Menconi and Cox, 1994). Of the 15 samples collected, one (7%) exceeded CDFG's suggested criterion.

Diazinon was detected on February 12, 17, and 19. Potential sources of pesticide contamination in surface waterways include runoff resulting from storm and irrigation events, direct deposition, and deposition in rainwater itself. The temporal distribution of the diazinon detections in relationship to rainfall and discharge indicates that all three detections occurred well after the last seasonal storm and while flows were declining (Figure 8). The presence of diazinon in western tributaries of the San Joaquin River after storm events has been previously documented at levels as high as 3.8 ug/L (Domagalski, 1995; Ross, 1996). Additionally, Ross (1996) has found organophosphorus insecticides in rainwater at concentrations as high as 1.9 ug/L, however, the timing of these detections precludes contamination due to storm-related runoff or wet deposition. Determining the source of flood water flows during this season is beyond the scope of this program, and therefore, no quantitative evaluation of the diazinon source is made.

Carbofuran (2,3-Dihydro-2,2-dimethyl-7-benzofuranyl methyl-carbamate) was detected on March 3 and 5. It is a systemic, broad spectrum, carbamate insecticide used to control various soil and foliar pests. In the Orestimba Creek drainage basin, specifically, all reported use of carbofuran was on alfalfa. Numeric criteria for the protection of freshwater aquatic life have not yet been established for carbofuran. CDFG has suggested an interim water quality criterion of 1.5 ug/L for the protection of aquatic organisms (Menconi and Gray, 1992). Neither of the carbofuran detections exceeded this criterion.

Dimethoate (O,O-dimethyl S-methylcarbamoylmethyl phosphorodithioate) was detected on February 12. It is a systemic, organophosphorus insecticide-acaricide used to control a wide range of pests on numerous crops. Reported use of dimethoate in the Orestimba Creek drainage basin was for assorted row crops. Numeric criteria for the protection of freshwater aquatic life have not yet been established for dimethoate. CDFG has, however, suggested that previously recorded levels of dimethoate in the Sacramento-San Joaquin River system do not pose a significant hazard to aquatic organisms (Siepmann and Yargeau, 1996).

San Joaquin River near Vernalis

No detectable pesticide residues were found in background samples collected during the first week of December. Water samples from the SJR near Vernalis were found to have diazinon residues in 3 of the 24 (12 %) samples collected. The maximum concentration was 0.070 ug/L. No other pesticides were detected there throughout the monitoring period.

CDFG has suggested that "freshwater aquatic organisms should not be affected unacceptably if the four-day average concentration does not exceed 0.04 ug/L..." (Menconi and Cox, 1994). This criterion was exceeded on three consecutive sampling days (12%), and the diazinon concentration fell below measurable amounts 5 days after the initial detection. Temporal distribution of the diazinon detections in relationship to rainfall and discharge indicates that the detections occurred after a seasonal storm event on January 20 - 22, the first detection of which occurred on January 24 (Figure 9). Elevated concentrations of dormant spray pesticides have previously been observed at Vernalis on 12 consecutive days, initially detected approximately one day following a storm event (Kuivila and Foe, 1995). The lag in response time for this year's detections, the lower diazinon concentrations, and the absence of chlorpyrifos and methidathion, cannot be accounted for in this report but were likely due in part to flood conditions which contributed a significant source of dilution water and altered pesticide use patterns.

Quality Control

Results from the laboratory's continuing QC are presented in Appendix C and blind spike results are presented in Appendix D. Since samples for both the San Joaquin (study 155) and Sacramento River (study 154) studies were analyzed at the same time, the tables for all QC results contain data from both studies. Table entries in Appendix C with asterisks indicate that the spike analyzed with the extraction set fell below the lower control limit and the resultant concentration may have been under estimated. Table entries in Appendix D with asterisks indicate that the blind spiked sample recovery was below the lower control limit.

Recoveries for fonofos were particularly poor. Additional work on fonofos will be done to improve recoveries, however, if satisfactory results cannot be attained by the start of the next monitoring season, it will be removed from the screen. There was some difficulty with the diazinon analysis; 5 of 23 extraction set spikes fell below the lower control limit. Diazinon concentrations in the samples collected on February 3, 5, 19, March 5 and 7 – all reported as none detected – may have been underestimated.

Mass Transport

Pesticide loads were calculated by multiplying the daily mean discharge volume at the sampling site times the instantaneous pesticide concentration of individual samples from that site. The integrated load over the period of observation is the total mass of the detected pesticide transported past the monitoring site. The estimated mass of diazinon, carbofuran, and dimethoate transported to the SJR from Orestimba Creek was 7.87, 6.68, and 2.93 lbs, respectively. The estimated mass of diazinon transported in the SJR past Vernalis was 85.8 lbs. Because the typical mechanism for the off-site movement of diazinon was substantially altered by flooding, no comparison of mass transport with previous study findings is made. The above estimated values for pesticide mass transported will be used as indicators of the success of changes in orchard management practices implemented in the watershed.

Toxicity Tests

Orestimba Creek

Ceriodaphnia dubia survival ranged from 40 to 100 percent for 96-hour acute toxicity samples from Orestimba Creek (Table 3). Split samples collected on January 29 were significantly different from the control (Dunnett's test, $p<0.05$) indicating that these samples were acutely toxic to the test species. There were no pesticides detected in those samples, and all water quality parameters were within acceptable limits. Based on the data collected, no determination can be made on the cause of the mortality. Raw data for acute bioassays performed by ATL are presented in Appendix E. Additionally, the bioassay performed on the split February 3 sample, provided to the CVRWQCB and tested by the University of California at Davis (UCD), displayed 100 percent survival, as did the control. This data was critical in filling the toxicological data gap in DPR's monitoring that resulted from the inadvertent termination of the bioassay by CDFG's ATL. The February 26 split sample, provided to the CVRWQCB and tested by UCD, also displayed 100 percent survival, as did the control, and was consistent with ATL's results. Seven percent (1 in 14) of the samples collected at Orestimba Creek were acutely toxic.

The highest measured concentration of diazinon, 0.092 ug/L, along with dimethoate at 0.082 ug/L, was observed in the February 12 samples. Other organophosphorus pesticides have shown additive toxicity to *C. dubia* (CDFG, 1992), however, these two samples demonstrated 85 and 100 percent survival indicating minimal, if any, additive effects. Diazinon was also present in the samples collected on February 17 at 0.04 ug/L, one-half the CDFG suggested criterion. The depressed survival rates for those toxicity tests were 80 and 60 percent in the two split samples. Given the data observed, no direct correlation between the lower survival rates and the presence of diazinon in these samples could be made.

In order to obtain a preliminary characterization of intralaboratory precision of acute toxicity tests performed on ambient water samples, split samples were sent to ATL with each primary toxicity sample. These data are presented in the "Acute Toxicity B" column of Table 3. Non-parametric statistical methods were to be used to examine the agreement between the determination of toxicity in split samples, and linear regression analysis was to be used to examine the agreement in proportion mortality. These statistical analyses were not performed due to the insufficient number of partial mortalities throughout the monitoring period.

San Joaquin River near Vernalis

Ceriodaphnia dubia displayed either 90 or 100 percent survival in 7-day chronic toxicity tests with water samples collected at the SJR near Vernalis (Table 3).

Statistical analysis (Fisher's Exact test) showed no significant differences between the samples and controls indicating no chronic toxicity. Diazinon was present above the suggested chronic criterion of 0.04 ug/L during two bioassays, one terminating on January 28 and the other on February 4. These bioassays displayed 90 and 100 percent survival, respectively. Raw data for chronic bioassays performed by ATL are presented in Appendix F. Additionally, two bioassays performed by UCD with split samples collected on February 3-7 and February 24-28 for CVRWQCB demonstrated 100 percent survival, as did the control.

Fecundity ranged from an average of 22.5 to 42.5 offspring per adult and 14.8 to 27.2 offspring per adult in field samples and controls, respectively (Figure 3). Observed fecundity represented an average 37.4 percent level of increased reproduction in the ambient samples over the laboratory control. Statistical analysis (Dunnett's test, $p<0.05$) of reproduction data indicated that, in 6 of 8 chronic tests, there was a significant difference between the control and sample. Reproduction data is often analyzed to determine whether or not there were potential detrimental effects due to exposure at sublethal levels of the toxicant(s) present. In all instances during this monitoring period, the reproduction in the sample was greater than that of the control (Figure 10). This observation is not unusual and can be partly attributed to nutritional benefits *C. dubia* derived from feeding on naturally occurring particulate matter (Stewart, 1996).

CONCLUSIONS

During the winter of 1996-97, water quality parameters measured at Orestimba Creek and the SJR near Vernalis were consistent with values from previous years and generally met established California objectives or Federal criteria. Discharge throughout the watershed was, however, substantially greater than previous years due to intense rainfall which resulted in breeched and broken levees, flooding, and reduced dormant spray insecticide use in Merced, San Joaquin, and Stanislaus counties.

At Orestimba Creek, diazinon, carbofuran, and dimethoate residues were found in surface water samples. Diazinon was detected most frequently and was the only pesticide to exceed recommended acute freshwater quality criteria. At the SJR near Vernalis, diazinon was the only pesticide detected and it exceeded the recommended chronic freshwater quality criterion. The maximum concentrations at both sites, however, were less than those found in previous studies during the equivalent time frame; this was largely due to flood conditions.

Pesticide mass transported to the SJR from Orestimba Creek was less than 8 lbs each of diazinon, carbofuran, and dimethoate. The estimated mass of diazinon transported in the SJR past Vernalis was an order of magnitude greater and was not compared to values measured in previous studies due to the inability to conclusively determine discharge sources under flood conditions.

Acute toxicity was observed on one day of sampling at Orestimba Creek, and no chronic toxicity was observed at the SJR near Vernalis. The toxicity of water samples provides the principle indicator of compliance regardless of the pesticide concentration level. However, since toxicity tests lack causal specificity, DPR in cooperation with CVRWQCB and CDFG prepared quantitative response limits (QRLs) for chlorpyrifos, diazinon, and methidathion. QRLs help DPR determine whether pesticide concentrations reach levels attributable to aquatic toxicity. QRLs neither present an enforceable standard nor supersede the CVRWQCB's narrative toxicity standard. Most importantly, QRLs provide a benchmark to gauge whether the concentrations of dormant spray pesticides correspond to verified aquatic toxicity. The proposed QRL values for acute and chronic exposures are as follows: chlorpyrifos – 0.04 and 0.02 ug/L, diazinon – 0.08 and 0.04 ug/L, and methidathion – 1.1 and 0.83 ug/L, respectively. The acute toxicity observed at Orestimba Creek could not be correlated with measured pesticide concentrations. This study will continue into its second year during winter 1997-98 as part of DPR's Dormant Spray Water Quality Program.

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