



# Department of Pesticide Regulation



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## MEMORANDUM

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DATE: June 20, 2003

SUBJECT: PRELIMINARY RESULTS OF STUDY #214: MONITORING THE  
OCCURRENCE AND CONCENTRATION OF ESFENVALERATE AND  
PERMETHRIN PYRETHROIDS

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### SCOPE OF THIS MEMORANDUM

This memorandum provides results of water sampling conducted in tributaries to the Sacramento and San Joaquin Rivers by the Department of Pesticide Regulation (DPR) for the Surface Water Protection Program. Information presented is from November 2002 through March 2003. Results from chemical analysis conducted by the California Department of Food and Agriculture (CDFA) and bioassays conducted by the California Department of Fish and Game (DFG) are also presented here.

The primary objectives of this monitoring project were to determine (a) if the insecticides esfenvalerate and permethrin are moving offsite into surface waters, during winter storm events, and if so, (b) the typical range of concentrations that may be observed. A secondary objective was to obtain more data on organophosphate (OP) insecticides and selected herbicide residues in surface water. This memorandum does not include an in-depth interpretation of the data, which will be provided in the final report.

### BACKGROUND

In the Sacramento and San Joaquin valleys there are more than 750,000 acres of almonds, nectarines, peaches, plums and prunes grown (Epstein et al., 2000). As part of integrated pest management, OP insecticides are applied on these tree crops, generally with dormant oil, to control the San Jose scale, the peach twig borer, aphids and other pests. This is done primarily between December and February when trees are dormant, allowing for better pesticide coverage to achieve effective control of pests.



The dormant-spray season coincides with seasonal rainfall, thus increasing the likelihood of insecticides to move offsite to surface water, either dissolved in water or attached to sediment. Various monitoring studies conducted by DPR and U.S. Geological Survey (USGS) have shown that detections of OPs such as diazinon and chlorpyrifos are frequently detected during dormant-spray seasons (Dileanis et al., 2002; Ross et al., 1996; Domagalski et al., 1997; Kratzer, 1998).

DPR is required to protect the environment, including surface water, from environmentally harmful pesticides (Food and Agricultural Code, section 11501), and has asked growers to voluntarily take measures to reduce water contamination from OPs during the rainy season (Bennett et al., 1998). Since 1992 the use of OPs during the dormant-spray season has been steadily decreasing, but they are being replaced by pyrethroids, specifically esfenvalerate and permethrin (Epstein et al., 2000).

The potential for environmental impacts to surface water from esfenvalerate and permethrin use is uncertain. Physico-chemical characteristics indicate a potential for esfenvalerate and permethrin to move offsite with sediment and the potential for an acute toxicity threat to aquatic organisms (Table 1 and 2).

## **MATERIALS AND METHODS**

### **Site Description**

Four monitoring sites were chosen that reflect areas with the heaviest historical applications of esfenvalerate and permethrin through the dormant-spray season (Figures 1-4). When evaluating the desirability of these sites for monitoring, previous detections of diazinon during dormant-spray seasons and the proximity of monitoring sites to application sites were also considered. All of the sites are dominated by agricultural inputs. In addition, site selection followed the general guideline in Standard Operating Procedure (SOP) FSWA002.00 (Bennett, 1997). The sites were:

- 1.) Wadsworth canal at South Butte road, a tributary that runs southeast into the Sutter Bypass canal which in turn flows into the Sacramento river
- 2.) Jack Slough at highway 70, a tributary that flows southeast into the Feather river which in turn flows into the Sacramento river
- 3.) Del Puerto creek at Vineyard road, a tributary that flows west into the San Joaquin river
- 4.) Highline canal at Griffith road, a tributary that flows east into the Merced River, which in turn flows into the San Joaquin River.

### **Sampling Plan**

Monitoring occurred during two storm events in the dormant-spray season of 2002-2003. The number and frequency of samples collected was dependent on the intensity and duration of the runoff event. Sufficient numbers of samples were collected to maximize the likelihood that peak concentrations of pesticides were captured.

Whole water collected from each site was analyzed for esfenvalerate and permethrin, currently used OPs, and selected herbicides (Table 3). Carbamates were not monitored due to the lack of detections in past dormant-spray monitoring.

Sediment samples were also collected and analyzed for esfenvalerate, permethrin, bifenthrin lambda cyhalothrin, cyfluthrin, and cypermethrin (Table 3). Background sediment samples were collected November 18<sup>th</sup> and 20<sup>th</sup>, 2002, prior to the start of dormant-spray applications. Sediment samples were then collected at the start and at the end of each water-sampling event, and again seven and fourteen days after each storm event.

Water samples were also analyzed for total suspended sediment and bioassays for acute toxicity to the sensitive aquatic species *Ceriodaphnia dubia* were conducted.

### **Sampling Method**

Each chemical screen, toxicity sample and suspended sediment sample was individually collected in 1-liter amber bottles. A total of 40 pesticide water samples were collected at three of the sites. All samples were collected by grab sample, as close to center channel as possible. The grab pole consisted of a 1-liter amber glass bottle at the end of an extended pole. Amber bottles were sealed with Teflon-lined lids.

Sediment samples were collected using either a hand scoop or a 24-inch long, by 2-inch diameter, Teflon cylindrical tube. When collecting with the hand scoop, the top 1-inch of submerged sediment was collected near the waters edge and placed into a 1-pint, clear glass jar. This was repeated within the same general area until the jar was approximately  $\frac{3}{4}$  full. When collecting with the tube, one end of the tube was thrust into the sediment near the waters edge and then removed. The top 1-2 inches of the sediment was collected in the tube and placed into a 1-pint, clear glass jar. This was repeated within the same general area until the jar was approximately  $\frac{3}{4}$  full.

All water samples were transported and stored on wet ice or refrigerated at 4°C until extraction for chemical analysis or toxicity testing. Sediment samples were transported on wet ice and then placed in a freezer until extraction. Dissolved oxygen (DO), pH, specific conductivity (EC), and water temperature were measured *in situ* at each site at the time of each grab sample.

### **Environmental Measurements**

Dissolved oxygen, EC and temperature were measured with an YSI® (Yellow Springs Instruments®) DO/EC meter (model 85). Water pH was measured with a Sentron® pH meter (model 1001) or a YSI® pH meter (model 60). Additionally, alkalinity, hardness, and ammonia were measured by the DFG aquatic toxicity lab. 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).

Rainfall and discharge data (where available) were also gathered for the study area. Rainfall measurements were obtained from the California Department of Water Resources database (CDEC), University of California, Davis, Statewide Integrated Pest Management Program, California Weather Databases (UCD IPM), and AccuWeather.com.

Discharge data were obtained from USGS gauging stations and the Central Valley Regional Water Quality Control Board (CVRWQCB). Rainfall, discharge and TSS information will be used to estimate pesticide loads and potential aqueous toxicity during similar storm events. This will be provided in the final report.

### **Pesticide Analysis**

Chemical analyses were performed by the California Department of Food and Agriculture's Center for Analytical Chemistry. The following was used to determine concentrations of pesticides:

- OPs - GC/FPD - gas chromatography/flame photometric detector
- Pyrethroids - GC/ECD - gas chromatography/electron capture detector, confirmed with GC/MS
- Triazines - LC/MS/MS – liquid chromatography/atmospheric pressure chemical ionization mass spectrometry

The pyrethroid water samples were extracted *in toto*, without filtration, and extracting solvent was used to rinse the sample bottles to insure complete removal of any pyrethroid adsorbed to the glass container.

Comprehensive chemical analytical methods will be provided in the final report. The reporting limit was determined as the lowest concentration of analyte that the method can detect reliably in a matrix blank. Method titles and reporting limits for this study are reported in Table 3.

### **Toxicity Tests**

The Department of Fish and Game's Aquatic Toxicology Laboratory performed aquatic toxicity tests. Acute tests were performed in undiluted, unfiltered 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).

### **Quality Control**

Quality control (QC) for the chemistry portion of this study was conducted in accordance with Standard Operating Procedure QAQC001.00 (Segawa, 1995) and consisted of a continuing QC program. Ten percent of the total number of water samples was submitted for chemistry analyses as field blanks and another ten percent as blind spikes. Blind spike and continuing QC results for each of the analytical screens are presented in Tables 4 through 8. There were no detections of any pesticides in any of the field blank samples (not in tables).

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.

## **RESULTS**

### **Environmental Measurements (Tables 9-10)**

#### Wadsworth Canal

During the first storm event on January 22, 2003, water temperature ranged from 11.0 to 11.8° C. Dissolved oxygen ranged from 8.64 to 8.78 mg/L, with percent saturation ranging from 81 to 84%, while both the pH measurements ranged from 6.44 to 7.56, and EC measurements ranged from 244.6 to 307.7 µS/cm. During the first hour of sampling both temperature and DO were at their lowest point and then increased during the sampling period. Both EC and pH were at their highest at the first hour and decreased during the sampling period. Hourly suspended sediment during the storm event ranged from 28.0 to 173.2 mg/L.

Storm events prior to the initial sampling date of January 22, 2003 had not been sampled due to the relatively few pesticide applications prior to those times. Total rainfall for January 21 through the 22<sup>nd</sup> for this area was 0.40 inches. There was no rainfall for 7 days prior to the 21<sup>st</sup>.

The local County Agricultural Commissioner's office confirmed the application of dormant spray insecticides during this time period.

During the second storm event on February 15 through the 16th, 2003, water temperature ranged from 11.6 to 14.6° C. The pH measurements ranged from 7.15 to 7.55. Dissolved oxygen and EC measurements were not measured during this storm event. During the first hour of sampling both temperature and pH were at their highest points and then decreased during the sampling period. Hourly suspended sediment during the storm event ranged from 7.6 to 3114.4 mg/L.

Total rainfall for February 15 through the 16<sup>th</sup> for this area was approximately 0.95 inches. Approximately 0.54 inches had fallen 2 days earlier on the 13<sup>th</sup>, but because there was no rainfall for 18 days prior to the 13<sup>th</sup>, this was not sufficient rainfall to cause significant runoff. The local County Agricultural Commissioner's office confirmed the application of dormant spray insecticides during this time period.

Discharge data for this site will be presented in the final report.

#### Jack Slough

During the first storm event on January 22, 2003, water temperature ranged from 10.5 to 11.0° C. Dissolved oxygen ranged from 9.42 to 11.51 mg/L, with percent saturation ranging from 88 to 107%. The pH measurements ranged from 7.0 to 7.39, and EC measurements ranged from 107.5 to 109.9 µS/cm. During this sampling event, temperature increased slightly by the end of the sampling period. Other water quality measurements (pH, EC, DO) fluctuated during this sampling period. Hourly suspended sediment during the storm event ranged from 66.0 to 80.4 mg/L.

Storm events prior to January 22, 2003 had not been sampled due to a lack of pesticide applications. Total rainfall for January 21 through the 22<sup>nd</sup> for this area was 0.40 inches (UCD IPM, 2003). There was no rainfall for 7 days prior to the 21<sup>st</sup>. The local County Agricultural Commissioner's office confirmed the application of dormant spray insecticides during this time period.

During the second storm event on February 15 through the 16th, 2003, water temperature ranged from 11.8 to 13.1° C. Dissolved oxygen ranged from 7.78 to 8.55 mg/L, with percent saturation ranging from 76 to 82%.

The pH measurements ranged from 7.09 to 7.56, and EC measurements ranged from 144.2 to 163.6  $\mu\text{S}/\text{cm}$ . Both temperature and EC were highest at the first hour of sampling and then decreased during the sampling period, while pH and DO fluctuated during this sampling period. Hourly suspended sediment during the storm event ranged from 80.0 to 300.0 mg/L.

Total rainfall for February 15 through the 16<sup>th</sup> for this area was approximately 0.95 inches. Approximately 0.54 inches had fallen 2 days earlier on the 13<sup>th</sup>, but because there was no rainfall for 18 days prior to the 13<sup>th</sup>, this was not sufficient rainfall to cause significant runoff. The local County Agricultural Commissioner's office confirmed the application of dormant spray insecticides during this time period.

Discharge data is not available for this site.

#### Del Puerto Creek

Due to the lack of rainfall in this area this site was only sampled on March 15<sup>th</sup>, 2003. Water temperature ranged from 13.7 to 19.8° C. Dissolved oxygen ranged from 8.2 to 8.96 mg/L, with percent saturation ranging from 85 to 93%. The pH measurements ranged from 8.29 to 9.03, and EC measurements ranged from 223.5 to 389  $\mu\text{S}/\text{cm}$ . During this sampling event, temperature had increased by the end of the sampling period. Other water quality measurements (pH, EC, DO) fluctuated during this sampling period. Hourly suspended sediment during the storm event ranged from 452.0 to 2708.8 mg/L.

Total rainfall for March 15<sup>th</sup> for this area was 0.96 inches. Prior to the 15<sup>th</sup>, the last precipitation was less than 0.25 inches February 24<sup>th</sup> and 27<sup>th</sup>, but because there was no rainfall for 11 days prior to the 24<sup>th</sup>, this was not sufficient rainfall to cause significant runoff. The local County Agricultural Commissioner's office confirmed the application of dormant spray insecticides during this time period.

Discharge data for this site will be presented in the final report.

#### Highline Canal

This site was not sampled due to the lack of rainfall and the use of the canal for mid-spring irrigation supply purposes.

## **Pesticide Concentrations and Toxicity (Tables 11-12)**

### Wadsworth Canal

During the storm event on January 22, 2002, there were no pyrethroid detections in any of the water or sediment samples collected. Trace\* amounts of chlorpyrifos were detected, and diazinon detections ranged from 0.106 to 0.130 ppb. Other detections during this storm event included the herbicides simazine, diuron, and norflurazon. There was no significant acute toxicity to *C. dubia* in any of the samples collected during this storm event.

During the storm event on February 15, 2003, there was one detection of Esfenvalerate (trace) and one permethrin detection (0.094 ppb), both occurring at the same time. Again, trace amounts of chlorpyrifos were detected and diazinon detections ranged from 0.102 to 0.246 ppb. At the time of detection of the two pyrethroids, and the highest detection of diazinon (0.246ppb), the acute toxicity test indicated 0% survival to *C. dubia*. Bioassay results for the sample collected during the following hour reported 60% survival to *C. dubia*. The only insecticide detected in that sample was diazinon at 0.176 ppb. Other detections during this storm event included the herbicides bromacil, diuron, and norflurazon. No sediment samples were collected during this storm event.

### Jack Slough

During the storm event on January 22, 2002, there were no pyrethroid detections in any of the water or sediment samples collected. Trace amounts of chlorpyrifos were detected, and diazinon detections ranged from 0.0978 to 0.138 ppb. There was significant acute toxicity to *C. dubia* (65% survival) in one sample. The diazinon detection at that time was 0.183 ppb. The herbicide diuron was also detected during this storm event.

During the storm event on February 15, 2003, there were no pyrethroid detections in any of the water or sediment samples collected. Diazinon detections ranged from 0.107 to 0.195 ppb. There was significant acute toxicity to *C. dubia* in three samples collected (60, 10, and 15% survival). Diazinon concentrations at these times were 0.195, 0.107, and 0.161 ppb, respectively. Other detections during this storm event included the herbicides diuron, bromacil and simazine.

### Del Puerto Creek

During the storm event on March 15<sup>th</sup>, 2003, esfenvalerate was detected in every sample. Detections ranged from trace amounts to 0.093 ppb. Both chlorpyrifos and diazinon were also detected with concentrations ranging from 0.0594 to 0.233 ppb and 0.0826 to 0.119 ppb, respectively. Other OP detections included dimethoate, ethoprop, and methyl parathion.



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Herbicide detections included simazine, diuron, hexazinone, norflurazon, metribuzin, bromacil and ACET.

There was significant acute toxicity to *C. dubia* in all samples collected (0% survival). There was one detection of bifenthrin in one sediment sample at this site (0.0242 ppb). There were no additional pyrethroid detections in any sediment samples collected at this site.

**\* Trace = An analyte concentration that falls between the reporting limit and method detection limit (DPR memo dated 7/17/02).**

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**TABLE 1. PHYSICAL CHARACTERISTICS AND ENVIRONMENTAL FATE OF DETECTED PESTICIDES**

<b>Pesticide</b>	<b>Koc</b>	<b>Solubility (mg/l)</b>	<b>Field Dissipation (half-life in days)</b>	<b>Soil Degradation - Aerobic (half-life in days)</b>	<b>Soil Degradation – Anaerobic (half-life in days)</b>	<b>Hydrolysis (half-life in days)</b>
Esfenvalerate	251,700 <sup>a</sup>	0.006 <sup>b</sup>	ND	38.6 <sup>b</sup>	90.4 <sup>b</sup>	>30 <sup>b</sup>
Permethrin	277,000 <sup>b</sup>	0.0055 <sup>b</sup>	ND	39.5 <sup>b</sup>	197 <sup>b</sup>	>30 - 242 <sup>b</sup>
Bifenthrin	237,000 <sup>b</sup>	0.000014 <sup>b</sup>	ND	96.3 <sup>b</sup>	425 <sup>b</sup>	>30 <sup>b</sup>
Lambda cyhalothrin	326,000 <sup>b</sup>	0.005 <sup>b</sup>	ND	42.6 <sup>b</sup>	ND	8.66 - >30 <sup>b</sup>
Cyfluthrin	124,000 <sup>b</sup>	0.0023 <sup>b</sup>	ND	11.5 <sup>b</sup>	33.6 <sup>b</sup>	1.84 - 183 <sup>b</sup>
Cypermethrin	310,000 <sup>b</sup>	0.004 <sup>b</sup>	ND	27.6 <sup>b</sup>	55.0 <sup>c</sup>	1.9 - 619 <sup>b</sup>
Diazinon	1,520 <sup>c</sup>	40 – 68.8 <sup>c</sup>	7-48 <sup>c</sup>	39	17	11.55 - 77.0 <sup>c</sup>
Chlorpyrifos	6,070-14,800 <sup>c</sup>	0.45 – 1.2 <sup>c</sup>	4-139 <sup>c</sup>	30.5	ND	15.75 - 77.0 <sup>c</sup>
Dimethoate	9-20 <sup>c</sup>	23,800 – 39,800 <sup>c</sup>	7 <sup>c</sup>	3	ND	4.5 - 157.5 <sup>c</sup>
Ethoprop	26-186 <sup>c</sup>	700-843 <sup>c</sup>	4-87 <sup>c</sup>	24	100	198.0 <sup>c</sup>
Methyl Parathion	6,300 <sup>c</sup>	55-60 <sup>c</sup>	1-30 <sup>c</sup>	ND	ND	33.0-69.3 <sup>c</sup>

ND - No data available

Sources:

- a. Dupont. Asana Technical Report. 2003
- b. Laskowski, D.A. 2002
- c. ARSUSDA. Pesticide Properties Database. 2003

**TABLE 2. TOXICITY OF DETECTED INSECTICIDES**

<b>Pesticide</b>	<i>Ceriodaphnia dubia</i> (ppb)	<i>Daphnia magna</i> (ppb)	<i>Oncorhynchus mykiss</i> (96hr LC50, ppb)
Esfenvalerate	ND	<b>0.24</b> <sup>a</sup>	0.26 <sup>a</sup>
Permethrin	<b>.55</b> <sup>b</sup>	<b>0.75</b> <sup>a</sup>	9.8 <sup>a</sup>
Bifenthrin	<b>0.07</b> <sup>b</sup>	<b>1.6</b> <sup>a</sup>	0.15 <sup>a</sup>
Lambda cyhalothrin	<b>.30</b> <sup>b</sup>	<b>0.23</b> <sup>a</sup>	0.44 <sup>a</sup>
Cyfluthrin	<b>.14</b> <sup>b</sup>	<b>.16</b> <sup>a</sup>	0.302 <sup>a</sup>
Cypermethrin	ND	<b>1.25</b> <sup>a</sup>	0.92 <sup>a</sup>
Diazinon	0.4 <sup>c</sup>	0.96 <sup>d</sup>	90-1650 <sup>d</sup>
Chlorpyrifos	0.08 <sup>c</sup>	0.1-1.7 <sup>d</sup>	7.1-27 <sup>d</sup>
Dimethoate	ND	<b>1700</b> <sup>e</sup>	6200-7500 <sup>d</sup>
Ethoprop	ND	44.0 <sup>d</sup>	1100-13800 <sup>d</sup>
Methyl Parathion	02.6 <sup>f</sup>	0.14-28.2 <sup>d</sup>	0.0022 – 0.161 <sup>d</sup>

ND - No data available

NOTES:

- Numbers in Normal print are for 48-hour EC50 toxicity tests.
- Numbers in **Bold** are for 48-hour LC50 toxicity tests.

Number ranges are for all studies listed in the indicated source and may represent 2-6 individual studies.

SOURCES:

- a. DPR Ecotox Database, 2003
- b. Mokry and Hoagland, 1990
- c. Sheipline, R. 1993
- d. U.S. EPA Ecotox Database, 2003
- e. Siepmann S. and T. Yargeau, 1996
- f. Menconi, M. and J.M. Harrington, 1992

**TABLE 3. CALIFORNIA DEPARTMENT OF FOOD AND AGRICULTURE, CENTER FOR ANALYTICAL CHEMISTRY  
 ORGANOPHOSPHATE AND TRIZINE/HERBICIDE PESTICIDES**

<b>Organophosphate Pesticides in Water Method: GC/FPD</b>		<b>Organophosphate Pesticides Water Method: GC/FPD</b>		<b>Triazines/Herbicides in Method: LC/MS/MS</b>	
<b><u>Compound</u></b>	<b><u>Reporting Limit</u></b> <b><u>(µg/L)</u></b>	<b><u>Compound</u></b>	<b><u>Reporting Limit</u></b> <b><u>(µg/L)</u></b>	<b><u>Compound</u></b>	<b><u>Reporting Limit</u></b> <b><u>(µg/L)</u></b>
Azinphos methyl	0.05	Phosmet	0.05	Atrazine	0.05
Chlorpyrifos	0.04	Thimet (Phorate)	0.05	Bromacil	0.05
Diazinon	0.04	Profenofos	0.05	Diuron	0.05
DDVP (dichlorvos)	0.05	Tribufos	0.05	Hexazinone	0.05
Dimethoate	0.05			Metribuzin	0.05
disulfoton	0.05			Norflurazon	0.05
ethoprop	0.05			Prometon	0.05
Fenamiphos	0.05			Prometryn	0.05
Fonofos	0.05			Simazine	0.05
Malathion	0.05			DEA	0.05
methidathion	0.05			ACET	0.05
Methyl Parathion	0.05			DACT	0.05

**TABLE 3. CALIFORNIA DEPARTMENT OF FOOD AND AGRICULTURE, CENTER FOR ANALYTICAL CHEMISTRY  
ORGANOPHOSPHATE AND TRIZINE/HERBICIDE PESTICIDES CONTINUED**

<b>Pyrethroid Pesticides in Surface Water</b>	
<b>Method: GC/ECD, confirmed with GC/MSD</b>	
<b><u>Compound</u></b>	<b><u>Reporting Limit (µg/L)</u></b>
Esfenvalerate	0.05
Permethrin	0.05
<b>Pyrethroid Pesticides in Sediment</b>	
<b>Method: GC/ECD, confirmed with GC/MSD (MG/G)</b>	
<b><u>Compound</u></b>	<b><u>Reporting Limit (µg/g)</u></b>
Fenvalerate/Esfenvalerate	0.011
Permethrin	0.01
Bifenthrin	0.01
Lambda Cyhalothrin	0.013
Cyfluthrin	0.011
Cypermethrin	0.011

**TABLE 4. BLIND SPIKE QUALITY CONTROL DATA**

Extraction Date	Sample Number	Screen	Pesticide	Spike Level	Recovery	Percent Recovery	Exceed CL <sup>a</sup>
1/23/03	97	PY	Permethrin	0.20	0.095	47.5	LCL <sup>b</sup>
Back-up blind spike results for 97			Permethrin	0.20	0.205	103	No
1/23/03	99	PY	Esfenvalerate	0.25	0.222	88.8	No
1/24/03	96	OP	Methidathion	0.25	0.244	97.6	No
1/24/03	98	OP	Diazinon	0.35	0.296	84.6	No
2/18/03	551	PY	Permethrin	0.30	0.297	99.0	No
2/18/03	624	PY	Permethrin	0.35	0.289	82.6	No
2/19/03	525	OP	Chlorpyrifos	0.25	0.217	86.8	No
2/19/03	626	OP	Malathion	0.20	0.165	82.5	No
2/19/03	552	OP	Diazinon	0.25	0.22	88.0	No
2/19/03	524	OP	Dimethoate	0.45	0.378	84.0	No
2/28/03	526	TR	Hexazinone	0.35	0.376	107	No
3/3/03	553	TR	Norflurazon	0.15	0.165	110	UWL
3/3/03	554	TR	Bromacil	0.20	0.255	127.5	UCL
3/3/03	625	TR	DEA	0.30	nd	nd <sup>c</sup>	LCL
3/17/03	343	PY	Esfenvalerate	0.35	0.419	120	No
3/18/03	345	TR	DACT	0.20	0.183	91.5	No
3/19/03	555	OP	Ethoprop	0.25	0.188	75.2	No

<sup>a</sup> CL=Control Limit; Upper CL (UCL), Lower CL (LCL).

<sup>b</sup> Chemist unsure whether problem occurred during extraction or when making blind spike. Back-up blind spike recovery was good, but bottles are spiked individually.

<sup>c</sup> The blind spike was spiked 10X lower than planned.



**TABLE 5. CONTINUING QUALITY CONTROL – ORGANOPHOSPHATE PESTICIDES**

Date	Numbers	Ethoprop	Diazinon	Disulfoton	Chlorpyrifos	Malathion	Methidathion	Fenamiphos	Methyl Azinphos	Dichlorvos	Phorate	Fonophos	Dimethoate	Methyl Parathion	Tribufos (DEF)	Profenofos
1/24/2003	(96),(98),101,108, 115,122,129,136, 143	74.4	79.2	77.8	83.9	89.1	87.4	83.3	81.5	80.7	87.2	92.1	98.3	103	101	108
1/24/2003	150,237,245,249, 256,263,270,277, 284	87.7	93.8	91.3	96.7	103	101	99.4	91.4	72.8	81.5	83.9	112	91.5	93.6	98.9
2/19/2003	165, 172, 179, 186, 193, 201, 208, 215	97.3	97.1	90.8	98.3	102	96.4	97.1	93.5	not analyzed	88.0	92.6	90.2	94.5	96.7	97.9
2/19/2003	626, 552, 525, 532, 600, 607, 614, 621	91.4	90.1	87.7	98.1	99	97.2	107	105	not analyzed	88.1	92.9	90.8	95	96.8	95.9
2/19/2003	225, 232, 235, 501, 508, 515, 522, 524	81.2	83.0	78.7	86.9	88.5	88.2	90.4	79.8	not analyzed	83.5	88.3	88.8	89.3	91.5	92.6
3/19/2003	304,312,319,326, 333,340,(555)	87.0	90.9	83.4	92.2	96.3	97.0	106	110	not analyzed	101	102	95.1	106	106	105
Average Recovery		86.5	89.0	85.0	92.7	96.3	94.5	97.2	93.5	76.8	88.2	92.0	95.9	96.6	97.6	99.7
Standard Deviation		8.0	6.7	5.9	6.1	6.3	5.5	9.1	12.2	5.6	6.8	6.0	8.7	6.6	5.2	5.8
CV		9.20	7.54	6.96	6.61	6.52	5.78	9.40	13.01	7.28	7.72	6.53	9.03	6.80	5.36	5.77
Upper Control Limit		123	147	119	121	126	128	125	137	106	110	113	117	119	126	125
Upper Warning Limit		113	130	109	112	116	117	115	122	98	102	105	108	111	116	115
Lower Warning Limit		71	63	68	77	76	75	77	64	67	74	76	73	77	75	74
Lower Control Limit		60	46	58	68	66	64	68	49	59	66	68	65	68	65	64

\*Highlighted cells are percent recoveries exceeding control limits

Sample numbers in ( ) are blind spikes.

Spike level = 0.1ppb (OP screen/Diazinon analysis in river water)

**TABLE 6. CONTINUING QUALITY CONTROL – TRIAZINE PESTICIDES**

Extraction Date	Sample Numbers	Spike	Percent Recovery												
			Atrazine	Simazine	Diuron	Prometon	Bromacil	Hexazinone	Metribuzin	Prometryn	DEA (Deethyl)	ACET (Deiso)	DACT	Norflurazon	Propazine (Surrogate)
1/29/2003	102,109,116,123,130,137,144,151	1	80.0	81.5	109	83.5	122	116	79.5	90.5	108	112	86.5	93.0	79.5
		2	75.5	82.5	109	81.0	108	110	95.5	87.0	104	107	92.5	87.5	77.0
2/24/2003	238, 245, 250, 257, 264, 271, 278, 285	1	105	106	108	94.0	112	108	98.0	102	99.0	106	122	120	102
		2	99.5	107	102	97.0	114	109	103	112	97.0	110	124	122	105
2/27/2003	166,173,180,187,194,202,209,216	1	86.5	86.0	101	74.5	97.5	83.5	89.5	91.0	81.5	82.0	91.0	98.5	91.5
		2	79.5	79.5	108	74.0	101	88.0	77.8	86.5	81.0	101	94.0	98.0	90.5
2/28/2003	226,233,290,502,509,516,523,(526)	1	86.0	93.0	125	84.5	112	94.5	99.5	85.5	86.5	80.0	103	99.0	89.5
		2	94.5	103.5	123	86.0	120	95.0	102	97.5	90.5	85.0	106	102	95.0
3/3/2003	(553,554,625)533,601,608,615,622	1	90.5	99.5	114	82.5	102	89.0	89.5	88.0	98.5	80.0	99.0	91.5	92.0
		2	95.5	100.0	117	94.0	106	93.5	108	102	100	88.5	111	99.0	104
3/18/2003	(345),338,331,324,317,310, 302	1	86.0	85.5	91.0	74.5	98.5	84.0	99.0	80.0	84.0	69.0	72.0	99.5	81.0
		2	86.0	92.0	139	80.5	104	86.5	82.5	87.5	78.5	83.0	77.5	105	86.5
Average Recovery			88.7	92.9	112	83.8	108	96	93.6	92.3	92.3	91.8	98.2	101	91.0
Standard Deviation			8.67	9.9	12.7	7.85	7.93	11.36	9.74	8.90	9.82	14.17	16.03	10.28	9.19
CV			9.77	10.6	11.3	9.36	7.35	11.78	10.41	9.64	10.65	15.45	16.33	10.15	10.10
Upper Control Limit			105	108	118	106	117	121	110	111	116	140	101	113	115
Upper Warning Limit			98.2	101	109	99.2	111	113	103	105	109	128	95.7	107	107
Lower Warning Limit			72.2	73.2	73.4	73.8	84.9	76.9	75.0	78.9	79.1	78.3	73.7	84.8	72.4
Lower Control Limit			65.8	66.3	64.4	67.4	78.4	68.1	68.0	72.4	71.7	66.0	68.2	79.2	63.8

\*Highlighted cells are percent recoveries exceeding control limits

Sample numbers in ( ) are blind spikes.

Spike Level = 0.2ppb (Triazine screen in river water)

**TABLE 7. CONTINUING QUALITY CONTROL – PYRETHROID PESTICIDES IN WATER**

Extraction Date	Sample Numbers	Percent Recovery	
		Permethrin	Esfenvalerate
1/23/2003	149,236,244,248,255,262,269,276,283	92.7	107
1/23/2003	(97),(99),100,107,114,121,128,135,142	95.0	102
2/14/2003	156,163,627, 637	79.0	95.0
2/18/2003	171,185,(624),(551),613,531,620,606,514,507	99.0	106
2/18/2003	224,164,200,178,192,295,214,207,231,234,	118	122
2/19/2003	500, 521	100	111
3/17/2003	300,308,315,322,329, 336,343	107	89.8
Average Recovery		98.7	105
Standard Deviation		12.12	10.56
CV		12.28	10.09
Upper Control Limit		127	131
Upper Warning Limit		117	121
Lower Warning Limit		76.0	80.2
Lower Control Limit		65.9	70.0

\*Highlighted cells are percent recoveries exceeding control limits

Sample numbers in ( ) are blind spikes.

Spike Level = 0.2ppb (Esfenvalerate and Permethrin total in river water with sediment)

**TABLE 8. CONTINUING QUALITY CONTROL – PYRETHROID PESTICIDES IN SEDIMENT**

Extraction Date	Sample Numbers	Percent Recovery					
		bifenthrin	lambda cyhalothrin	permethrin (cis&trans)	cyfluthrin 1-4	cypermethrin 1-4	fenvalerate/ esfenvalerate
11/22/2002	1,2,3, (w. 210 sample)	103	114	96.0	113	107	117
2/10/2003	4,5,10,11,14,15,20, 21	99.0	105	100.0	92.0	96.0	98.0
2/18/2003	12,99, 110	98.8	103	99.6	102	99.0	103
3/6/2003	7, 13, (215: 508- 515)	85.2	85.0	83.2	78.3	79.0	84.0
4/3/2003	6,8,9, 25,26	96.8	101	98.8	88.6	95.3	96.8
<b>Average Recovery</b>		97	102	96	95	95	100
<b>Standard Deviation</b>		6.7	10.5	7.1	13.2	10.2	11.9
<b>CV</b>		6.98	10.36	7.39	13.97	10.72	11.94
<b>Upper Control Limit</b>		142	158	133	152	173	149
<b>Upper Warning Limit</b>		131	145	123	139	154	137
<b>Lower Warning Limit</b>		88.9	90.9	81.2	88.4	76.2	87.4
<b>Lower Control Limit</b>		78.4	77.4	70.8	75.6	56.8	74.7

Sample numbers in ( ) are blind spikes.  
 Spike Level = 0.03ppm

**TABLE 9. RESULTS: WATER QUALITY MEASUREMENTS**

<b>Wadsworth Canal 1/22/2003</b>					<b>Jack Slough 1/22/03</b>				
<b>Time</b>	<b>Temp</b>	<b>pH</b>	<b>EC</b>	<b>DO</b>	<b>Time</b>	<b>Temp</b>	<b>pH</b>	<b>EC</b>	<b>DO</b>
15:35	11	7.56	307.7	8.64	15:45	10.5	7	109.2	11.51
16:32	11.8	7.11	302.7	8.66	16:45	10.6	7	109.8	11.5
17:25	11.7	7.08	287.8	8.78	17:45	10.6	7.05	109.7	11.3
18:30	11.8	7.04	274.3	8.72	18:45	10.7	7.1	109.2	10.95
19:35	11.8	6.75	260.2	8.75	19:45	10.8	7.1	108.4	10.79
20:35	11.8	6.72	255.1	8.78	20:45	10.9	7.02	109.9	10.46
21:40	11.8	6.44	246.5	8.77	21:45	11	7.39	109.1	9.42
22:35	11.8	6.45	244.6	8.73	22:45	11	7.2	107.5	11.15
<b>Wadsworth Canal 2/15-16/2003</b>					<b>Jack Slough 2/15-16/03</b>				
<b>Time</b>	<b>Temp</b>	<b>pH</b>	<b>EC</b>	<b>DO</b>	<b>Time</b>	<b>Temp</b>	<b>pH</b>	<b>EC</b>	<b>DO</b>
21:30	14.6	7.62	NA	NA	21:56	13.1	7.09	163.6	7.78
22:25	14.5	7.57	NA	NA	2300	13	7.36	163.4	7.84
23:30	14.3	7.57	NA	NA	24:00:00	12.9	7.34	162	8.16
24:30:00	14.1	7.53	NA	NA	1:00	12.8	7.38	157.8	8.31
1:30	13.8	7.55	NA	NA	2:00	12.7	7.56	152.3	8.36
2:30	12	7.15	NA	NA	3:00	12.6	7.52	150	8.38
3:30	11.9	7.15	NA	NA	4:00	12.4	7.52	145.2	8.44
4:30	11.6	7.16	NA	NA	5:00	12.1	7.46	142.6	8.06
5:30	11.8	7.36	NA	NA	6:00	11.8	7.43	142.2	8.55
<b>Del Puerto Creek 3/15/03</b>									
<b>Time</b>	<b>Temp</b>	<b>pH</b>	<b>EC</b>	<b>DO</b>					
9:30	13.7	8.59	223.5	8.65					
10:30	14.8	8.29	381	8.6					
11:25	16.1	8.67	385	8.96					
12:30	17.8	8.51	347.5	8.36					
13:30	18.9	9.03	363	8.35					
14:30	19.8	8.74	389	8.2					

**TABLE 10. RESULTS: TOTAL SUSPENDED SEDIMENT**

**Wadsworth - 1/22/2003**

Sample #	105	112	119	126	133	140	147	154
Time	15:35	16:32	17:25	18:30	19:35	20:35	21:40	22:35
Sediment (mg/L)	28	28	61.6	173.2	106	80.8	69.2	64.4

**Wadsworth Canal 2/15-16/03**

Sample #	169	176	183	190	197	505	512	519	529
Time	21:30	22:25	23:30	:30	1:30	2:30	3:30	4:30	5:30
Sediment (mg/L)	7.6	10	10.4	27.2	200	3114.4	1439.6	684.4	336.8

**Jack Slough - 1/22/2003**

	Time							
Sample #	241	297	253	260	267	274	281	288
Time	15:45	16:45	17:45	18:45	19:45	20:45	21:45	22:45
Sediment (mg/L)	73.6	71.6	73.6	78.8	80.4	63.6	70.8	66

**Jack Slough 2/15-16/03**

Sample #	205	212	219	229	293	604	611	618	637
Time	21:56	23:00	24:00:00	1:00	2:00	3:00	4:00	5:00	6:00
Sediment (mg/L)	80	82.4	84.8	93.2	126	159.6	230.8	247.6	300

**Del Puerto Creek 3/15/03**

Sample #	306	313	320	327	334	341
Time	9:20	10:20	11:20	12:20	13:20	14:20
Sediment (mg/L)	2708.8	1476	1216.8	727.6	557.6	452

**TABLE 11. RESULTS: PESTICIDE DETECTIONS IN WATER AND ACUTE TOXICITY (ppb)**

	Sampling time	Chlorpyrifos	Diazinon	Simazine	Diuron	Bromacil	Hexazinone	Metribuzin	Norflurazon	ACET	Dimethoate	Ethoprop	Methyl Parathion	Esfenvalerat	Permethrin	Acute toxicity (% survival)
<b>Wadsworth Canal</b>	15:35	trace	0.130	0.066	0.175	nd	nd	nd	0.052	nd	nd	nd	nd	nd	nd	95/100
Jan. 22, 2003	16:32	trace	0.130	nd	0.218	nd	nd	nd	0.053	nd	nd	nd	nd	nd	nd	100/100
	17:25	nd	0.116	nd	0.236	nd	nd	nd	0.077	nd	nd	nd	nd	nd	nd	95/100
	18:30	trace	0.117	nd	0.317	nd	nd	nd	0.091	nd	nd	nd	nd	nd	nd	100/100
	19:35	nd	0.106	0.078	0.194	nd	nd	nd	0.09	nd	nd	nd	nd	nd	nd	100/100
	20:35	trace	0.115	nd	0.186	nd	nd	nd	0.113	nd	nd	nd	nd	nd	nd	90/100
	21:40	trace	0.114	nd	0.149	nd	nd	nd	0.093	nd	nd	nd	nd	nd	nd	100/100
	22:35	trace	0.111	nd	0.151	nd	nd	nd	0.093	nd	nd	nd	nd	nd	nd	100/100
Feb. 15-16, 2003	21:30	trace	0.103	nd	0.077	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	100/100
	22:25	trace	0.103	nd	0.133	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	100/100
	23:30	trace	0.103	nd	0.091	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	95/100
	0:30	trace	0.102	nd	0.115	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	95/100
	1:30	trace	0.106	nd	6.12	0.923	nd	nd	0.374	nd	nd	nd	nd	nd	nd	95/100
	2:30	nd	0.246	nd	1.05	0.381	nd	nd	0.243	nd	nd	nd	nd	trace	0.094	0/100
	3:30	nd	0.176	nd	1.5	0.324	nd	nd	0.121	nd	nd	nd	nd	nd	nd	60/100
	4:30	nd	0.19	nd	1.678	0.121	nd	nd	0.052	nd	nd	nd	nd	nd	nd	95/100
	5:30	trace	0.13	nd	0.521	nd	nd	nd	0.063	nd	nd	nd	nd	nd	nd	95/100

Trace = An analyte concentration that falls between the reporting limit and method detection limit (DPR memo dated 7/17/02).

% survival = % survival in sample / % survival in control

**TABLE 11. RESULTS: PESTICIDE DETECTIONS IN WATER AND ACUTE TOXICITY (ppb) CONTINUED**

	Sampling time	Chlorpyrifos	Diazinon	Simazine	Diuron	Bromacil	Hexazinone	Metribuzin	Norflurazon	ACET	Dimethoate	Ethoprop	Methyl Parathion	Esfenvalerate	Permethrin	Acute toxicity (% survival)
<b>Jack Slough</b>	15:45	trace	0.126	nd	0.196	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	100/100
Jan. 22, 2003	16:45	trace	0.113	nd	0.183	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	65/100
	17:45	trace	0.098	nd	0.186	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	90/100
	18:45	trace	0.129	nd	0.19	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	85/100
	19:45	trace	0.111	nd	0.176	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	90/100
	20:45	trace	0.127	nd	0.263	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	85/100
	21:45	trace	0.129	nd	0.274	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	80/100
	22:45	trace	0.138	nd	0.198	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	100/100
Feb. 15-16, 2003	23:00	nd	0.167	nd	0.21	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	95/100
	0:00	nd	0.178	nd	0.265	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	100/100
	1:00	nd	0.161	nd	0.275	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	80/100
	2:00	nd	0.142	nd	0.213	0.135	nd	nd	nd	nd	nd	nd	nd	nd	nd	100/100
	3:00	nd	0.197	nd	0.192	0.192	nd	nd	nd	nd	nd	nd	nd	nd	nd	90/100
	4:00	nd	0.195	nd	0.26	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	60/100
	5:00	nd	0.107	0.246	0.348	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	10/100
	6:00	nd	0.161	0.415	0.326	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	15/100
<b>Del Puerto Creek</b>	9:20	nd	0.083	2.281	2.819	nd	0.09	0.142	1.387	0.112	nd	trace	trace	0.062	nd	0/95
March 15, 2003	10:20	0.059	0.096	1.943	4.184	0.246	0.316	nd	2.021	0.08	trace	trace	trace	0.093	nd	0/95
	11:20	0.233	0.119	3.787	4.288	0.463	3.564	nd	3.034	0.147	trace	trace	trace	0.087	nd	0/95
	12:20	0.169	0.109	1.155	5.516	nd	1.032	nd	3.536	nd	0.201	nd	trace	0.057	nd	0/95
	13:20	0.104	0.111	0.404	5.524	nd	0.382	nd	1.51	nd	0.302	nd	nd	trace	nd	0/95
	14:20	0.115	0.092	0.243	5.94	nd	0.288	nd	1.143	nd	0.25	nd	nd	trace	nd	0/95

Trace = An analyte concentration that falls between the reporting limit and method detection limit (DPR memo dated 7/17/02).  
 % SURVIVAL = % SURVIVAL IN SAMPLE / % SURVIVAL IN CONTROL



**TABLE 12. RESULTS: PESTICIDE DETECTIONS IN SEDIMENT ( $\mu\text{g/g}$ , wet weight basis)**

<b>Site 1. Wadsworth Canal</b>		Bifenthrin	Lambda	Cyfluthrin	Cypermethrin	Esfenvalerate	Permethrin	Wet weight	Dry weight
Time	Date							grams	grams
10:30	11/18/2002	nd	nd	nd	nd	nd	nd	23.04	12.12
16:45	1/22/2003	nd	nd	nd	nd	nd	nd	21.94	14.65
22:55	1/22/2003	nd	nd	nd	nd	nd	nd	20.74	14.14
13:50	1/29/2003	nd	nd	nd	nd	nd	nd	18.02	12.26
13:10	2/5/2003	nd	nd	nd	nd	nd	nd	18.23	12.87
NO SEDIMENT SAMPLES WERE COLLECTED DURING THE SECOND STORM EVENT ON 2/15/03									
<b>Site 2. Jack Slough</b>									
Time	Date							grams	grams
10:00	11/18/2002	nd	nd	nd	nd	nd	nd	21.99	12.17
15:45	1/22/2003	nd	nd	nd	nd	nd	nd	18.89	10.1
22:45	1/22/2003	nd	nd	nd	nd	nd	nd	20.49	8.22
14:30	1/29/2003	nd	nd	nd	nd	nd	nd	24.42	11.96
13:50	2/5/2003	nd	nd	nd	nd	nd	nd	24.01	12.54
12:50	2/13/2003	nd	nd	nd	nd	nd	nd	25.02	11.62
21:56	2/15/2003	nd	nd	nd	nd	nd	nd	25	5.98
6:00	2/16/2003	nd	nd	nd	nd	nd	nd	25	14.24
12:00	2/24/2003	nd	nd	nd	nd	nd	nd	20.54	9.69
11:55	3/3/2003	nd	nd	nd	nd	nd	nd	20.31	7.44

**TABLE 12. RESULTS: PESTICIDE DETECTIONS IN SEDIMENT ( $\mu\text{g/g}$ , wet weight basis) CONTINUED**

Site 3. Del Puerto Creek		Bifenthrin	Lambda	Cyfluthrin	Cypermethrin	Esfenvalerate	Permethrin	Wet weight	Dry weight
Time	Date	$\mu\text{g/g}$ (ppm)						grams	grams
10:30	11/20/2002	nd	nd	nd	nd	nd	nd	22.55	15.87
9:10	3/15/2003	0.0242	nd	nd	nd	nd	nd	20.61	13.92
9:30	3/15/2003	nd	nd	nd	nd	nd	nd	21.25	12.38
13:15	3/15/2003	nd	nd	nd	nd	nd	nd	20.53	13.01
10:20	3/21/2003	nd	nd	nd	nd	nd	nd	20.13	14.87
9:15	3/28/2003	nd	nd	nd	nd	nd	nd	20.19	13.64

Figure 1

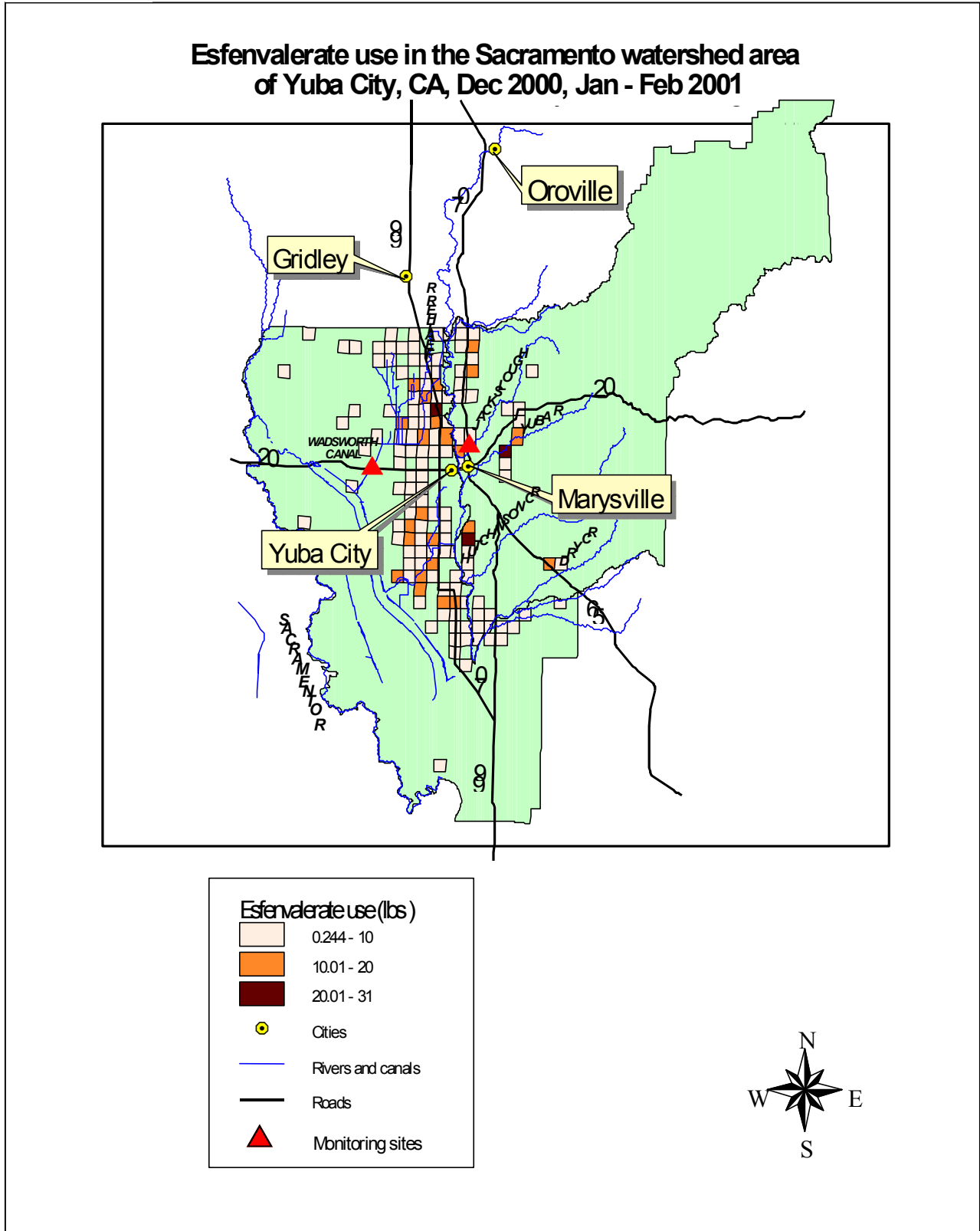


Figure 2

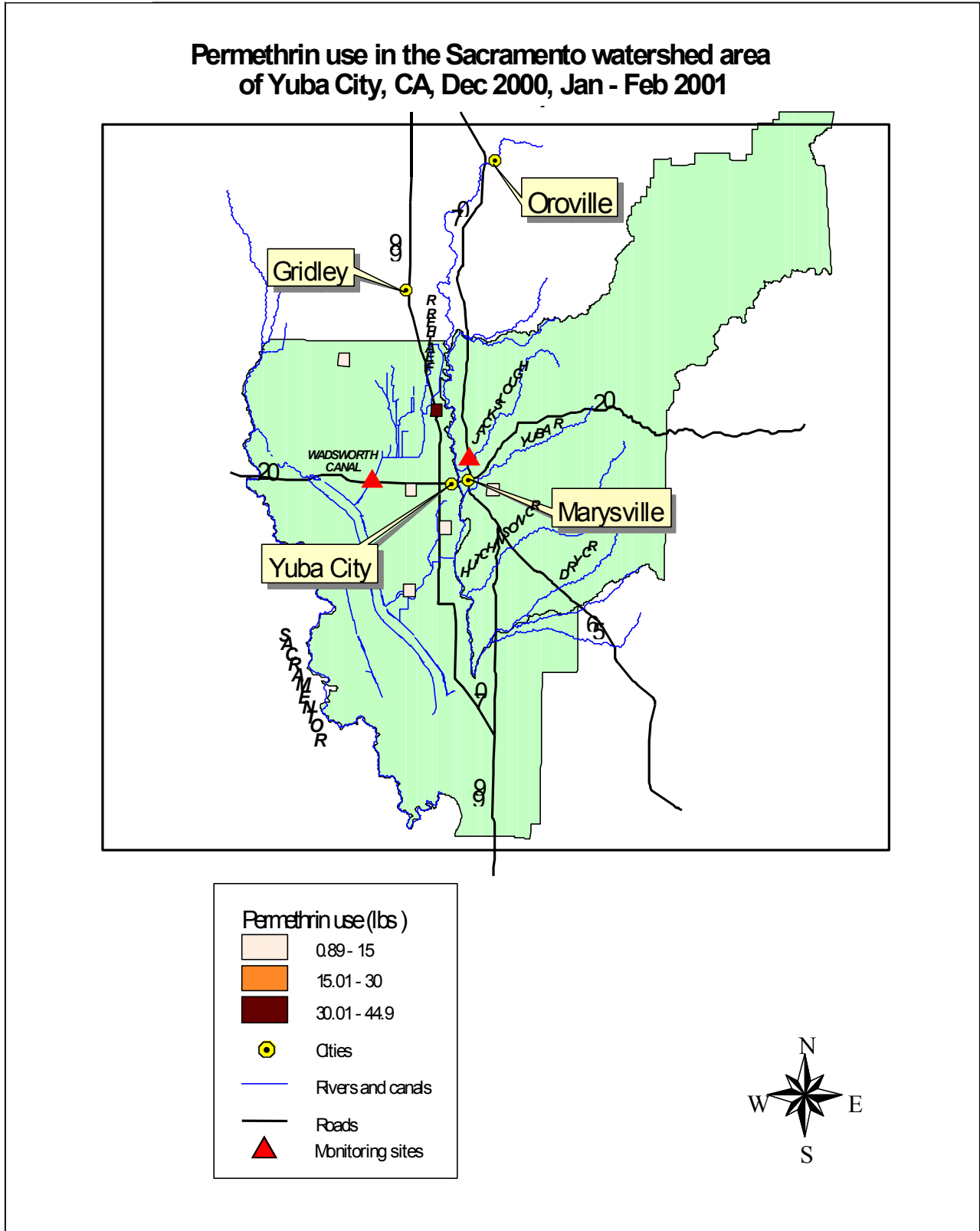


Figure 3

**Esfenvalerat use in the San Joaquin watershed area  
of Modesto, CA, Dec 2000, Jan - Feb 2001**

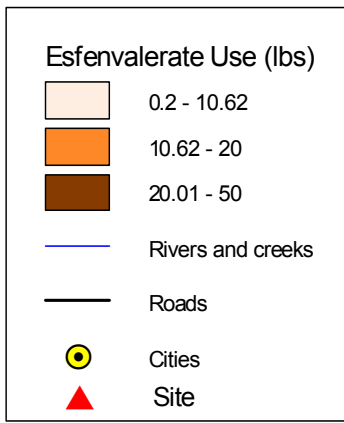
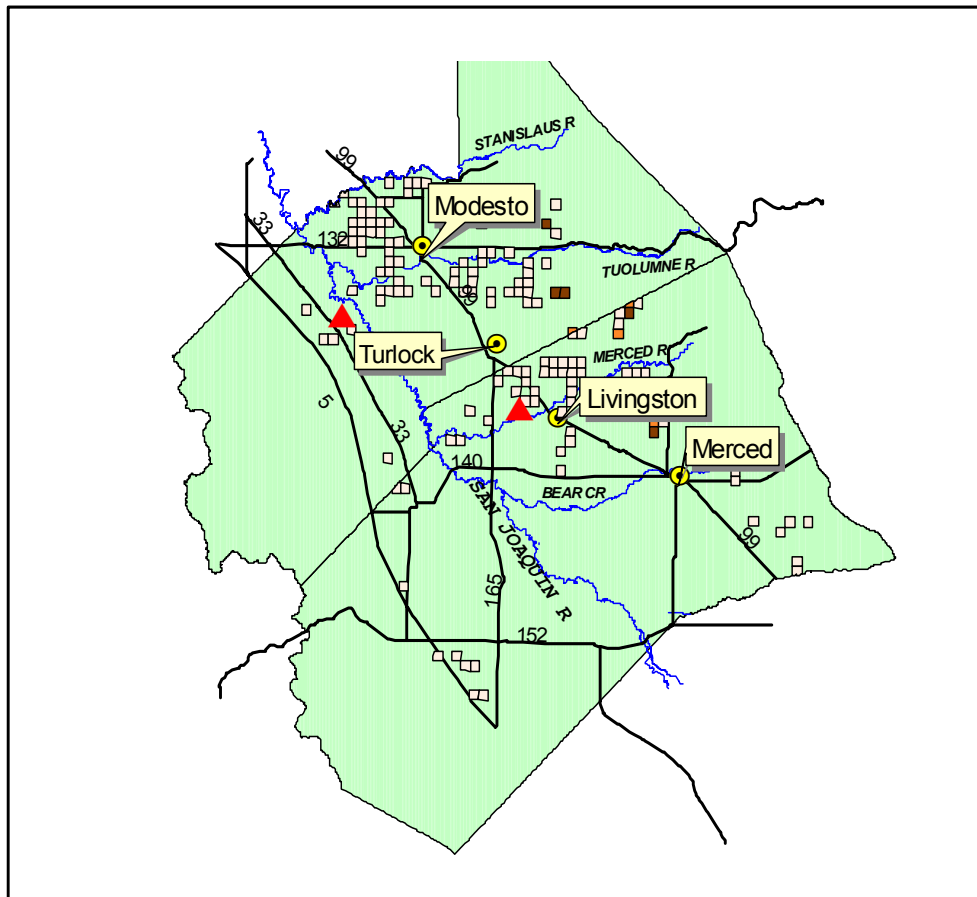


Figure 4

Permethrin use in the San Joaquin watershed area  
of Modesto, CA, Dec 2000, Jan - Feb 2001

