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MEMORANDUM

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DATE: January 5, 1999

SUBJECT: PRELIMINARY RESULTS OF ACUTE AND CHRONIC TOXICITY TESTING OF SURFACE WATER MONITORED IN THE SAN JOAQUIN RIVER WATERSHED, WINTER 1997-98

SCOPE OF THIS MEMORANDUM

This memorandum provides results of water sampling conducted on the San Joaquin River (SJR) by the Department of Pesticide Regulation (DPR) for the Dormant Spray Water Quality Project. Information presented is from December 1, 1997 to March 6, 1998 and includes results from chemical analyses conducted by the California Department of Food and Agriculture (CDFA) and bioassays conducted by the California Department of Fish and Game (DFG). This memorandum summarizes one year of a five-year study begun in 1996, designed to monitor dormant spray insecticides (chlorpyrifos, diazinon, and methidathion) in the SJR watershed. In an effort to obtain more information about pesticide residues in surface water, samples were analyzed for additional insecticides as well as selected herbicides. This memorandum does not include an in-depth interpretation of the data which will be provided in the final report.

BACKGROUND

The SJR flows from the Sierra Nevada Mountain Range, the flow then heads north through the San Joaquin Valley and terminates in the Sacramento-San Joaquin Delta. 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 river basin including tributary watersheds, drains approximately 15,880 square miles (Central Valley Regional Water Quality Control Board [CVRWQCB], 1994). Runoff from rainfall occurring in the San Joaquin Valley and Sierra Nevada foothills during the rainy season, October to March, creates short term increases in river discharge. With little significant rain from June to September, river discharge during the summer is composed of dam releases of snow-melt water which is subsequently used for agricultural, urban, recreational, and wildlife purposes.

The dormant spray season for nut and stone fruit trees coincides with the rainy season. During this period dormant spray insecticides, mainly chlorpyrifos, diazinon, and methidathion, are applied along with weed oil to control peach twig borer, San Jose scale, European red mite, and brown mite pests. Rainfall and subsequent surface runoff from agricultural areas provides a mechanism for off-site movement of pesticides to the SJR. From 1988 to 1990, the 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. 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). The toxicity found in these studies was in violation of 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).

The DPR 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. Of these positive samples 2, 13, and 1 percent respectively, exceeded the LC_{50} for *C. dubia* indicating potential acute toxicity to this organism (Ross, et al., 1997). In addition, in a 1993 CVRWQCB study, diazinon concentrations in the SJR at Vernalis ranged from 0.148 to 1.07 μg/L on 12 consecutive days, and the authors concluded that chronic toxicity due to diazinon might be problematic at this site (Kuivila and Foe, 1995). Diazinon was also detected at levels acutely toxic to *C. dubia* in Orestimba Creek, a tributary to the SJR, during the 1992-93 dormant spray period (Domagalski, 1995). Consequently, methods designed to reduce the mass of dormant spray insecticides leaving target areas have been under investigation by DPR and growers (Ross, et al., 1997; Ando, 1996; Anonymous, 1996; Biermann, 1996).

During the winter of 1996-97, DPR conducted toxicity monitoring at two sites in the SJR Watershed (Bennett et al., 1998). The first half of winter was unusually wet due to flooding, followed by unseasonably dry weather during the second half of winter. Water samples from Orestimba Creek contained residues of diazinon, carbofuran, and dimethoate in 20, 13, and 7 percent of the 15 samples collected, respectively. The maximum diazinon, carbofuran, and dimethoate concentrations detected were 0.092, 0.238, and 0.082 ug/L, respectively. Twelve percent of the 24 water samples from the SJR near Vernalis contained diazinon residues, with a maximum concentration of 0.070 ug/L. *Ceriodaphnia dubia* survival ranged from 40 to 100 percent for acute toxicity tests from Orestimba Creek. Only one of these samples collected on January 29, 1997 was significantly different than the control. However, there were no pesticides detected in this sample. Chronic toxicity was not detected in the 8 weekly sets of water samples collected from the SJR near Vernalis.

A recently published U.S. Geological Survey (USGS) report of an investigation of pesticides in storm runoff from agricultural areas at a site along the Tuolumne River and from urban drains in Modesto, California found six different pesticides in the predominantly agricultural samples, and 15 different pesticides in the mainly urban runoff samples (Kratzer, 1998). Diazinon and chlorpyrifos were the insecticides detected in agricultural runoff in 100 and 88 percent of the 8 samples, respectively. Diazinon, carbaryl, chlorpyrifos, and malathion were each detected in 100 percent of the 10 urban samples collected. The herbicides simazine, napropamide, and dacthal were detected in 100 percent of the 8 samples collected from the agricultural runoff site. Metolachlor was also found in 88 percent of the samples. Simazine, dacthal, and trifluralin were detected in all the samples collected in the urban runoff, and metolachlor, EPTC, benfluralin, pendimethalin, prometon, napropamide, and propanil were detected in 10 to 90 percent of the samples.

This study is part of a five-year effort to monitor the occurrence of aquatic toxicity to *C. dubia* in the SJR watershed. Monitoring is conducted specifically during winter months for organophosphate and carbamate insecticides that are historically applied to dormant nut and stone fruit orchards (Table 1). These insecticides have been found to enter the SJR with surface water runoff. Orestimba Creek, a small tributary of the SJR, was monitored for acute toxicity since historically small tributaries carry higher insecticide concentrations then the mainstem of the SJR. Orestimba Creek contains runoff from the coastal range and agricultural areas in the valley floor. SJR at Vernalis, a site downstream from agriculture and urban areas, yet above tidal influence from the delta, was examined for chronic toxicity. In addition to gain more information about pesticide residues in state surface waters, samples will also be analyzed for selected herbicides (Table 1). A companion study was also conducted to monitor pesticide levels and toxicity in the Sacramento River (Nordmark, 1998). Long-term monitoring of acute and chronic toxicity will help scientists at DPR evaluate the effectiveness of programs designed to decrease the runoff of dormant spray insecticides.

MATERIALS AND METHODS

Site Description

One site each was selected for acute and chronic toxicity monitoring. Acute toxicity was monitored in Orestimba Creek, a western tributary to the SJR, where runoff in the winter is composed of drainage from the Coastal Range and from agricultural areas in the watershed (Figure 1). Samples for chronic toxicity were collected from the SJR near Vernalis, where discharges from the River's major agricultural tributaries, including the Merced, Tuolumne, and Stanislaus Rivers, are received. Discharge records for both monitoring sites were available from collocated gaging stations.

Sample Collection

Background samples were collected during the week of December 1, 1997, prior to the onset of the dormant spray season. Dormant-season sampling began on January 7, 1998, and continued through March 6, 1998, when dormant-spray applications ceased.

Chemical analyses were performed on each water sample that was collected for acute and chronic tests. Pesticides included in our analyses were chosen based on historical use during the dormant spray season in the watershed (DPR, 1995), previous detections in the watershed, and to standardize analyses between the Sacramento and SJR studies. For this study, organophospahate and carbamate insecticides, and soil applied herbicides (triazine herbicides, diuron, and bromacil) were analyzed in three separate screen analyses with diazinon being analyzed in a fourth analysis (Table 1).

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 begin the chronic toxicity tests. Water collected on Wednesday and Friday was used to renew chronic test water (see below).

Water samples were collected at both Orestimba Creek at River Road and the SJR near Vernalis using a depth-integrated sampler (D-77), equipped with a Teflon® bottle and nozzle. A center channel water sample was collected at the Orestimba Creek site until February 2, 1998, when the discharge pipe just up stream from the the River Road Bridge began to flow. Thereafter, water was collected at three locations, spaced evenly across Orestimba Creek on the downstream side of the bridge. On one occasion (January 12, 1998) discharge was so low that the D-77 sampler could not be used and a center channel grab sample was collected using a clean stainless steel bucket. Three locations across the stream's width were used to collect samples from the SJR at the Vernalis site, with sample collection weighted more heavily on the west side of the river where a greater portion of flow occurs. At both sites, sub-samples were composited in a larger 38-liter stainless steel container until 12 liters were collected. This composited sample was stored on wet ice until it was delivered to DPR's West Sacramento field office later that day.

Samples were transported to the field office and split using a Geotech® 10-port splitter, into nine 1-liter amber glass bottles with Teflon® lined caps. For both sites, two 1-liter samples were submitted to DFG for toxicity testing. Four 1-liter samples were submitted for chemical analyses: one each for the organophosphate, carbamate, diazinon, and herbicide analyses. Two 1-liter backups were stored at West Sacramento and one-liter was used for acidification purposes (see below). Samples designated for organophosphate and carbamate chemical analysis were preserved by acidification with 3N hydrochloric acid to a pH of between 3.0 to 3.5. Most organophosphate and carbamate pesticides are sufficiently preserved at this pH (Ross et al., 1996). Diazinon, however, rapidly degrades under acidic conditions and therefore was analyzed from a separate un-acidified sample. Herbicide samples are stable enough without acidification so were not acidified.

Samples were stored in a 4°C refrigerator until transported to the appropriate laboratory (on wet ice) for analysis. All primary samples were delivered to the testing laboratory the same day they were collected with the exception of when there was a Monday holiday, then samples were delivered early on Tuesdays.

Environmental Measurements

Temperature and dissolved oxygen (DO) were measured *in situ,* and pH and electrical conductivity (EC) were measured on site. Water temperature and DO were measured with an YSI (Yellow Springs Instruments®) DO meter (model 57). Water pH was measured with a Sentron® pH meter (model 1001) or the Orion® Quickcheck (model 106) pH meter. EC was measured with an Orion® conductivity meter (model 142). Additionally, alkalinity, hardness, and ammonia were measured by DFG's aquatic toxicity lab (ATL) upon delivery of their 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).

Daily rainfall and discharge data were also gathered for the study area. Daily rainfall measurements were obtained courtesy of the Modesto Irrigation District office in Modesto, California about 15 miles east of the Vernalis site (Modesto Irrigation District, 1998) and Yancey Lumber and Hardware in Patterson, California, eight miles north west of the Orestimba Creek site (Figure 1) (Kittridge, 1998). Discharge data were collected at collocated gaging stations at both the SJR at Vernalis and Orestimba Creek at River Road. Preliminary data for these two gaging stations were transmitted courtesy of USGS. Rainfall and discharge 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, if they should be undertaken.

Pesticide Analysis and Toxicity Tests

Pesticide analyses were performed by the CDFA Center for Analytical Chemistry. The organophosphate insecticides were analyzed using gas chromatography (GC) equipped with a flame photometric detector. The carbamate insecticides were analyzed using high performance liquid chromatography (HPLC), post column-derivatization and a fluorescence detector. The herbicides (triazine herbicides, diuron, and bromacil) were analyzed by both HPLC equipped with a UV detector and by GC equipped with a nitrogen phosphorus detector. The pesticides and reporting limits are listed in Table 1. Detailed analytical methods will be provided in the final report.

Quality control (QC) for the chemistry portion of this study was conducted in accordance with Standard Operating Procedure QAQC001.00 (DPR, 1996) and consisted of a continuing QC program, plus the submission of five rinse blanks of the splitting equipment and 32 blind spikes submitted for the Sacramento and San Joaquin studies. Blind spike and continuing QC results for each of the analytical screens are presented in Tables 2 though 6. Study 166 and 167 refer to the Sacramento and SJR studies, respectively. There were no detections of any pesticides in any of the five rinse blank samples (not in tables). The 32 blind spikes were submitted for both studies along with the regular field samples. The blind spikes contained 58 chemical analytes (Table 2). More detailed quality control data, including method development, the establishment of control limits, spike recoveries and analysis of QC will be included in the final report.

Toxicity Tests

For Orestimba Creek, two samples (1 primary/1 quality control) per collection event 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 *C. dubia* in accordance with current U. S. Environmental Protection Agency procedures (U.S. EPA, 1993). From the SJR, one sample per collection event 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. EPA (1994) procedures. Test organisms used in chronic testing were placed in sample water on day one of the testing, with test water replenished on days three and five with new water collected from the site on Wednesdays and Thursdays. 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 female adult (fecundity) for the chronic tests.

RESULTS

The following results include data collected during a wet season (DWR, 1998) which included almost daily measurable rains from the end of December through the end of February. River discharge remained high from January through the end of sampling in March compared to historical levels for these months (Anderson et al., 1995). Any interpretation of the results by the reader should take into account that conditions during the monitoring period were not necessarily characteristic of an average winter season.

Environmental Measurements

Orestimba Creek

Temperature measurements at the Orestimba Creek site ranged between 9.2 and 13° C (Figure 2). DO ranged from 9.6 to 11 mg/L (Figure 2), with percent saturation ranging from 88 to 98 percent. pH ranged between 6.9 and 8.5, and EC measurements ranged from 301 to 1,119 μS/cm. Alkalinity ranged from 94 to 230 mg/L and hardness was between 122 and 510 mg/L. Ammonia concentrations ranged from below the detection limit of 50 μg/L to 2,100 μg/L.

During the weekly monitoring period from January 5 to March 4, 1998, rainfall reported at Patterson, California totaled 11.8 inches (Kettridge, 1998) (Figure 3). Discharge at the USGS gaging station along Orestimba Creek at River Road ranged from no flow to 2,250 cfs. These data are provisional and subject to change.

San Joaquin River near Vernalis

Water temperature measurements at the SJR site ranged from 9.5 to 13°C (Figure 4). DO ranged from 7.0 to 11 mg/L (Figure 4), with percent saturation ranging from 65 to 95 percent. pH ranged from 7.1 to 8.3, and EC measurements were between 177 and 800. Alkalinity ranged from 46 to 122 mg/L and hardness from 48 to 182 mg/L. Ammonia concentrations ranged from the detection limit of 50 μg/L to 818 μg/L.

During the weekly monitoring period from January 5 to March 6, 1998, discharge at the SJR site ranged from 1,960 to 35,000 cfs (Figure 5). SJR discharge was near the flood warning stage for several weeks during the sampling period. Rainfall data collected by the Modesto Irrigation District totaled 12.7 inches during the same period (MID, 1998).

Pesticide Concentrations and Toxicity Data

Pesticide Concentrations

Orestimba Creek

Of the eight organophosphates analyzed, chlorpyrifos, diazinon, and methyl parathion were detected in Orestimba Creek (Table 7). Chlorpyrifos and methyl parathion were each detected once at 0.093 and 0.190 parts per billion (ppb) in the same sample collected January 26, 1998, respectively. Diazinon was detected in three of 18 samples (17 percent) collected at the Orestimba Creek site with concentrations ranging from 0.059 to 0.139 ppb (Table 7). Diazinon was detected on January 12, and then again in the samples collected on February 2, and 4. Four of the nine herbicides analyzed were detected in Orestimba Creek. Bromacil was detected in three of the 18 samples (17 percent) with concentrations ranging from 0.066 to 0.115 ppb. Cyanazine was detected in one of 18 samples (6 percent) at 0.25 ppb. Diuron was detected in six of 18 samples (33 percent) ranging from 0.078 to 0.388 ppb and simazine was detected in five of 18 samples (28 percent) ranging from 0.063 to 0.711 ppb. Three of the samples had three herbicide detections. These samples were collected on December 1, 1997, January 12, and January 19, 1998. After February 4, 1998, there were no detections of any pesticides.

For acute toxicity tests, three of 18 samples had significantly reduced survival compared to the control. The three samples were collected on January 21, and February 4, and 23. On January 21 and February 23, pesticides analyzed in this study were all below detection limits. On February 4, diazinon, diuron, and simazine were detected. Possible relationships between the occurrence of pesticides and aquatic toxicity will be investigated in the final report.

San Joaquin River

Of the eight organophosphates analyzed, diazinon, and methidathion were detected. Diazinon was detected in the SJR in 10 of 30 samples collected at Vernalis (Table 6). These detections came in two groupings. The first detection occurred on January 7 and was at the detection limit. There was no detection January 9. On January 12, 14, and 16 diazinon was again detected at concentrations ranging from 0.063 to 0.102 ppb. The second group of detections began on January 30 and continued through February 11 with concentrations ranging from 0.042 to 0.093 ppb. Methidathion was detected in three samples (10 percent) collected January 7, 12, and February 2. The three detections ranged from 0.053 to 0.112 ppb and coincided with diazinon detections. The herbicides bromacil, cyanazine, diuron, and simazine were also detected in the SJR.

Bromacil and cyanazine were detected in four (13 percent) and two of 30 samples (7 percent), respectively. Diuron was detected in all samples at concentrations ranging from 0.056 to 2.95 ppb. Simazine was detected in 16 samples (53 percent) with levels ranging from 0.050 to 0.470 ppb.

There was no *C. dubia* survival in the chronic toxicity test sample collected on February 2 with renewal water collected February 4. The survival decreased from 90 to 40 percent between 72 and 96 hours. After 96 hours the sample fell to zero percent survival while the corresponding control had 100 percent survival. The sample collected February 2 had detectable levels of diazinon, methidathion, diuron, and simazine. The other chronic toxicity tests had survivals ranging from 80 percent to 100 percent with corresponding control survival from 80 percent to 100 percent. In addition, there were three failed tests (January 26, February 9, and February 16) that resulted from poor survival in the control. The samples were retested from 6 to 8 days after collection. Retest data are presented and the status is indicated in table 7. Statistical analysis of reproduction data will be included in the final report as it may be used, in conjunction with chemical data, to identify potential sub-lethal effects in the test organisms.

Please contact me if you have any questions.

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Table 1. California Department of Food and Agriculture, Center for Analytical Chemistry organophosphate and carbamate insecticide and herbicide screens for the San Joaquin River toxicity monitoring study.

Organophosphate Pesticides in Surface Water by GC Method: GC/FPD		**N-Methyl Carbamate in Surface Water by HPLC Method: HPLC/Post Column-fluorescence**		**Herbicides in Surface Water by HPLC Method: HPLC/UV detection and GC/Nitrogen Phosphorus detection (NPD)**	
Compound	**Reporting Limit (µg/L)**	**Compound**	**Reporting Limit (µg/L)**	**Compound**	**Reporting Limit (µg/L)**
Chlorpyrifos	0.04	Carbaryl	0.05	Atrazine	0.05
Diazinon[1]	0.04	Carbofuran	0.05	Bromacil	0.05
Dimethoate (Cygon)	0.05			Diuron	0.05
Fonofos	0.05			Cyanazine	0.2
Malathion	0.05			Hexazinone	0.2
Methidathion	0.05			Metribuzin	0.2
Methyl parathion	0.05			Prometon	0.05
Phosmet	0.05			Prometryn	0.05
				Simazine	0.05

[1] Diazinon was analyzed from a separate, unpreserved, split sample. Other OP and CB chemical samples were preserved with 3N HCl to a pH of 3-3.5 to retard analyte degradation. See text.

Table 2. Blind Spike Recoveries for the San Joaquin River and Sacramento River Studies.

Extraction Date	Study Number	Sample Number	Screen	Chemical	Spike Level	Recovery	Percent Recovery
1/9/98	[a]166	496	Triazine	Diuron	0.2	0.205	103
				Metribuzin	0.5	0.512	102
1/7/98	167	73	Organophosphate	Fonofos	0.2	0.197	98.5
				Malathion	0.5	0.536	107
				Phosmet	0.1	0.101	101
1/14/98	167	435	Triazine	Atrazine	0.5	0.417	83.4
				Simazine	0.2	0.165	82.5
1/13/98	166	86	Carbamate	Carbaryl	0.1	0.101	101
				Carbofuran	0.2	0.198	99.0
1/14/98	167	85	Diazinon	Diazinon	0.5	0.493	98.6
1/14/98	166	87	Organophosphate	Chlorpyrifos	0.2	0.184	92.0
				Methidathion	0.1	0.098	98.0
1/20/98	166	497	Triazine	Hexazinone	0.5	0.454	90.8
				Cyanazine	0.5	0.537	107
1/20/98	167	86	Organophosphate	Chlorpyrifos	0.2	0.183	91.5
				Methidathion	0.2	0.23	115
				Dimethoate	0.1	0.109	109
1/29/98	166	498	Triazine	Hexazinone	0.5	0.483	96.6
				Simazine	0.1	0.113	113
1/27/98	167	209	Carbamate	Carbaryl	0.2	0.173	86.5
				Carbofuran	0.1	0.0983	98.3
1/26/98	167	208	Organophosphate	Methyl Parathion	0.2	0.19	95.0
				Chlorpyrifos	0.1	0.093	93.0
1/26/98	167	210	Diazinon	Diazinon	0.2	0.1	50.0 *
1/29/98	167	211	Organophosphate	Fonofos	0.2	0.157	78.5
				Chlorpyrifos	0.2	0.16	80.0
2/2/98	166	499	Triazine	Bromacil	0.2	0.207	104
				Prometryn	0.5	0.465	93.0
2/2/98	167	213	Diazinon	Diazinon	0.1	0.079	79.0
2/2/98	167	212	Organophosphate	Dimethoate	0.2	0.203	102
				Methidathion	0.1	0.103	103
2/9/98	167	215	Diazinon	Diazinon	0.3	0.287	95.7
2/9/98	167	214	Organophosphate	Fonofos	0.1	0.094	94.0
				Phosmet	0.2	0.346	173/90 **
2/9/98	166	424	Triazine	Atrazine	0.2	0.187	93.5
				Diuron	0.5	0.433	86.6
2/10/98	167	216	Carbamate	Carbaryl	0.3	0.306	102
				Carbofuran	0.2	0.208	104
2/11/98	167	461	Triazine	Metribuzin	0.5	0.517	103
2/13/98	167	217	Organophosphate	Dimethoate	0.1	0.099	99.0
				Methidathion	0.2	0.197	98.5
2/17/98	166	244	Organophosphate	Chlorpyrifos	0.1	0.103	103
				Malathion	0.2	0.21	105
2/13/98	166	246	Diazinon	Diazinon	0.1	0.106	106
2/23/98	166	449	Triazine	Hexazinone	0.5	0.617	123
				Prometryn	0.3	0.267	89.0
2/23/98	166	450	Triazine	Bromacil	0.2	0.211	106
				Prometon	0.5	0.442	88.4
2/23/98	166	248	Diazinon	Diazinon	0.1	0.084	84.0
2/23/98	166	247	Organophosphate	Fonofos	0.2	0.176	88.0
				Phosmet	0.1	0.114	114
2/25/98	167	265	Organophosphate	Dimethoate	0.2	0.179	89.5
				Methidathion	0.1	0.094	94.0
2/24/98	166	249	Carbamate	Carbaryl	0.1	0.1	100
				Carbofuran	0.2	0.2	100
2/26/98	166	252	Diazinon	Diazinon	0.2	0.180	90.0
2/26/98	166	250	Organophosphate	Chlorpyrifos	0.2	0.114	57.0 *
				Methyl Parathion	0.2	0.176	88.0

[a] 166 refers to the study number for the Sacramento River, 167 refers to the SJR.

* sample may have been spiked at half the reported spike level

**a backup of this blind spike was run, resulting in a 90% recovery

Table 3. Continuing Quality Control- Organophosphate Screen

Extraction Date	Sample Numbers	Percent Recovery							
		Chlorpyrifos	Diazinon	Dimethoate	Fonofos	Methyl Parathion	Malathion	Methidathion	Phosmet
12/2/98	166-1, 6. 167-6.	101	92.0	115	94.0	105	103	108	115
12/4/98	166-11,16. 167-4, 11, 16.	92.0	85.0	101	90.0	93.0	100.0	104	113
12/8/98	166-21. 167-11,21.	102	103	112	105	107	106	110	116
1/5/98	166-26, 31. 167-26.	97.0	87.5	108	80.9	104	105	107	114
1/7/98	166-36, 41. 167-31, 73.	84.0	96.0	109	86.0	103	99.0	111	111
1/12/98	166-46, 51.	90.0	92.0	113	86.0	104	95.0	114	98.8
1/14/98	166-62, 67, 54, 59, 87. 167-41, 46, 51, 56.	103	102	97.2	97.8	106	105	109	101
1/20/98	166-74, 84, 79. 167-61, 66, 71, 86.	94.0	94.0	100	92.0	108	104	95.0	94.8
1/22/98	166-91, 96. 167-90, 95, 100.	91.3	92.3	103	94.1	102	99.2	86.8	94.2
1/26/98	166-101, 106. 167-105, 208.	90.0	96.0	112	84.0	111	107	93.0	101
1/27/98	166-109, 114. 167-110, 115.	102	93.0	102	94.3	111	106	117	115
1/29/98	166-119, 124. 167-120, 125, 211.	91.0	88.0	114	92.0	109	103	86.0	116
2/2/98	166-129. 167-130, 135, 212.	94.0	90.0	107	89.0	108	107	91.0	92.6
2/3/98	166-134, 139 167-140,145	92.0	92.0	113	89.0	107	103	91.0	92.6
2/5/98	166-144,149. 167-74, 79.	92.5	85.0	102	96.8	99.5	97.0	102	92.0
2/9/98	166-154,159. 167-84,214.	89.0	89.0	84.0	86.0	109	98.0	97.0	107
2/11/98	166-162, 167. 167-159.	79.0	77.0	85.0	87.0	87.0	83.0	83.0	92.4
2/13/98	166-172, 177. 167-164, 169, 217.	98.6	95.0	102	89.0	101	97.6	105	114
2/17/98	166-182,244,196,201. 167-174,157,179,184.	92.0	98.0	96.0	92.0	106	98.0	99.0	105
2/20/98	166-187, 192. 167-189,194,199.	87.0	91.0	100	85.0	95.0	92.0	92.0	103
2/23/98	166-207, 247. 167-204.	98.5	89.0	96.5	91.9	102	99.0	100	91.0
2/25/98	166-212, 217. 167-219, 224, 265.	85.0	94.0	96.0	89.0	99.0	97.0	98.0	97.4
2/26/98	166-222,227,232,250. 167-229,234.	90.0	98.0	84.0	99.0	98.0	104	90.4	84.0
3/4/98	166-240,254. 167-244, 249.	103	99.6	100	94.8	101	102	103	98.2
3/2/98	166-235. 167-239.	84.0	92.0	71.0	94.0	88.0	97.0	89.8	79.0
3/6/98	166-259,264. 167-254,259.	96.0	99.0	94.0	99.0	96.0	101	102	91.0
3/10/98	166-269,274. 167-266	87.2	86.0	85.2	96.0	91.2	91.2	96.8	91.4
Average Recovery		92.4	92.1	100	91.5	102	99.9	99.1	101
Standard Deviation		6.13	5.68	11.22	5.51	6.83	5.55	9.16	10.83
CV		6.63	6.17	11.20	6.02	6.70	5.55	9.24	10.74
Upper Control Limit		116	122	116	102	116	114	124	118
Upper Warning Limit		110	113	110	100	110	109	116	113
Lower Warning Limit		83	78	86	94	85	87	83	95
Lower Control Limit		76	69	80	92	79	81	75	90

*Highlighted cells are percent recoveries exceeding control limits

Table 4. Continuing Quality Control- Carbamate Screen

Extraction Date	Sample Numbers	Percent Recovery	
		Carbofuran	Carbaryl
12/4/98	166-2,7,12,17. 167-2,7,12,17.	102	95.8
12/10/98	166-22. 166-22.	88.4	86.4
1/8/98	166-27,32,37,42. 167-27 32.	98.6	94.0
1/13/98	166-47,52,63,68,86. 167-37,42,47.	99.4	97.2
1/16/98	166-55,60. 167-52,57.	95.5	94.5
1/21/98	166-75,80,85. 167-62,67,72.	95.5	94.5
1/27/98	166-92,97,102,107. 167-91,96,101,106,209.	86.2	89.4
1/29/98	166-110,115,120,125. 167-11,116,121,126.	98.4	99.4
2/3/98	166-130,135,140. 167-131,136,141,146.	94.4	99.6
2/5/98	166-145,150. 167-75,80.	92.0	96.1
2/10/98	166-155,160,163,168. 167-150,155,160,216	96.4	96.2
2/17/98	166-173, 178, 183, 197, 202. 167-165, 170, 175, 180, 185.	86.4	87.4
2/19/98	166-188, 193. 167-190, 195, 200.	90.0	95.8
2/24/98	166-208,205,213,218,249 167-249,220,225	104	110
3/3/98	166-223,228,233,236 167-230,235,240	*116	114
3/5/98	166-241,255,260,265 167-245,250,255,260	111	104
3/9/98	166-270,275 167-267	96.0	91.2
Average Recovery		91.7	96.8
Standard Deviation		8.0	7.3
CV		8.7	7.5
Upper Control Limit		113	124
Upper Warning Limit		108	116
Lower Warning Limit		89	83
Lower Control Limit		84	75

*Highlighted cells are percent recoveries exceeding control limits

Table 5. Continuing Quality Control- Diazinon Analysis

Extraction Date	Sample Numbers	Percent Recovery
		Diazinon
12/2/97	166-3, 8 167-3,8	89.0
12/4/97	166-13,18 167-13,18	88.0
12/8/97	166-23, 167-23	104
1/5/98	166-28, 33 167-28	96.0
1/7/98	166,38,43 167-33	95.0
1/12/98	166-48,53 167-38	103
1/14/98	166-64,69,56,61 167-43,53,58,85	103
1/20/98	166-76,81,88 167-63,68,87	103
1/22/98	166-93,98 167-92,97,102	91.0
1/26/98	166-105,108 167-107,210	93.0
1/27/98	166-111,116 167-112,117	102
1/29/98	166-121, 126 167-122,127	97.0
2/5/98	166-146, 151 167-76,81	80.5
2/3/98	166-136,141 167-142,147	97.0
2/9/98	166-156,161. 167-151,215.	83.0
2/11/98	166-164,169 167-156,161	91.0
2/13/98	166-174,179 167-166,171	101
2/18/98	166-184, 198,203,246 167-176,181,186	80.0
2/20/98	166-189,194 167-134,191,196,201	104
2/23/98	166-143,209,248 167-206	96.0
2/25/98	166-214,219 167-221,226	80.0
2/26/98	166-224,229,234,252. 167-231,236.	100
3/2/98	166-237. 167-241.	98.2
3/5/98	166-261,266. 167-256,261.	96.0
3/10/98	166-271,276. 167-268.	98.0
Average Recovery		94.7
Standard Deviation		7.3
CV		7.7
Upper Control Limit		109
Upper Warning Limit		104
Lower Warning Limit		86
Lower Control Limit		81

Table 6. Continuing Quality Control- Triazine/Diuron/Bromacil Screen

Extraction Date	Sample Numbers	Percent Recovery								
		Hexazinone	Cyanazine	Metribuzin	Atrazine	Simazine	Diuron	Prometon	Bromacil	Prometryn
12/4/97	166-400, 401, 402, 403. 167-400, 401, 402, 403.	111	103	86.4	102	112	90.0	96.0	89.6	98.4
12/11/97	166-404, 5, 10, 15, 20. 167-404, 5, 10, 15, 20, 25.	115	117	98.4	101	105	99.6	104	98.4	107
1/9/98	166-405, 406, 407, 408, 496. 167-405, 407.	98.4	100	89.2	104	110	97.6	105	98.4	94.0
1/14/98	166-409, 411, 484. 167-407, 408, 409, 435.	98.4	111	85.2	96.0	102	88.0	97.2	97.2	99.6
1/20/98	166-485,486,487,497. 167-410,411,412.	101	102	100	89.2	88.0	88.8	86.0	95.2	84.0
1/28/98	166-488,489,490,491. 167-413,414,415,416,417.	110	117	116	86.5	90.3	108	92.8	113	101
1/29/98	166-492, 493,494, 495, 498. 167-418,419,420.	107	111	97.9	105	103	98.6	99.2	112	101
2/2/98	166-412, 413, 414, 499. 167-421, 422, 423, 424.	100	110	97.2	95.4	98.0	92.8	91.2	104	87.4
2/3/98	166-415, 416. 167-425, 426.	98.8	110	95.6	89.0	94.8	90.6	88.2	107	89.2
2/9/98	166-417, 418, 419, 420, 424. 167-427, 428, 429.	99.6	95.6	105	95.0	86.4	83.4	88.2	90.8	86.4
2/11/98	166-421, 422. 167-430, 431, 461.	97.5	101	99.0	107	104	92.7	79.9	101	82.0
2/13/98	166-423, 425. 167-432, 433.	94.8	118	106	105	102	99.8	104	103	105
2/18/98	166-426, 427, 428. 167-436, 437, 438.	89.2	110	99.8	92.4	102	83.8	104	103	105
2/20/98	166-429, 430. 167-439, 440, 441.	95.2	111	101	108	84.4	97.2	84.8	108	84.8
2/23/98	166-431, 449, 450. 167-442.	106	117	80	86.8	101	90.0	89.2	101	91.2
2/26/98	166-432,433,435,437. 167-443,444,445,446.	109	102	100	84.0	98.0	99.2	104	103	96.8
3/3/98	166-436,438,439. 167-447,448,449.	101	115	103	95.6	94	95.6	92	102	91.2
3/5/98	166-440,441. 167-450,451.	102	113	111	84.4	90.8	85.2	82.4	93.6	91.6
3/9/98	166-442,443. 167-452.	101	98.8	108	88.3	96.6	89.1	89.6	92.1	100.4
Average Recovery		102	109	98.8	97.4	98.0	93.2	93.6	101	94.5
Standard Deviation		6.36	7.12	8.76	8.07	7.72	6.45	8.13	6.70	7.76
CV		6.25	6.56	8.87	8.29	7.88	6.92	8.69	6.65	8.21
Upper Control Limit		123	121	105	121	126	117	111	115	115
Upper Warning Limit		115	114	101	114	126	108	104	109	108
Lower Warning Limit		84.5	87.4	84.5	85.0	86.4	74.6	75.9	86.5	79.1
Lower Control Limit		76.8	80.7	80.4	77.7	78.5	66.2	68.9	80.9	71.9

*Highlighted cells are percent recoveries exceeding control limits

Table 7. Concentrations of pesticides (ppb) detected in samples from Orestimba Creek and the San Joaquin River, winter 1997-98.

	ORESTIMBA CREEK at RIVER ROAD								SAN JOAQUIN RIVER near VERNALIS							
Sampling Date	Chlorpyrifos	Diazinon	Methyl Parathion	Bromacil	Cyanazine	Diuron	Simazine	Acute Toxicity (percent survival[1])	Diazinon	Methidathion	Bromacil	Cyanazine	Diuron	Simazine	Chronic Toxicity (percent survival[1])	Chronic Toxicity (offspring per female[1])
12/1/97	*nd*	*nd*[2]	*nd*	*nd*	0.254	0.165	0.074	95/90	*nd*	*nd*	*nd*	0.678	1.440	0.470		
12/3/97	*nd*	*nd*	*nd*	0.066	*nd*	0.078	*nd*	100/100	*nd*	*nd*	*nd*	*nd*	0.596	0.086		
12/5/97									*nd*	*nd*	*nd*	0.222	0.524	0.107	100/90	20/15
1/5/98	*ns*	*ns*[3]	*ns*	*ns*	*ns*	*ns*	*ns*	*ns*	*nd*	*nd*	0.058	*nd*	0.318	0.053		
1/7/98	*ns*	*ns*	*ns*	*ns*	*ns*	*ns*	*ns*	*ns*	0.040	0.053	*nd*	*nd*	1.231	nd		
1/9/98									*nd*	nd	0.088	*nd*	0.817	nd	90/80	37/15
1/12/98	*nd*	0.139	*nd*	0.115	*nd*	0.388	0.711	100/100	0.063	0.054	0.050	*nd*	2.527	0.072		
1/14/98	*nd*	*nd*	*nd*	*nd*	*nd*	*nd*	0.093	100/100	0.086	*nd*	*nd*	*nd*	2.950	0.125		
1/16/98									0.102	*nd*	0.053	*nd*	1.575	0.163	90/100	15/15
1/19/98	*nd*	*nd*	*nd*	0.097	*nd*	0.079	0.063	100/95	*nd*	*nd*	*nd*	*nd*	0.406	0.066		
1/21/98	*nd*	*nd*	*nd*	*nd*	*nd*	*nd*	*nd*	*65/100	*nd*	*nd*	*nd*	*nd*	0.056	0.291		
1/23/98									*nd*	*nd*	*nd*	*nd*	0.240	nd	80/80	33/16
1/26/98	0.093	*nd*	0.190	*nd*	*nd*	*nd*	*nd*	95/95	*nd*	*nd*	*nd*	*nd*	0.252	nd	control died/failed test	
1/28/98	*nd*	*nd*	*nd*	*nd*	*nd*	*nd*	*nd*	100/100	*nd*	*nd*	*nd*	*nd*	0.142	0.050		
1/30/98									0.084	*nd*	*nd*	*nd*	0.205	nd	(90/80)[4]	(25/15)
2/2/98	*nd*	0.110	*nd*	*nd*	*nd*	0.086	*nd*	95/100	0.047	0.112	*nd*	*nd*	0.330	0.088		
2/4/98	*nd*	0.059	*nd*	*nd*	*nd*	0.179	0.075	*0/90	0.093	*nd*	*nd*	*nd*	1.351	0.194		
2/6/98									0.067	*nd*	*nd*	*nd*	0.519	0.236	0/100	0.9/15
2/9/98	*nd*	*nd*	*nd*	*nd*	*nd*	*nd*	*nd*	45/90	0.048	*nd*	*nd*	*nd*	0.574	0.140	control died/failed test	
2/11/98	*nd*	*nd*	*nd*	*nd*	*nd*	*nd*	*nd*	40/95	0.042	*nd*	*nd*	*nd*	0.525	0.126		
2/13/98									*nd*	*nd*	*nd*	*nd*	0.352	0.057	(90/80)	(31/30)
2/16/98	*nd*	*nd*	*nd*	*nd*	*nd*	*nd*	*nd*	100/95	*nd*	*nd*	*nd*	*nd*	0.221	*nd*	control died/failed test	
2/18/98	*nd*	*nd*	*nd*	*nd*	*nd*	*nd*	*nd*	90/95	*nd*	*nd*	*nd*	*nd*	0.202	*nd*		
2/20/98									*nd*	*nd*	*nd*	*nd*	0.249	*nd*	(90/100)	(20/28)
2/23/98	*nd*	*nd*	*nd*	*nd*	*nd*	*nd*	*nd*	*55/90	*nd*	*nd*	*nd*	*nd*	0.275	*nd*		
2/25/98	*nd*	*nd*	*nd*	*nd*	*nd*	*nd*	*nd*	100/100	*nd*	*nd*	*nd*	*nd*	0.215	*nd*		
2/27/98									*nd*	*nd*	*nd*	*nd*	0.211	*nd*	100/90	20/17
3/2/98	*nd*	*nd*	*nd*	*nd*	*nd*	*nd*	*nd*	95/100	*nd*	*nd*	*nd*	*nd*	0.178	*nd*		
3/4/98	*nd*	*nd*	*nd*	*nd*	*nd*	*nd*	*nd*	95/100	*nd*	*nd*	*nd*	*nd*	0.105	*nd*		
3/6/98									*nd*	*nd*	*nd*	*nd*	0.152	*nd*	80/100	28/30

1) Two numbers are reported for all toxicity tests. The first number is the result from the sample and the second is the result from the corresponding control. Asterisks indicate ambient sample significantly different than the laboratory control (Dunnett's test, p,0.05) 2) nd=none detected 3) ns=not sampled due to no flow 4) retest data in parenthesis

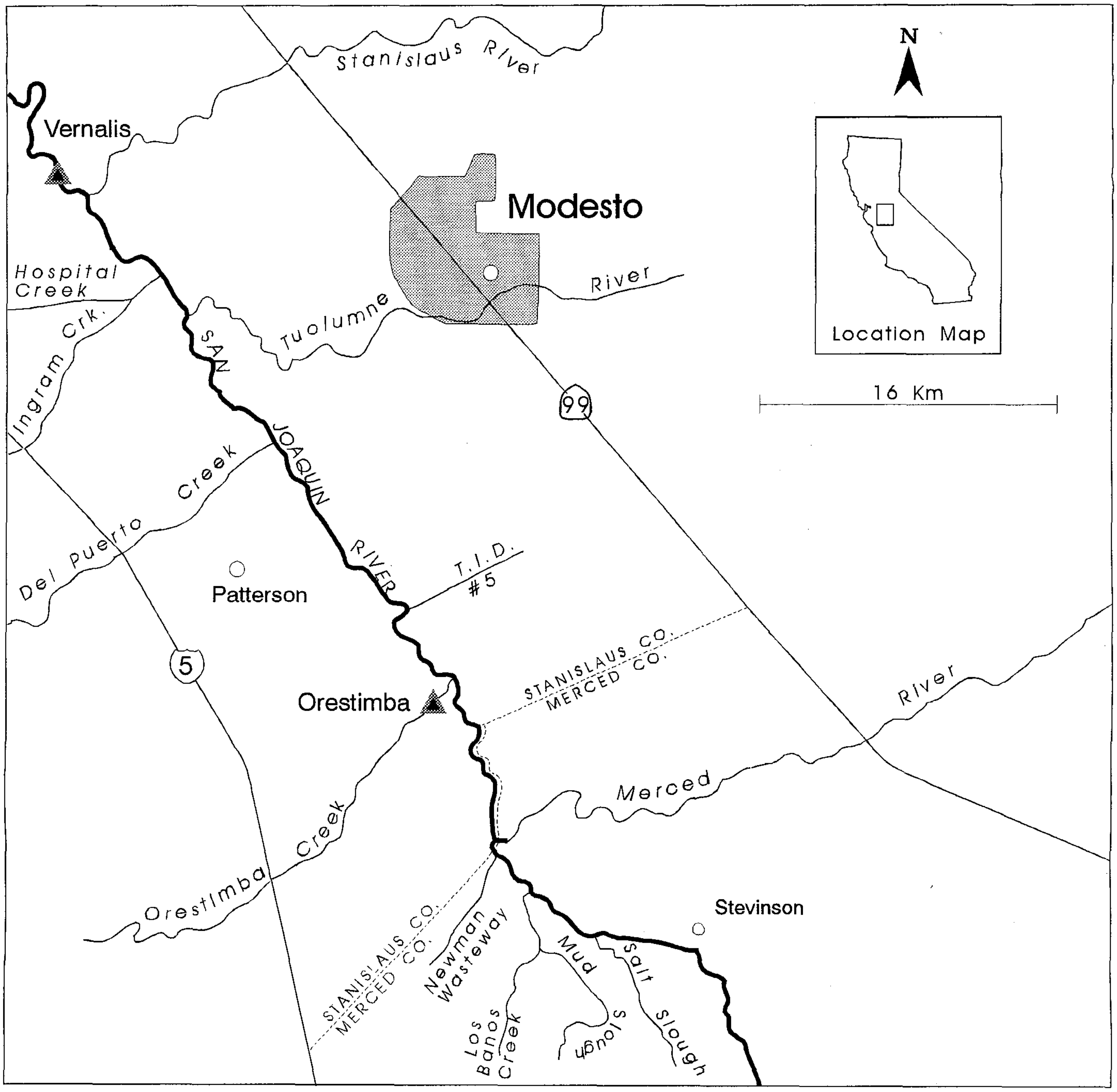

Figure 1. Location of toxicity sampling sites (▲) and rainfall data stations (○)in the San Joaquin River watershed: Winter 1997-98.

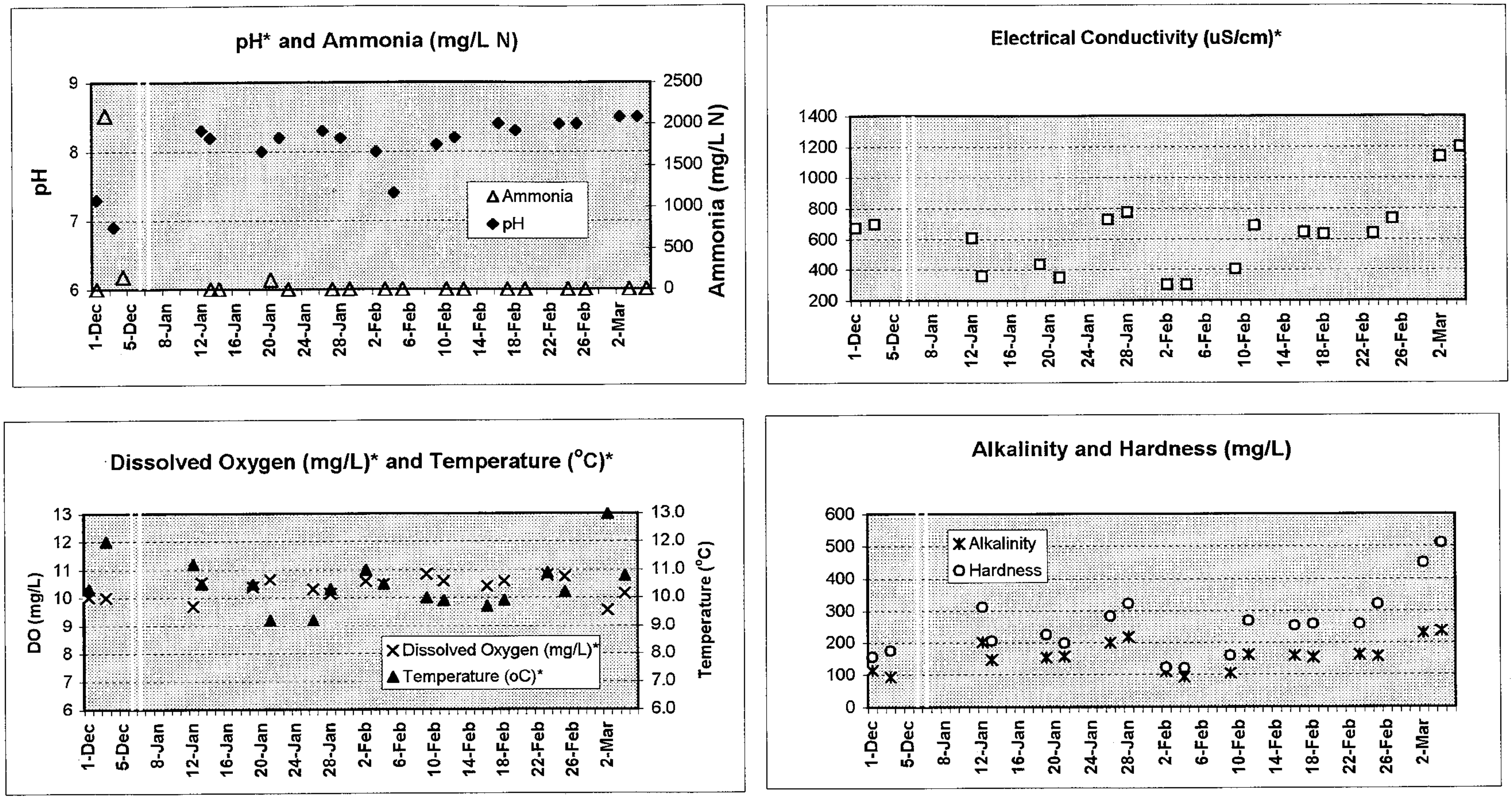

Figure 2. Environmental measurements for the Orestimba Creek at River Road. Data collected from December 1 through 5, 1997 and January 5 through March 4, 1998. Data were collected twice each week during the study period. * Denotes measurements made on site. Double bar denotes a break in sampling between background and dormant season samples.

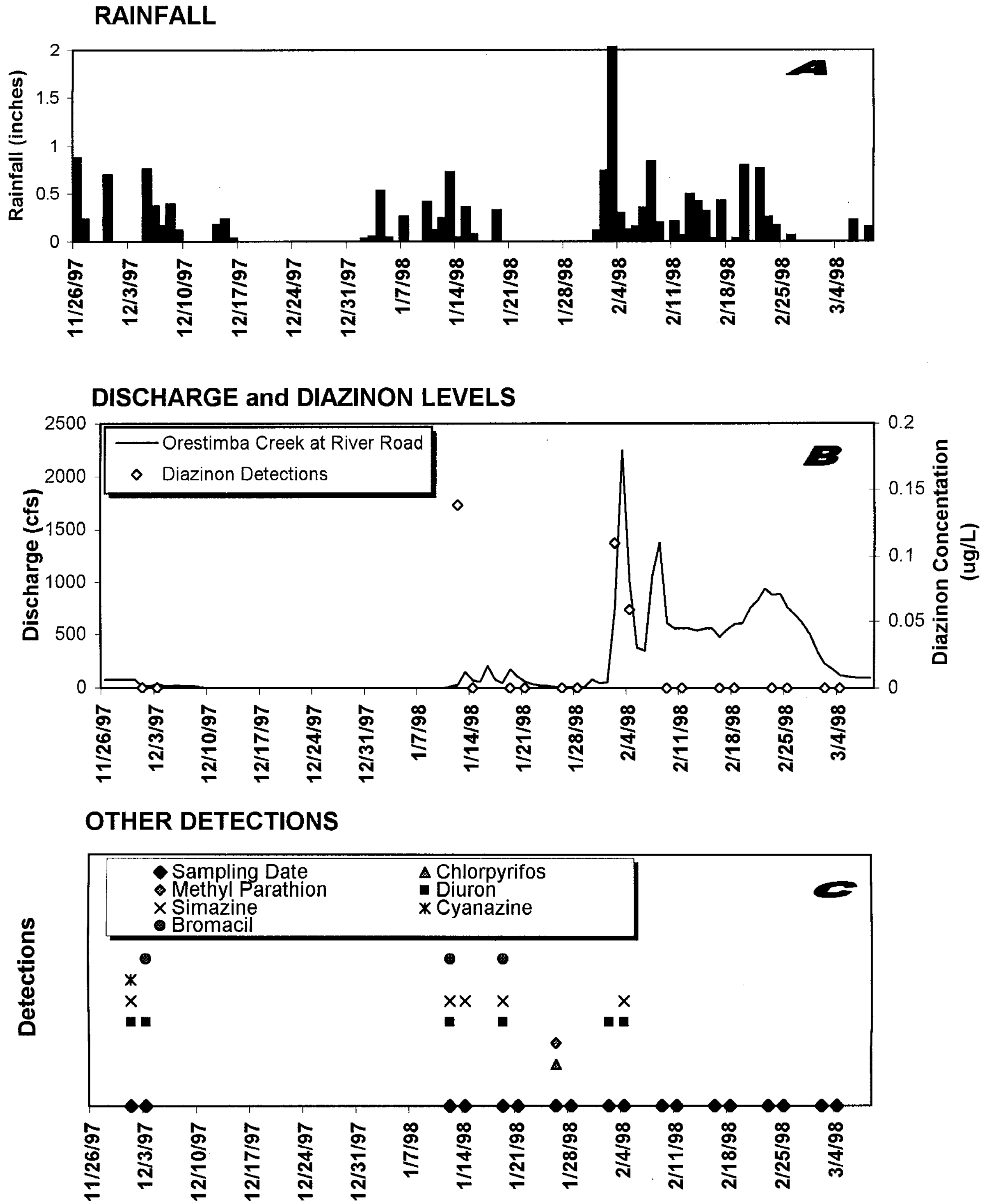

Figure 3. (A) Rainfall measured at Patterson; (B) discharge and diazinon were measured in Orestimba Creek at River Road; (C) detections of other insecticides and herbicides, winter 1997-98.

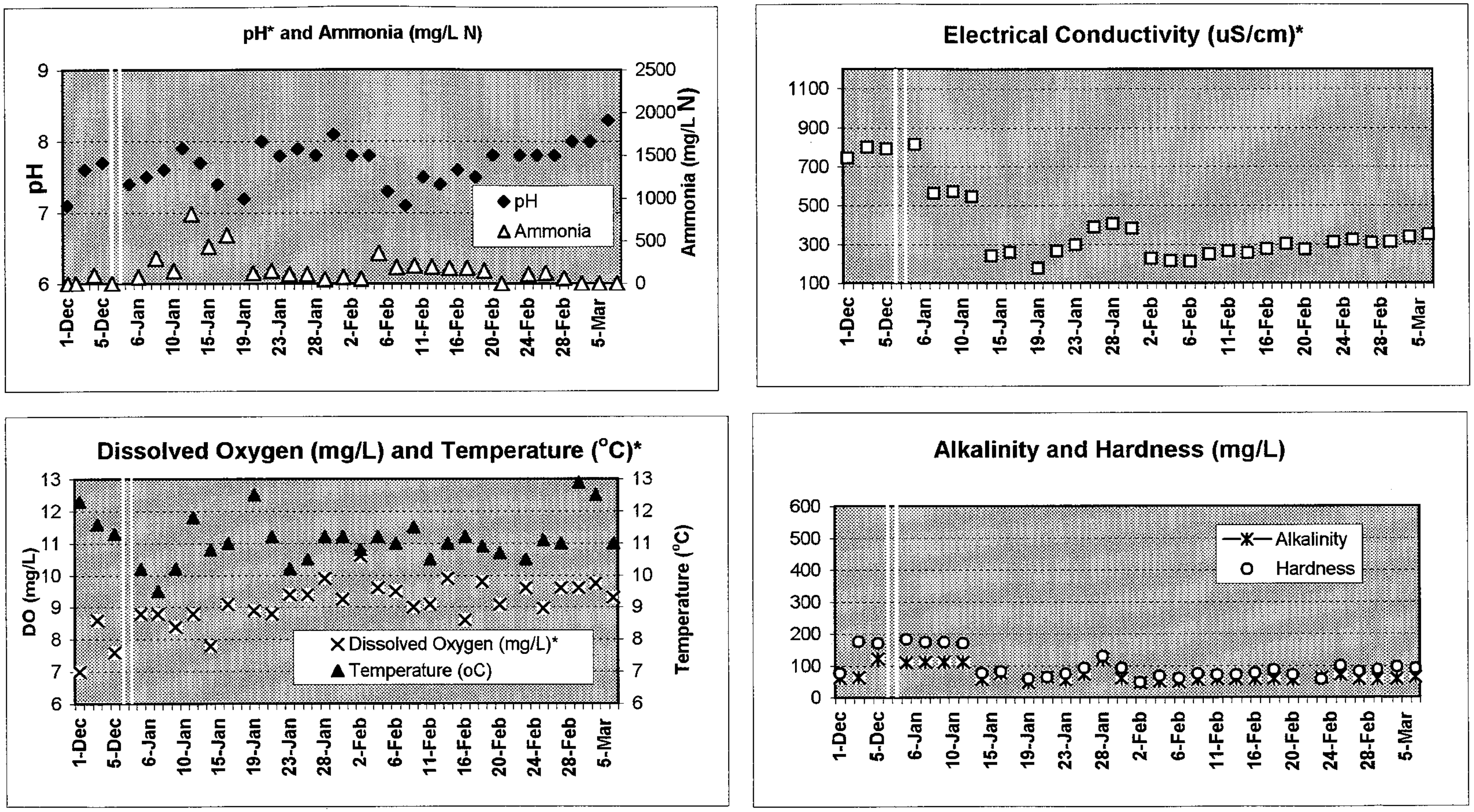

Figure 4. Envrionmental measurments for the San Joaquin River at Vernalis, CA. Data collected from December 1 through December 5, 199 and January 5 through March 6, 1998. Measurements were collected three times per week during the study period. *Denotes measurements made on site. Double bar denotes a break in sampling between background and dormant season samples.

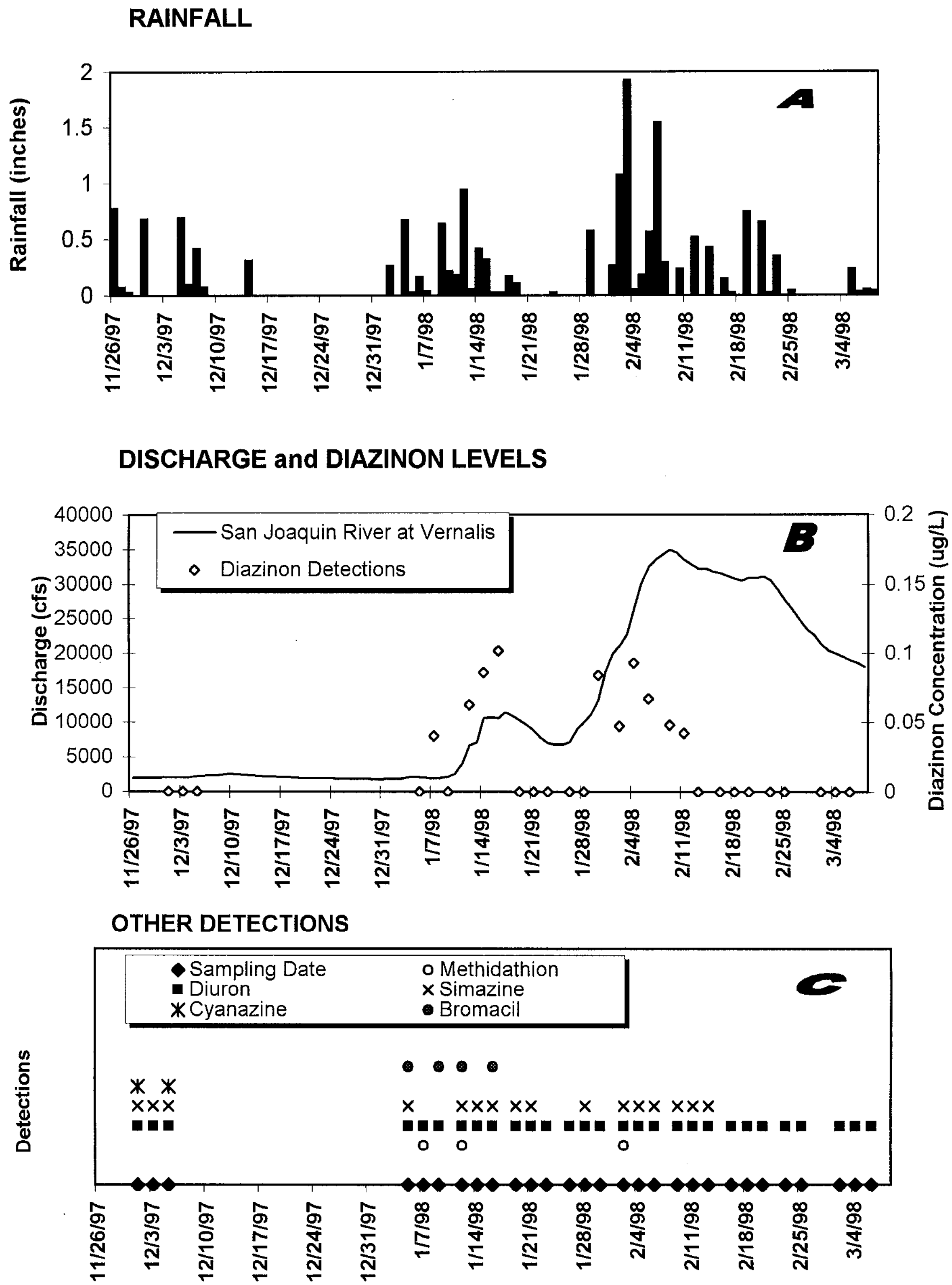

Figure 5. (A) Rainfall measured at Modesto; (B) discharge and diazinon concentrations measured in the San Joaquin River near Vernalis; (C) detections of other insecticides and herbicides, winter 1997-98 .

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