THE OCCURRENCE AND CONCENTRATION OF ESFENVALERATE AND PERMETHRIN IN WATER AND SEDIMENT IN THE SACRAMENTO AND SAN JOAQUIN WATERSHEDS

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ABSTRACT

This study was conducted to determine whether pyrethroid insecticides, particularly esfenvalerate and permethrin, were moving offsite into surface waters, during winter storm events, and to characterize typical concentration ranges that might be observed. Additional objectives included the collection of further storm runoff monitoring data for (a) the known organophosphate (OP) surface water contaminants diazinon and chlorpyrifos, and (b) selected herbicides. Dormant spray OP insecticides have been widely detected in California surface water during the rainy season. While the use of OP dormant sprays has been steadily decreasing in recent years, they are being replaced by pyrethroids such as esfenvalerate and permethrin. Four monitoring sites were chosen, two in the Sacramento watershed and two in the San Joaquin watershed, which reflected areas with the heaviest historical applications of esfenvalerate and permethrin through the dormant-spray season. Whole water grab samples (runoff water plus suspended sediment) and bed sediment samples were collected for pesticide analysis during runoff events. Bioassays were also conducted for acute toxicity to the sensitive aquatic species *Ceriodaphnia dubia*. There were detections of permethrin and/or esfenvalerate in seven of 40 whole water samples, with concentrations ranging up to 0.094 µg/L. While significant toxicity to *Ceriodaphnia dubia* was observed in every water sample containing pyrethroids, these same samples also contained both OPs and herbicides. Organophosphate concentrations in five of seven of these samples were sufficient to account for the observed toxicity. The remaining two samples may have demonstrated toxicity due to synergistic effects between the pyrethroids, OPs and herbicides, or toxicity may be attributable to additional constituents that were not determined. Probabilistic estimation of dissolved phase pyrethroid concentrations in the positive samples suggests that bioavailable pyrethroid concentrations were lower than available aquatic freshwater LC50s, however such toxicity data are limited for esfenvalerate. Of the fifteen bed sediment samples collected, the pyrethroid bifenthrin was detected in one sample (0.0242µg/g); there were no other pyrethroid detections in bed sediment. This study shows that pyrethroid pesticides are sufficiently mobile to move off-site in measurable amounts during rain-induced runoff events, however their potential toxicity to biological communities is not fully understood.

ACKNOWLEGMENTS

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Thanks also to the California Department of Food and Agriculture who conducted chemical analysis and the California Department of Fish and Game who conducted toxicity tests.

DISCLAIMER

The mention of commercial products, their source, or use in connection with material reported herein is not to be construed as an actual or implied endorsement of such product.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

I. Introduction

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, organophosphate (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. These applications occur primarily between late-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 sorbed to sediment. Various monitoring studies conducted by the Department of Pesticide Regulation (DPR) and U.S. Geological Survey (USGS) have shown that dormant spray 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). 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. While pyrethroids have the potential to be acutely toxic to aquatic species, their physico-chemical properties indicate that they are primarily associated with sediment in aquatic systems (Tables 1 and 2). Though sorption to sediment mitigates their acute toxicity by reducing short-term bioavailability, the effect is poorly understood, and data on long-term effects on chronic toxicity is very limited.

The physio-chemical properties of pyrethroids reflect that they have a strong tendency to sorb to organic carbons with the potential to continuously move offsite attached to sediment. There is a potential for acute toxicity to sediment-dwelling aquatic organisms, or those that live just above the sediment. Muir et al. (1985) found that the midge *Chironomus tentans* became immobilized after being exposed to greater than 0.005μg/g concentrations of four different pyrethroids (fenvalerate, permethrin, deltamethrin, cypermethrin). Any accumulation of pyrethroids by larvae was suggested by the author to be due to the uptake of the dissolved portion in the pore water.

In a water only environment, Schulz and Leiss (2001b) showed a significant change in emergence success for the macroinvertebrate *Limnephilus lunatus*. This occurred at concentrations of 0.001µg/L or greater. Total emergence at the end of the experiment (240 days after exposure) showed significant reduction of emergence at 0.1µg/L in a water only environment.

Schulz and Dabrowski (2001) found mortality increased significantly in benthic macroinvertebrates when exposed to both fenvalerate (0.2µg/L) and predatory fish. The authors suggested this was due to toxicological impairment of nymphs by the pesticide, causing them to be unable to effectively avoid predators and become easy prey for fish.

The primary objectives of this monitoring project were to determine if pyrethroid insecticides, particularly esfenvalerate and permethrin, are moving offsite into surface waters at measurable concentrations during winter storm events, and to evaluate typical concentration ranges that might be observed. An additional objective was to obtain more data on OP insecticides and selected herbicide residues in surface water.

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 5-8). Two were located in the Sacramento watershed and two in the San Joaquin watershed. 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 which in turn flows into the Sacramento River
3.) Del Puerto creek at Vineyard road, a tributary that flows westerly into the San Joaquin River
4.) Highline canal at Griffith road, a canal that flows easterly into the Merced River, which in turn flows into the San Joaquin River.

Sampling Plan
Monitoring occurred during three 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). Water samples were also analyzed for total suspended sediment and bioassays were conducted for acute toxicity to the sensitive aquatic species *Ceriodaphnia dubia*. Toxicity to *C. dubia* is used as a screening tool to indicate the presence of bioavailable contaminants at concentrations that may negatively impact aquatic organisms.

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

Sampling Method
Each water sample, toxicity sample and suspended sediment sample was individually collected in 1-liter amber bottles as opposed to collection of large water volumes and subsequent splitting into 1-liter sample bottles. This was done to minimize adsorption and loss of pesticides in samples by exposing samples to as few containers and sampling equipment as possible. A total of 39 water samples were collected. All samples were grab samples, collected 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. The amber sample 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 water's edge and placed into a 1-pint, clear glass jar. This was repeated within the same general area until the jar was approximately ¾ full. When collecting with the tube, one end of the tube was thrust into the submerged sediment near the waters edge and then removed. The top 1-inch 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 ¾ full.

All water samples were transported on wet ice and then 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).

Rainfall and discharge data (where available) were also gathered for the study areas. Rainfall measurements and observations 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 U.S. Geological Survey (USGS) gauging stations and the Central Valley Regional Water Quality Control Board (CVRWQCB).

Pesticide Analysis and Toxicity Tests

Analysis

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

- OPs - GC/FPD - gas chromatography/flame phometric detector
- Pyrethroids - GC/ECD - gas chromatography/electron capture detector, confirmed with GC/ MSD - gas chromatography/mass selective detector
- 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. The reporting limit was determined as the lowest concentration of analyte that the method can detect reliably in a matrix blank as described in SOP QAQC001 (Segawa, 1995). Method titles, method detection limits and reporting limits for this study are reported in Table 3. Comprehensive chemical analytical methods are provided in appendices 2-5. Concentrations are reported as nd (below detection limit), trace, or a numerical concentration in $\mu g\ L^{-1}$. A trace detection is a detection where the analyte concentration is between the method detection limit and the reporting limit, and where the detection is due to the particular analyte in the chemist's best professional judgment (Appendix 1).

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, 2002a). Significant toxicity is defined as a difference of 30 percent or greater between survival of test organisms and control organisms. An additional requirement is that control organism survival must be equal or greater than 90 percent.

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. The numbers of field blanks and blind spikes submitted for chemical analysis were each approximately ten percent of the total number of water samples. In addition, there were 278 matrix spikes analyzed and compared to established warning and control limits for each analytical method. Quality Control results are presented in Tables 4 though 8.

3. Results

Quality Control

Two blind spikes were below the lower control limit (permethrin and DEA). The permethrin spike was repeated with a back up spike and the results were within the control limits. The DEA spike was not repeated. Two spikes exceeded the upper control limit, norflurazon and bromacil. Because herbicides were not the primary focus of this study, backup samples of those in the affected extraction sets were not re-analyzed for herbicides.

There were a total of 278 continuing QC spikes analyzed. Of the 134 spikes analyzed for pyrethroids and OPs, none fell outside the control limits. Of the 144 spikes analyzed for triazines, 14 were over the upper control limit, indicating the possibility that the herbicide analytical results may be positively biased in some cases.

Twenty-four field blanks were each analyzed for all pesticides in the pyrethroid, OP and triazine screens. There were no detections (data not shown).

Environmental Measurements

Wadsworth Canal

The first sampling event occurred on January 22, 2003. Storm events prior to this date had not been sampled due to the relatively few pesticide applications. During this storm event, samples and water quality measurements were collected hourly for 8 hours. Total rainfall for January 21 through the 22nd for this area was 0.40 inches (UCD IPM, 2003). There was no rainfall for 7 days prior to the 21st.

The local County Agricultural Commissioner's office confirmed the application of dormant spray insecticides prior to this storm event. Discharge at this site during this period was not available. Suspended sediment samples ranged from 28.0 to 173.2 mg/L, peaking at the fourth hour of the sampling event.

During the second storm event on 15-16 February 2003, samples and water quality measurements were collected hourly for 9 hours. Total rainfall for 15-16 February for this area was approximately 0.95 inches (UCD IPM, 2003). The local County Agricultural Commissioner's office confirmed the application of dormant spray insecticides prior to this storm event. Approximately 0.54 inches had fallen 2 days earlier on the 13th, but because there was no rainfall for 18 days prior to the 13th, this was not considered sufficient rainfall to cause significant runoff to sample at that time. Discharge on 15-16 February ranged from 15.78 CFS at the beginning of the sampling event to 52.97 CFS at the end of the sampling period (CVRWQCB, 2003; Figure 1). Suspended sediment ranged from 7.6 to 3114.4 mg/L, peaking at the sixth hour.

Jack Slough

During the first storm event on January 22, 2003, samples and water quality measurements were collected hourly for 8 hours. Water quality measurements were relatively constant throughout the sampling period. Suspended sediment samples collected during the sampling period ranged from 66.0 to 80.4 mg/L, peaking at the fifth hour. Storm events prior to January 22, 2003, had not been sampled due to a lack of pesticide applications. Total rainfall for 21-22 January for this area was 0.40 inches (UCD IPM, 2003). There was no rainfall for 7 days prior to the 21st. The local County Agricultural Commissioner's office confirmed the application of dormant spray insecticides prior to this storm event.

During the second storm event on 15-16 February 2003, samples and water quality measurements were collected hourly for 8 hours. Suspended sediment ranged from 80.0 to 300.0 mg/L, peaking at the last hour. Total rainfall for 15-16 February for this area was approximately 0.95 inches (UCD IPM, 2003). The local County Agricultural Commissioner's office confirmed the application of dormant spray insecticides prior to this storm event. Approximately 0.54 inches had fallen 2 days earlier on the 13th, but because there was no rainfall for 18 days prior to the 13th, this was not considered sufficient rainfall to cause significant runoff to sample at that time.

Discharge data is not available for this site.

Del Puerto Creek

Due to the lack of rainfall in this area this site was sampled only once on 15 March 2003. Samples and water quality measurements were collected hourly for 6 hours. Dissolved oxygen, pH and EC all fluctuated during the sampling period. Suspended sediment ranged from 452.0 to 2708.8 mg/L, peaking at the first hour.

Total rainfall for March 15th for this area was 0.88 inches (UCD IPM, 2003). Prior to the 15th, the last precipitation was less than 0.25 inches February 24th and 27th, but because there was no rainfall for 11 days prior to the 24th, this was not considered sufficient rainfall to cause significant runoff to sample at that time. The local County Agricultural Commissioner's office confirmed the application of dormant spray insecticides prior to this storm event.

Discharge ranged from less than 5 CFS to approximately 20 CFS over the sampling period (USGS, 2003; Figure 2). Although discharge data is available for this site, it is an underestimate due to the proximity of the sampling point to the gauging station. The gauging station is approximately 1-2 miles upstream of the sampling point, and there is at least one discharge of runoff water between these two points. This additional inflow of water is well below the gauging station and is not included in the discharge measurement.

Highline Canal

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

Pesticide Concentrations and Toxicity (Tables 11-12)

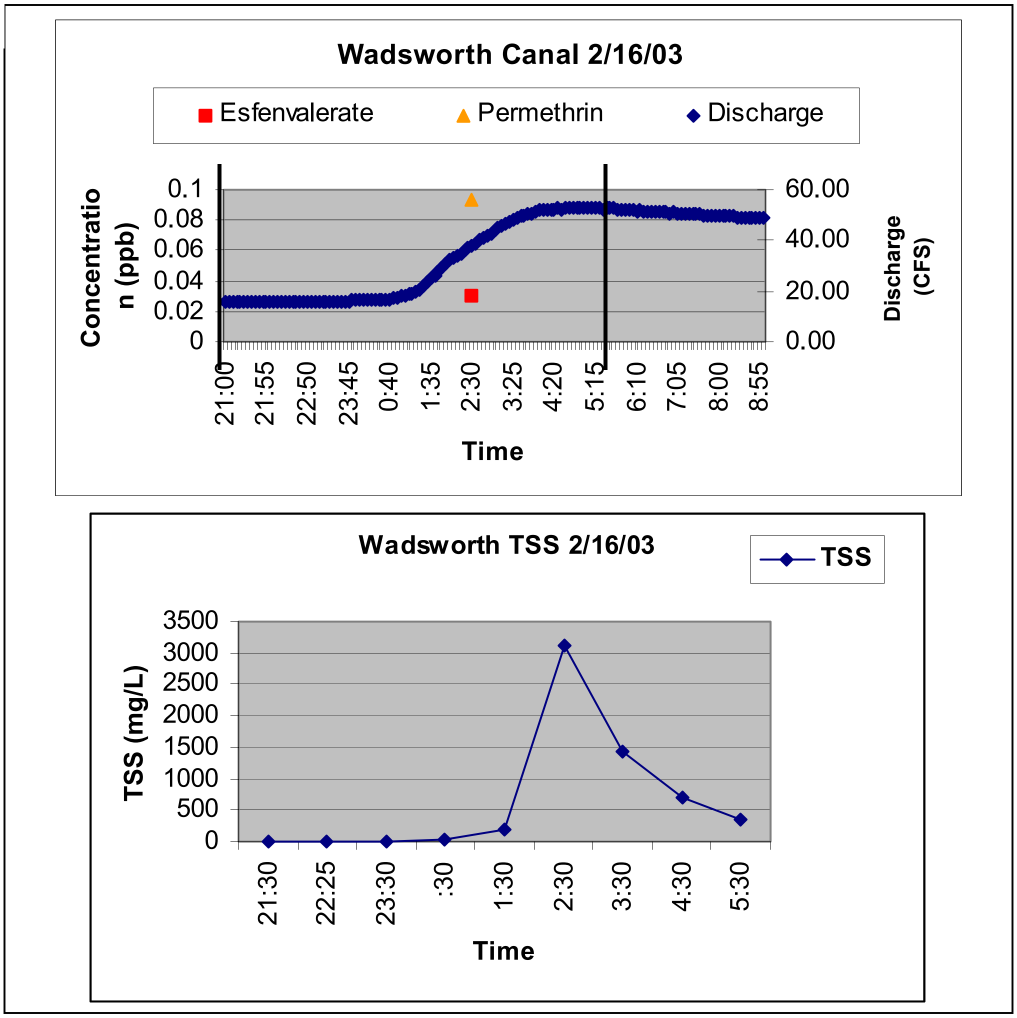
Wadsworth Canal

During the first storm event on January 22, 2003, 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 μg/L. Other detections during this storm event included the herbicides simazine, diruon, and norflurazon. There was no significant acute toxicity to *C. dubia* in any of the samples collected.

During the second storm event on February 15, 2003, there was one detection of esfenvalerate (trace) and one permethrin detection (0.094 μg/L), both occurring at the sixth hour of the 9-hour sampling period.

Discharge data was obtained after the second storm event. Due to the strong sorption properties of pyrethroids to sediment, total suspended sediments (TSS) were also measured. It is evident that peak runoff concentrations were obtained at the time of peak discharge and peak TSS levels. (Figure1).

Figure 1



Also detected were diazinon concentrations ranging from 0.102 to 0.245 µg/L, trace amounts of chlorpyrifos, and the herbicides diuron, bromacil, and norflurazon. At the sixth hour sampling, the estimated dissolved phase concentration of permethrin (0.015µg/L) was well below the *C. dubia* LC50 (0.55µg/L; Table 2). However, the *C. dubia* bioassay results demonstrated that the sample was acutely toxic (0% survival). Though diazinon was detected at this time, chlorpyrifos was not. The diazinon concentration was also less than the *C. dubia* LC50 (0.436µg/L), therefore permethrin or diazinon alone was apparently not responsible for the observed toxicity. The following hour's sample showed 60% survival of C. dubia. At this time there were no pyrethroid detections, but diazinon was detected at 0.176µg/L. The presence of pyrethroids or chlorpyrifos below the reporting limit is possible. The observed toxicity may have been due to the presence of unmeasured constituents or the possible additive or synergistic interactions between measured constituents.

Pape-Lindstrom and Lydy (1997) reported synergistic effects of the herbicide atrazine on the toxicity of OPs, and Denton et al. (2003) reported that the combined effects of diazinon and the pyrethroid esfenvalerate on larval fathead minnows were greater than additive, and suggested that synergism was occurring. The cause of toxicity here cannot be determined from the existing data.

No sediment samples were collected during this storm event.

Jack Slough

During the first 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 µg/L. There was significant acute toxicity to *C. dubia* (65% survival) in one sample. This sample had a diazinon detection of 0.113 µg/L and a trace detection of chlorpyrifos. These concentrations were below the *C. Dubia* LC50 (Table 2), yet possible additive interactions may have been occurring, accounting for the observed toxicity. Diazinon and chlorpyrifos possess a common mode of action, and have been shown to display additive properties (Bailey et al., 1997). The herbicide diuron was also detected in every sample. While the acute diuron toxicity data for C. dubia is not available, diuron is generally considered to be less toxic to aquatic invertebrates than insecticides such as diazinon.

During the second 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 0.195µg/L. 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 µg/L, respectively. Other detections during this storm event included the herbicides diuron, bromacil and simazine.

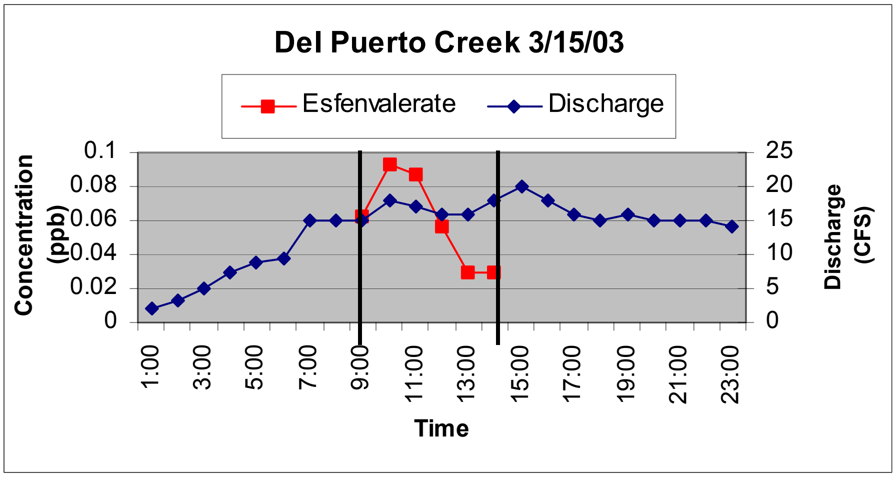
Again, diazinon alone was apparently not responsible for the observed toxicity. Toxicity may have been due to possible additive or synergistic interactions occurring, or possible toxic unmeasured constituents being present. Observed toxicity cannot be determined from the data obtained.

Del Puerto Creek

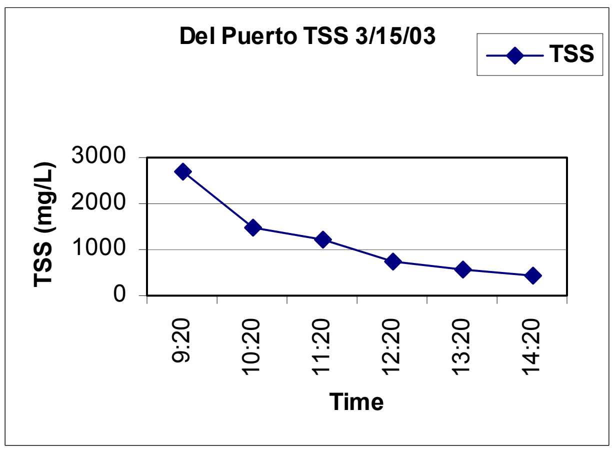
During the storm event on 15 March 2003, esfenvalerate was detected in every sample.

Discharge data was obtained after the sampling event. Due to the strong sorption properties of pyrethroids to sediment, total suspended sediments (TSS) were also measured. It is evident that peak runoff concentrations were obtained at the time of peak discharge and peak TSS levels. (Figure 2).

Figure 2



The time between the two black lines is when sampling took place.



Esfenvalerate detections ranged from trace amounts to 0.093 µg/L. Both chlorpyrifos and diazinon were also detected with concentrations ranging from 0.0594 to 0.233 µg/L and 0.0826 to 0.119 µg/L, respectively. Other OP detections included dimethoate, ethoprop, and methyl parathion. Herbicide detections included simazine, diuron, hexazinone, norflurazon, metribuzin, bromacil and ACET.

At Del Puerto creek the estimated dissolved phase concentrations of esfenvalerate ranged from 0.00346 µg/L to 0.03728 µg/L. Acute toxicity, *C. dubia* LC50, for esfenvalerate is unknown. Bioassays for *C. dubia* demonstrated acute toxicity in all six samples collected at Del Puerto Creek during this runoff event (0% survival). Major water chemical conditions (dissolved oxygen and pH) were within tolerable ranges for *C. dubia* (U.S. EPA 2001, 2002b). Chlorpyrifos concentrations exceeded the *C. dubia* LC50 (0.038 µg/L, Table 2) in all but the initial sample in which chlorpyrifos was not detected (Table 11).

The presence of chlorpyrifos in the initial sample at a level below the method detection limit is possible. In addition, diazinon was detected in all samples (Table 11), although always at concentrations below the *C. dubia* LC50 (0.436 µg/L, Table 2). Other OPs detected included dimethoate, ethoprop, and methyl parathion, which may have contributed to the observed toxicity. The following herbicides were also detected, simazine, diuron, bromacil, hexazinone, metribuzin, norflurazon, and ACET.

Bifenthrin was detected in one sediment sample (0.0242 µg/L). There were no additional pyrethroid detections in any sediment samples collected at this site.

Chlorpyrifos concentrations alone can account for much of the observed toxicity. The presence of other OPs including diazinon, as well as the pyrethroid esfenvalerate, in every sample, suggests that additive or synergistic interactions may be occurring as well.

4. Discussion

Pyrethroid Detections In Water

The physio-chemical properties of pyrethroids reflect that they are hydrophobic and have high K_{OC}s, therefore they tend to sorb strongly to suspended sediment organic carbons (Table 1). One benefit of strong sorption is reduced bioavailability, thereby mitigating acute toxicity. While this effect is not fully understood, it is commonly believed that the bioavailable fraction is limited to that which is in the dissolved phase (Lamoureux and Brownawell, 1999). In this study we estimated freely dissolved phase pyrethroid concentrations in each water sample and compared these to available water-aquatic toxicity data.

The estimation procedure yields a probabilistic estimate of freely dissolved pyrethroid concentration from whole water (suspended sediment + water) analytical data, the distribution of a particular pyrethroids measured organic carbon sorption coefficient (K_{OC}), the distribution of measured organic carbon fraction of suspended sediment in California Central Valley agriculturally-dominated tributaries, and each sample's measured suspended sediment concentration (Table 10).

The probabilistic estimate is calculated using Monte Carlo techniques by assuming organic carbon-based sorption equilibrium between the pyrethroid sorbed to suspended sediment and that freely dissolved in the water sample. A more detailed description of this method is given in Spurlock, 2003.

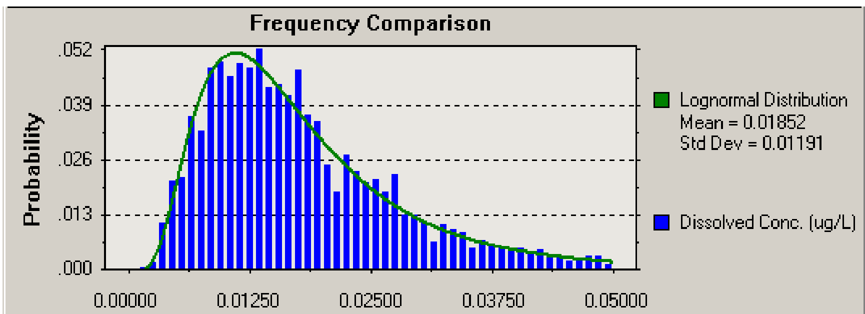
Using the permethrin detection of 0.094 µg/L found on 15 February at Wadsworth canal, the estimated dissolved phase concentration at that time was 0.00699 µg/L to 0.03229 µg/L. This is the 10 to 90th percentile range, with the 50th percentile range being 0.01503 µg/L (Figure 3).

Figure 3.

Estimated Dissolved Phase Permethrin Concentration: Wadsworth Canal: February 16, 2003, 02:30

Percentiles

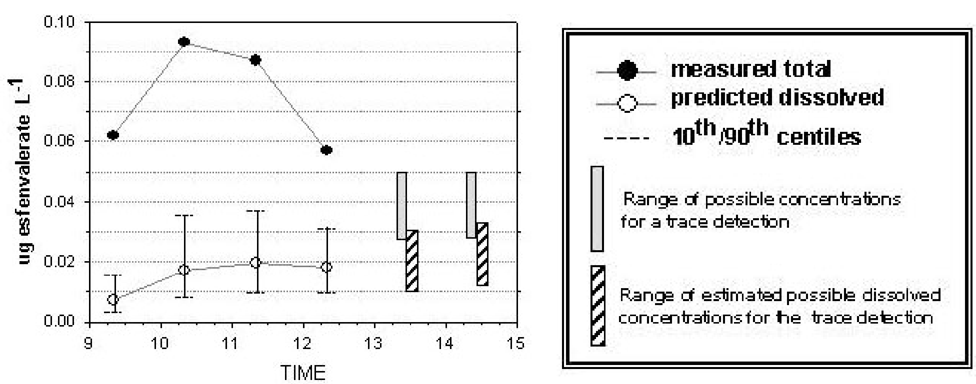
Percentile	Value
0%	0.00209
10%	0.00699
20%	0.00895
30%	0.01092
40%	0.01299
50%	0.01503
60%	0.01761
70%	0.02063
80%	0.02472
90%	0.03229
100%	0.09343



Spurlock, 2003

At Del Puerto Creek, using the esfenvalerate detections of 0.057 to 0.093µg/L found on March 15th, the estimated dissolved phase concentrations ranged from 0.00346 to 0.03728µg/L (10 to 90th percentile of estimates), with the 50th percentile ranging from approximately 0.005 to 0.02 µg/L (Figure 4).

Figure 4. **Estimated Dissolved Phase Esfenvalerate Concentration: Del Puerto Creek, March 15, 2003, 09:00 to 13:00**



Spurlock, 2003

Pyrethroid Detections in Sediment

Of the 21 sediment samples collected there was one pyrethroid detection (bifenthrin at 0.0242µg/g). Pyrethroid sediment toxicity LC_{50}'s are currently being developed. The bifenthrin 10-day LC_{50} for the test species *Hyalella azteca* has been determined to be 0.17 µg/g organic carbon (Amweg et al., 2004).

Total Suspended Sediment

Total suspended sediment levels increased substantially at all sites during the rain-induced runoff events. At Del Puerto Creek sediment levels ranged from 452 mg/L to 2708.8 mg/L. Previous TSS levels at this site during the dormant season were 8.1 and 8.9 mg/L, with spring observations as high as 370 mg/L (CVRWQCB, 2003).

5. Conclusion

In this study, both esfenvalerate and permethrin were detected in unfiltered water samples collected during a storm induced runoff event. Bifenthrin was also detected in one sediment sample. It is evident that pyrethroids are able to move offsite during a rain induced runoff event.

Typical concentrations of esfenvalerate and permethrin ranged from trace to 0.094ug/L. Discharge in the tributaries sampled reached a maximum of approximately 55 cfs and total suspended sediments were as high as 3114.4 mg/L. Due to the physical characteristics of pyrethroids, their tendency to sorb to suspended sediments (organic carbons), and the low concentrations detected, it is probable that measurable concentrations may not be detected in a larger river system such as the Sacramento or San Joaquin River.

Concentrations detected were below acute toxicity LC50 levels, yet, mortality of the test species *C. dubia* was often times 100%. A significant number of OPs were detected as well which may have contributed to the observed toxicity. Detections of diazinon and chlorpyrifos often exceeded DFG water quality standards, and chlorpyrifos levels often exceeded LC50 acute toxicity levels for the test species *C. dubia*. Toxicity may have also been due to possible additive or synergistic interactions occurring, or possible toxic unmeasured constituents being present.

The detection of pyrethroids in combination with other pesticides, as well as the increasing use of pyrethroids as they replace common OPs, should necessitate continual monitoring. Planned studies by DPR (Starner, 2004) will further examine typical concentrations of pyrethroids found in runoff (water and sediment) during normal irrigation.

Another study (Spurlock, 2004) will help to better understand the bioavailability of pyrethroids in sediment. They will also further determine and explain distributions of concentrations in sediment.

Concentrations of pyrethroids detected in this study coincided with TSS peak levels. Recent studies suggest that pyrethroids in sediment are bioavailable to aquatic organisms and toxicity is possible (Conrad et al., 1999;Pereira et al., 1995). The tendency of these pesticides to sorb to sediments would dictate sediment toxicity testing in addition to sediment monitoring in future studies.

Although not an objective in this study, many herbicides were detected at all sites. Diuron was detected in every sample collected. These results are similar to those of past studies. While the acute diuron toxicity data for *C. dubia* is not available, diuron is generally considered to be less toxic to aquatic invertebrates than insecticides.

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Figure 5 Esfenvalerate use in the Sacramento watershed area of Yuba City, CA, Dec 2000, Jan - Feb 2001

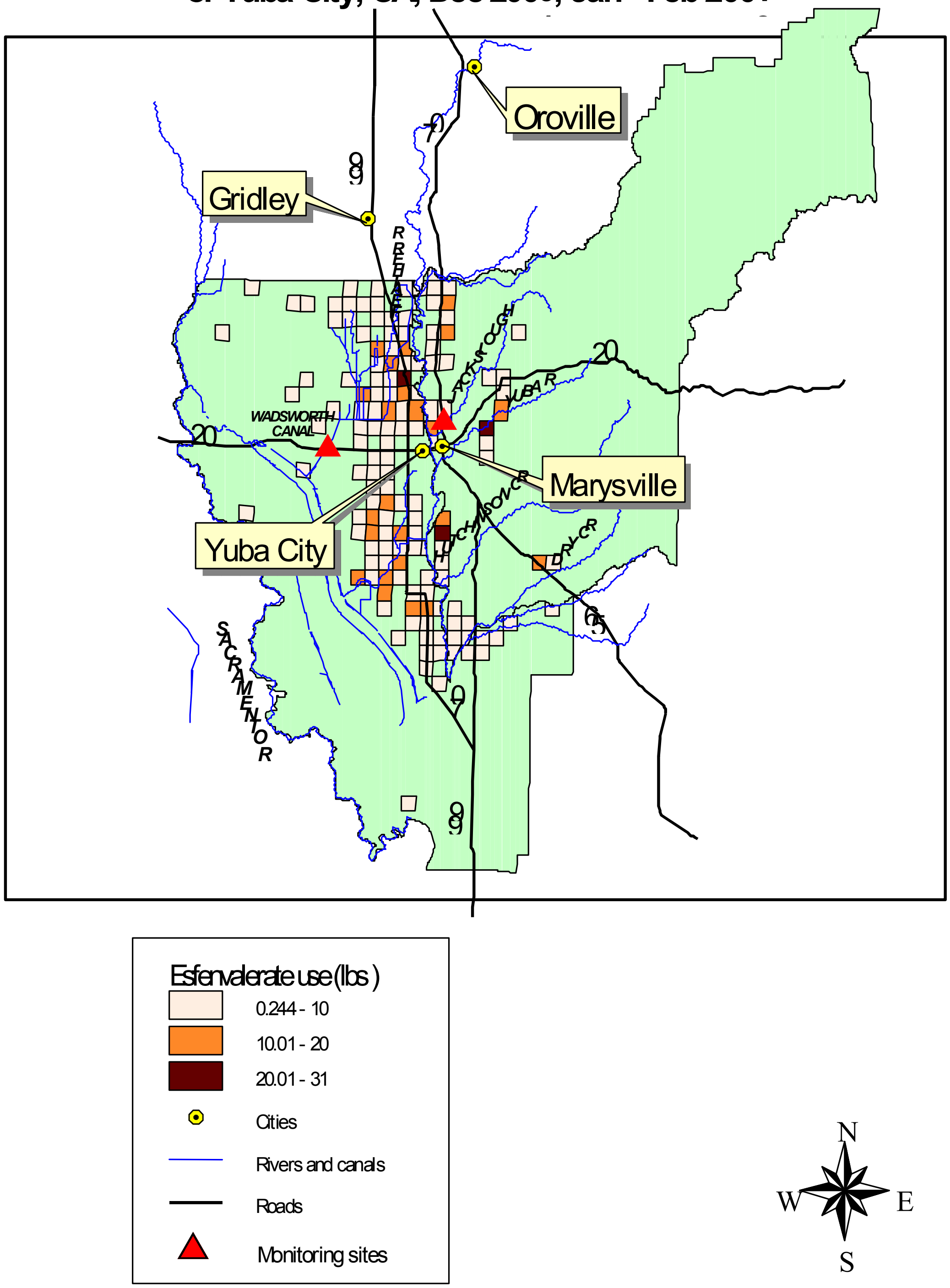

Figure 6 **Permethrin use in the Sacramento watershed area of Yuba City, CA, Dec 2000, Jan - Feb 2001**

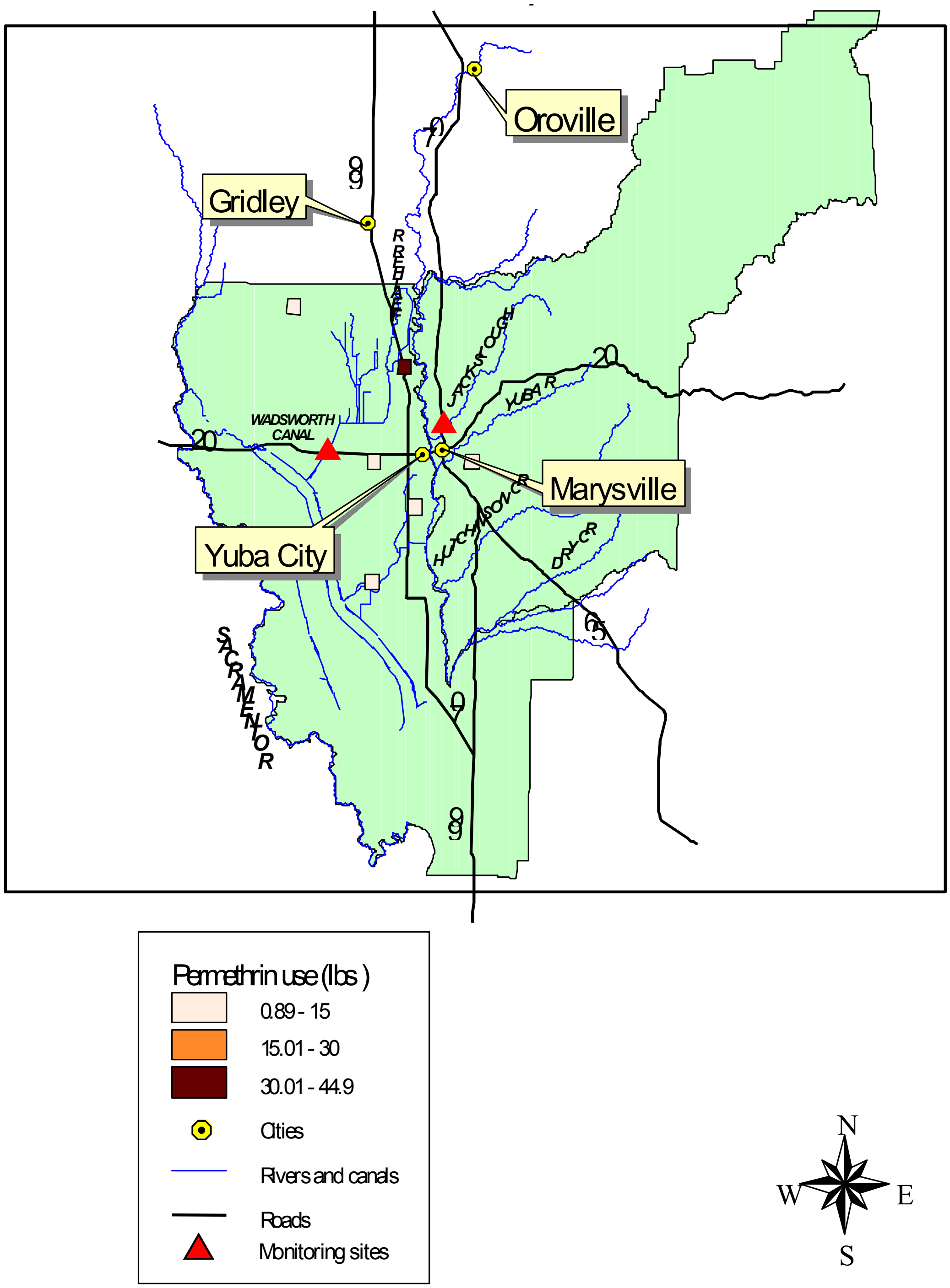

Figure 7 **Esfenvalerat use in the San Joaquin watershed area of Modesto, CA, Dec 2000, Jan - Feb 2001**

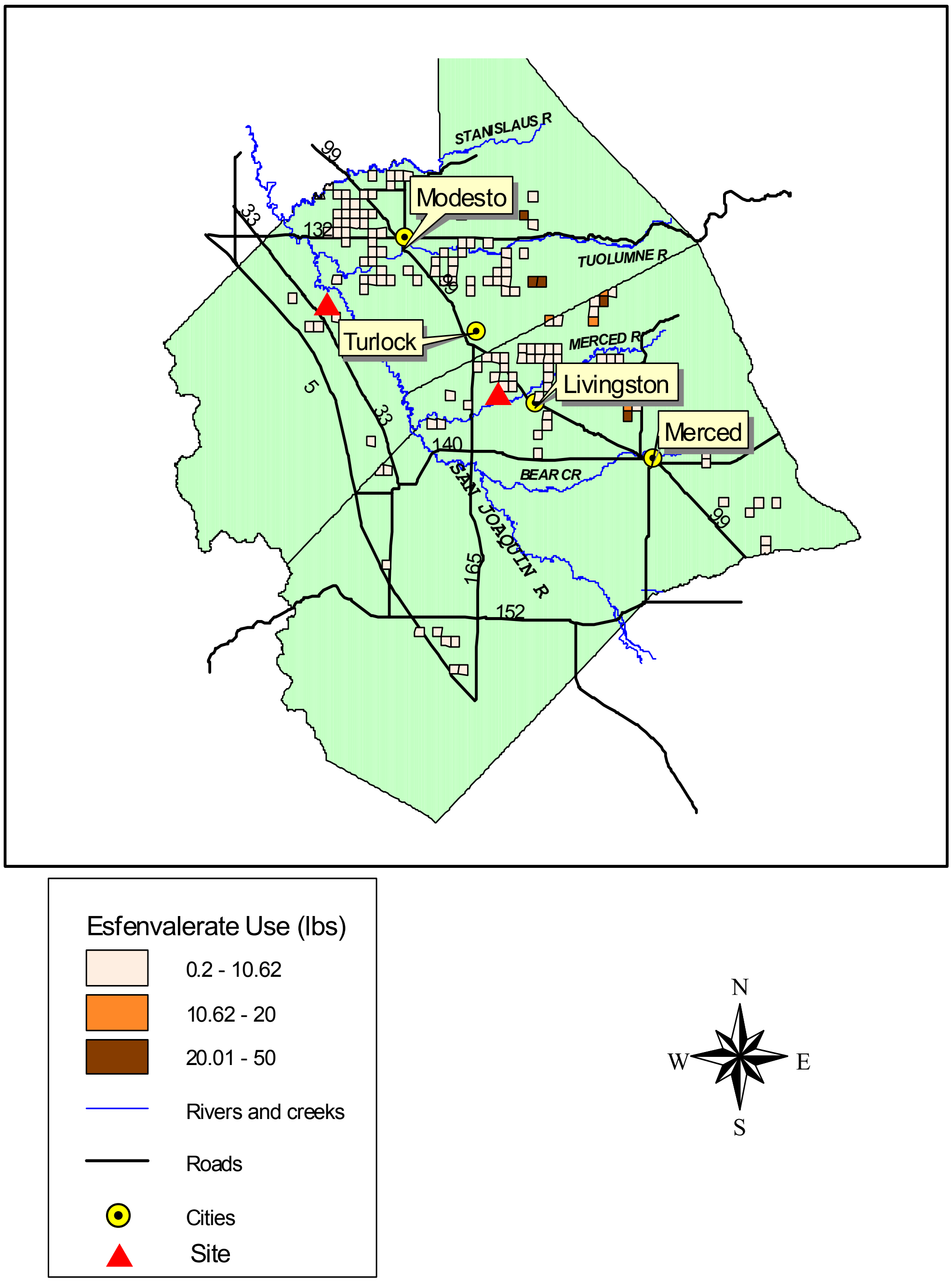

Figure 8 Permethrin use in the San Joaquin watershed area of Modesto, CA, Dec 2000, Jan - Feb 2001

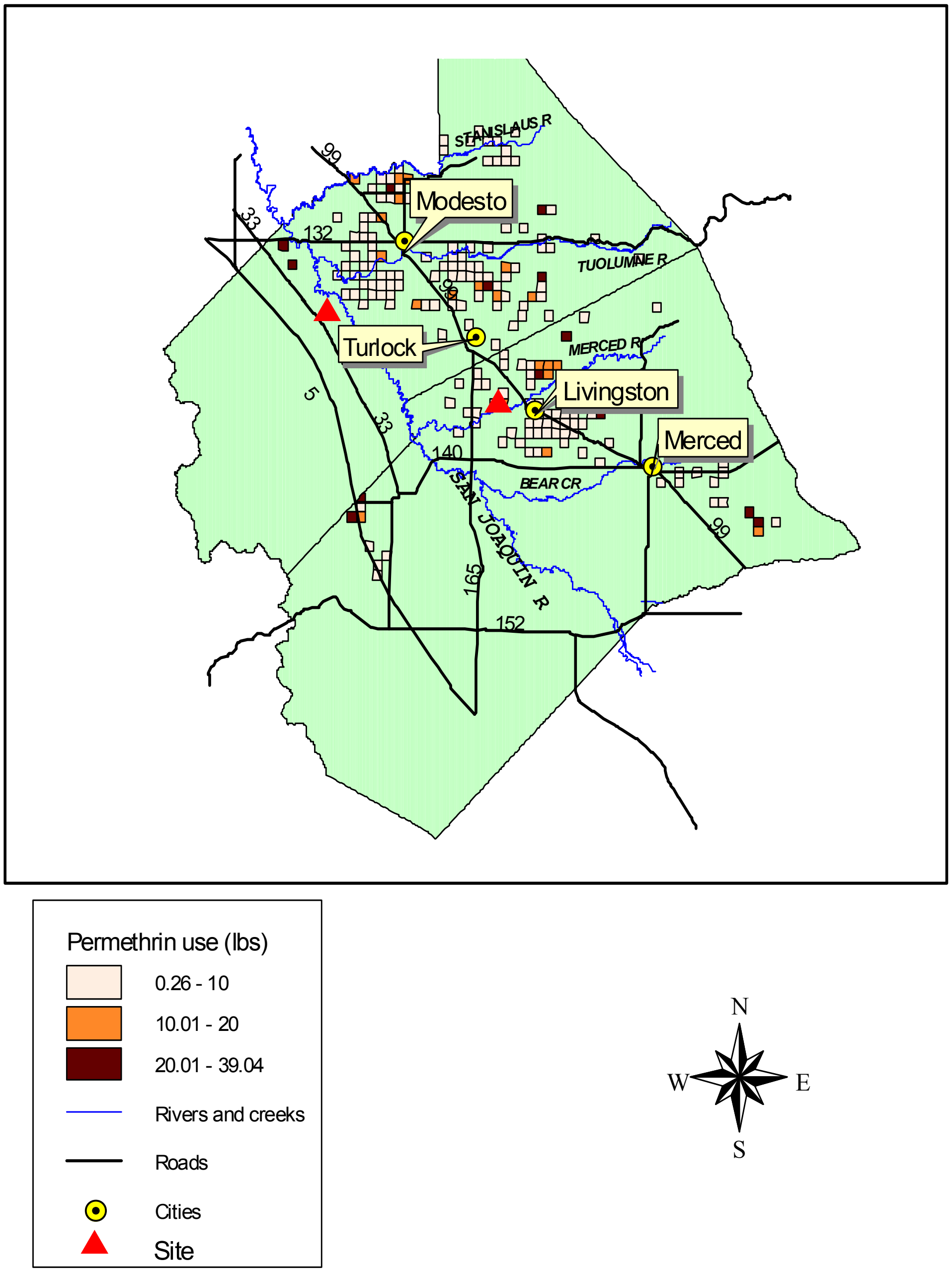

TABLE 1. PHYSICAL CHARACTERISTICS AND ENVIRONMENTAL FATE OF DETECTED PESTICIDES

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

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

Pesticide	***Ceriodaphnia dubia*** (µg/L)	***Daphnia magna*** (µg/L)	***Oncorhynchus mykiss*** (96hr LC50, µg/L)
Esfenvalerate	ND	**0.24** [a]	0.26[a]
Permethrin	**.55**[b]	**0.75** [a]	9.8 [a]
Bifenthrin	**0.07**[b]	**1.6** [a]	0.15 [a]
Lambda cyhalothrin	**.30**[b]	**0.23** [a]	0.44 [a]
Cyfluthrin	**.14**[b]	**.16** [a]	0.302 [a]
Cypermethrin	ND	**1.25** [a]	0.92 [a]
Diazinon	0.436[c]	0.96 [d]	90-1650[d]
Chlorpyrifos	0.038[e]	0.1-1.7[d]	7.1-27[d]
Dimethoate	ND	**1700**[f]	6200 - 7500 [d]
Ethoprop	ND	44.0[d]	1100-13800[d]
Methyl Parathion	02.6[g]	0.14-28.2[d]	0.0022 – 0.161[d]
Diazinon Freshwater Criterion Maximum Concentration (CMC)			0.08[h]
Chlorpyrifos CMC			0.02[h]

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. CA Dept. of Fish & Game, 1998
d. U.S. EPA Ecotox Database, 2003
e. CA Dept. of Fish & Game, 1999
f. Siepmann S. and T. Yargeau, 1996
g. Menconi, M. and J.M. Harrington, 1992
h. Siepmann and Finlayson, 2002

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

Organophosphate Pesticides in Water
Method: GC/FPD

Compound	Method Detection Limit (µg/L)	Reporting Limit (µg/L)
Azinphos methyl	0.0099	0.05
Chlorpyrifos	0.0109	0.04
Diazinon	0.011	0.04
DDVP (dichlorvos)	0.0098	0.05
Dimethoate	0.0079	0.04
disulfoton	0.0093	0.04
ethoprop	0.0098	0.05
Fenamiphos	0.0125	0.05
Fonofos	0.008	0.04
Malathion	0.0117	0.04
methidathion	0.0111	0.05
Methyl Parathion	0.008	0.03
Thimet (Phorate)	0.0083	0.05
Profenofos	0.0114	0.05
Tribufos	0.0142	0.05

Triazines/Herbicides in Water Method: LC/MS/MS

Compound	Method Detection Limit (µg/L)	Reporting Limit (µg/L)
Atrazine	0.020	0.05
Bromacil	0.031	0.05
Diuron	0.220	0.05
Hexazinone	0.040	0.05
Metribuzin	0.025	0.05
Norflurazon	0.019	0.05
Prometon	0.016	0.05
Prometryn	0.016	0.05
Simazine	0.013	0.05
DEA	0.010	0.05
ACET	0.030	0.05
DACT	0.016	0.05

Pyrethroid Pesticides in Sediment
Method: GC/ECD, confirmed with GC/MSD (ŲG/G)

Fenvalerate/Esfenvalerate	8.0	10.0
Permethrin	6.0	10.0
Bifenthrin	7.0	10.0
Lambda Cyhalothrin	9.0	10.0
Cyfluthrin	8.0	10.0
Cypermethrin	8.0	10.0

Pyrethroid Pesticides in Surface Water
Method: GC/ECD, confirmed with GC/MSD

Fenvalerate/Esfenvalerate	0.028	0.050
Permethrin	0.0049	0.050

TABLE 4. BLIND SPIKE QUALITY CONTROL DATA (μg/L)

Extraction Date	Sample Number	Screen	Pesticide	Spike Level	Recovery	Percent Recovery	Exceed CL[a]
1/23/03	97	PY	Permethrin	0.20	0.095	47.5	LCL[b]
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	UCL
3/3/03	554	TR	Bromacil	0.20	0.255	127.5	UCL
3/3/03	625	TR	DEA	0.30	nd	nd[c]	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

[a] CL=Control Limit; Upper CL (UCL), Lower CL (LCL).

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

[c] 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	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 = 0.1µg/L (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 = 0.2µg/L (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 = 0.2µg/L (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
Average Recovery		97	102	96	95	95	100
Standard Deviation		6.7	10.5	7.1	13.2	10.2	11.9
CV		6.98	10.36	7.39	13.97	10.72	11.94
Upper Control Limit		142	158	133	152	173	149
Upper Warning Limit		131	145	123	139	154	137
Lower Warning Limit		88.9	90.9	81.2	88.4	76.2	87.4
Lower Control Limit		78.4	77.4	70.8	75.6	56.8	74.7

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

TABLE 9. WATER QUALITY MEASUREMENTS

Wadsworth Canal 1/22/2003						**Jack Slough 1/22/03**				
Time	**Temp**	**pH**	**EC**	**DO**		**Time**	**Temp**	**pH**	**EC**	**DO**
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
Wadsworth Canal 2/15-16/2003						**Jack Slough 2/15-16/03**				
Time	**Temp**	**pH**	**EC**	**DO**		**Time**	**Temp**	**pH**	**EC**	**DO**
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
Del Puerto Creek 3/15/03										
Time	**Temp**	**pH**	**EC**	**DO**						
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. 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. PESTICIDE DETECTIONS IN WATER AND ACUTE TOXICITY (µg/L)

	Sampling time	Chlorpyrifos	Diazinon	Simazine	Diuron	Bromacil	Hexazinone	Metribuzin	Norflurazon	ACET	Dimethoate	Ethoprop	Methyl Parathion	Esfenvalerate	Permethrin	Acute toxicity (% survival)
Wadsworth Canal	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; Appendix I). % survival = % survival in sample / % survival in control

TABLE 11. CONTINUED: PESTICIDE DETECTIONS IN WATER AND ACUTE TOXICITY (µg/L)

	Sampling time	Chlorpyrifos	Diazinon	Simazine	Diuron	Bromacil	Hexazinone	Metribuzin	Norflurazon	ACET	Dimethoate	Ethoprop	Methyl Parathion	Esfenvalerate	Permethrin	Acute toxicity (% survival)
Jack Slough	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
Del Puerto Creek	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. PESTICIDE DETECTIONS IN SEDIMENT (µg/g, wet weight basis)

Site 1. Wadsworth Canal		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									
Site 2. Jack Slough									
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. CONTINUED: PESTICIDE DETECTIONS IN SEDIMENT (µg/g, wet weight basis)

Site 3. Del Puerto Creek		Bifenthrin	Lambda	Cyfluthrin	Cypermethrin	Esfenvalerate	Permethrin	Wet weight	Dry weight
Time	Date	µg/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