

# SURFACE AND GROUND WATER MONITORING OF PESTICIDES USED IN THE RED IMPORTED FIRE ANT CONTROL PROGRAM

March 2005

Johanna Levine, Environmental Monitoring  
Dave Kim, Environmental Monitoring  
Kean S. Goh, Environmental Monitoring  
Carissa Ganapathy, Environmental Monitoring  
Jean Hsu, CDFA Center for Analytical Chemistry  
Hsiao Feng, CDFA Center for Analytical Chemistry  
Paul Lee, CDFA Center for Analytical Chemistry



California Environmental Protection Agency  
California Department of Pesticide Regulation  
Environmental Monitoring Branch  
1001 I Street  
Sacramento, CA 95812

**EH05-02**

## **Abstract**

In 1999, the Department of Pesticide Regulation (DPR) entered into an interagency agreement with the California Department of Food and Agriculture (CDFA) to monitor pesticide treatments for Red Imported Fire Ant (RIFA) control. The objective of the monitoring was to develop data on potential concentrations of bifenthrin, fenoxycarb, hydramethylnon, pyriproxyfen, chlorpyrifos, and diazinon in surface water entering from treatments to control fire ants. Surface waterways containing residential and agricultural irrigation runoff were monitored on a monthly basis with additional samples collected during the first significant storm events of the 1999–2000 and 2000–2001 rain seasons. In addition to surface water monitoring, ground water samples were collected in high infestation areas.

Monthly surface water sampling was conducted at ten sites over approximately three years (1999–2002). Bifenthrin, a pyrethroid, was detected in six sites with most detections found in water originating from two nursery sites where residues were found in 97% of all samples collected. In contrast, organophosphates, especially diazinon, were detected at all ten sites with most detections found in water originating from urban and integrated sites where residues were found in 89% of samples. Toxicity at the nursery sites was attributed to RIFA insecticide applications, whereas toxicity in water samples from the urban/residential and integrated sites could not be attributed solely to the fire ant treatments.

Two rain events were monitored over the course of the study. The first took place in the Upper Newport Bay watershed and the second was conducted at the most southern sites in an area that had a high number of applications by the Orange County Fire Ant Authority. Diazinon was detected in all water samples collected for both rain events. Bifenthrin was detected in all samples collected from the nursery sites during the first rain event. All water samples collected during the first rain event resulted in 100% mortality to *C. dubia*. No toxicity samples were collected during the second rain event, but toxicity was inferred because concentrations of residues detected in the second rain event were comparable to the previous rain event's.

Well monitoring was conducted in ten wells; five in Orange County and five in Riverside County. All samples had no detectable residue of any of the chemicals tested; no toxicity tests were conducted.

## **Acknowledgments**

The authors of this report would like to acknowledge the following persons and entities for their contribution.

Logistics and site selection:

- Mohammad Azhar, Muhammad Azhar, John Blasius, Gene Drake, Craig Hanes,

Basil Ibewiro, Russ Mally, Cesar Paredes, David Quimayousie, Joan Scheiman, and Mohammed Zubaidy, CDFA, Pest Detection/Emergency Projects Branch, and Pest Exclusion Branch.

- John Kabashima, Darren Haver, and Christina Smith, University of California Cooperative Extension, South Coast Research and Extension Center.
- Les Greenberg, University of California, Riverside.
- Kathy Boyle and Jahan Motakef, DPR, Enforcement Branch.
- Erick Burres and Brian Finlayson, California Department of Fish and Game.
- John Ellis, Deputy Agricultural Commissioner of Orange County.
- Larry Shaw, Richard Bowen, Dick Meyer, and Doug Mathews, Orange County Vector Control/Fire Ant Authority.
- Dale Dillon and Cesar Sarmiento, Orange County, Public Facilities and Resources Department.
- Toby Mancini and Jo-Anne Newton, El Modeno Gardens.
- George Gutman, Hines Nursery.
- Bill Russell, Bordier's Nursery.
- Henry Sakaida, Sakaida Nursery
- Terry Yasutake, T Y Nursery.

Principle Chemists:

- Jane White, Jean Hsu, Hsiao Feng, Paul Lee, Jorge Hernandez, Tina Mok, David Hirano, CDFA, Center for Analytical Chemistry.

Sample analysis:

- Irene Aguilar, Cathy Cooper, Jim Echelberry, Tuong Le, John Medina, Tina Mok, Liana Ortiz, Janice Temple, Duc Tran, Aurora Vasquez, and Teresa Woroniecka, CDFA, Center for Analytical Chemistry.
- George Faggella, Donald Guy, and Frank Riley, California Department of Fish and Game, Aquatic Toxicity Lab.

Sample collection, transport and storage:

- Nina Bacey, Shifang Fan, Andy Fecko, Roger Sava, Valerie Walsh, Pam Wofford, and Jesse Ybarra, DPR, Environmental Monitoring Branch.

And for his expert review:

- John Troiano, DPR, Environmental Monitoring Branch.

**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

Abstract.....	i
Acknowledgments.....	i
Table of Contents.....	iii
List of Tables.....	iv
List of Figures.....	v
Introduction.....	1
Materials and Methods.....	2
Irrigation Surface Water Sampling.....	2
Sampling Sites.....	2
Irrigation Runoff Sampling Frequency and Methods.....	4
Physical and Chemical Measurements of Water Quality.....	5
Pesticide Analysis and Toxicity Testing.....	5
Rain Runoff Surface Water Monitoring.....	8
Sampling Sites.....	8
Sampling Frequency and Methods.....	8
Chemical Analysis and Toxicity Sampling.....	8
Ground Water Monitoring.....	8
Sampling Sites.....	8
Sampling Frequency and Methods.....	9
Chemical Analyses.....	10
Quality Control.....	13
Results and Discussion.....	14
Pesticide Use.....	14
Monthly Surface Water Sampling.....	20
Continuing Quality Control.....	20
Physical and Chemical Measurements of Water Quality.....	21
Pesticide Analyses.....	23
Toxicity Testing.....	28
Relationship Between Chemical Constituents and Toxicity Testing.....	31
Rain Event Monitoring.....	36
Continuing Quality Control.....	36
Discharge and Rainfall Information.....	36
Physical and Chemical Measurements of Water Quality.....	38
Pesticide Analysis.....	39
Toxicity Testing.....	39
Ground Water Monitoring.....	41
Continuing Quality Control.....	41
Pesticide Analysis.....	42
Summary.....	42
References.....	43

## List of Tables

Table 1. Surface water sampling sites in Orange County, California.....	3
Table 2. Pesticide active ingredients, common product names, and mode of action of chemicals used in the RIFA control program .....	7
Table 3. Minimum detection limit (ppb) for the insecticide active ingredients.....	7
Table 4. Ground water sampling sites in Riverside and Orange Counties, California .....	9
Table 5. Pesticide use (pounds active ingredient) in Riverside and Orange Counties 1999-2001 .....	14
Table 6. Average continuing QC recoveries in surface water. ....	21
Table 7. Mean of monthly sampling physical and chemical water quality measurements..	22
Table 8. Percent of samples with positive detections. Numbers in parentheses are the mean of the positive detections.....	27
Table 9. Percent mortality of <i>C. dubia</i> in water samples collected in Orange County.....	29
Table 10. LC <sub>50</sub> 's of insecticides (ppb) for three aquatic species. <sup>1</sup> .....	30
Table 11. LC <sub>50</sub> 's (mg/L)* of chemical water quality parameters for <i>C. dubia</i> . ....	30
Table 12. Additional constituents and water quality factors that may have caused toxicity to those samples identified as false negatives with respect to lack of organophosphate toxic units.....	33
Table 13. Additional constituents and water quality factors that may have caused toxicity to those samples identified as false negatives with respect to lack of bifenthrin toxic units.....	35
Table 14. Mean physical and chemical water quality measurements for rain runoff sampling.....	38
Table 15. Average continuing QC recoveries for the RIFA insecticides in ground water. ..	42

## List of Figures

Figure 1. Surface water sampling sites, gauging stations, and weather stations .....	4
Figure 2. Riverside County well sampling sites .....	11
Figure 3. Orange County well sampling sites.....	12
Figure 4. Bifenthrin pesticide use for 1999-2001 in Orange County .....	15
Figure 5. Fenoxycarb, hydramethylnon, and pyriproxyfen use for 1999-2001 in Orange County .....	16
Figure 6. Chlorpyrifos use for 1999-2001 in Orange County.....	17
Figure 7. Bifenthrin use for 1999-2001 in the Coachella Valley, Riverside County.....	18
Figure 8. Fenoxycarb, hydramethylnon, and pyriproxyfen use for 1999-2001 in the Coachella Valley, Riverside County.....	19
Figure 9. Chlorpyrifos and diazinon use for 1999-2001 in the Coachella Valley, Riverside County .....	20
Figure 10. Insecticide concentration for sites A-D .....	24
Figure 11. Insecticide concentrations for sites E-H.....	25
Figure 12. Insecticide concentrations for sites I and J.....	26
Figure 13. Observed vs. predicted toxicity from analytical concentrations of diazinon, chlorpyrifos, malathion, and methidathion .....	32
Figure 14. Observed vs. predicted toxicity from analytical concentrations of bifenthrin ....	33
Figure 15. Hourly precipitation (represented by bars) from three Alert stations and water discharge (solid line) measured at San Diego Creek at Campus Drive for the January 2000 rain event.....	37
Figure 16. Hourly precipitation (represented by bars) from two Alert stations and water discharge (solid line) measured at Oso Creek at Crown Valley Parkway for the October 2000 rain event.....	37
Figure 17. January 2000 rain event concentrations .....	40
Figure 18. October 2000 rain event concentrations.....	41

## Introduction

The Red Imported Fire Ant (RIFA), *Solenopsis invicta* Buren, is a widespread pest in 11 southeastern states: Alabama, Arkansas, Florida, Georgia, Louisiana, Mississippi, North Carolina, Oklahoma, South Carolina, Tennessee, and Texas. In these regions, the pest has caused billions of dollars in damage to agriculture and has had a major impact on public safety and the environment (CDFA, 2004). California infestations were discovered in 1998, when Nevada officials notified CDFA that nursery products shipped from an Orange County commercial nursery to Las Vegas contained RIFA. This discovery triggered a broad survey of nurseries, open space, and residential communities in southern California, culminating with state and federal officials placing Orange County and portions of Los Angeles County and Riverside County under quarantine. The quarantine limits the movement of articles including plants and soil, and requires commercial nursery growers to take steps to ensure their products are free of RIFA. It is believed that the infestations in Southern California may stem from the shipment of infested nursery stock from southeastern states. Fruit orchard infestations in the agricultural regions of California's San Joaquin Valley have been traced back to colonies that hitchhiked on beehives shipped to California from Texas (CDFA, 2004).

Since the discovery in 1998, CDFA, County Agricultural Commissioners, District Vector Control, and other agencies have been pursuing aggressive eradication programs. These programs have used ground applications of insecticides, which may include bifenthrin, chlorpyrifos, diazinon, fenoxycarb, hydramethylnon, and pyriproxyfen. The granular bait treatments use a metabolic inhibitor (hydramethylnon) or an Insect Growth Regulator (pyriproxyfen or fenoxycarb) broadcast over entire areas or applied to individual mounds. Baits are composed of a carrier, soybean oil or corn grit, and the toxicant. Ant foragers find the bait, carry it back to the colony, and feed it to other members of the colony eventually affecting all members of the colony. Nurseries within the quarantine area follow approved treatment protocols which ensure nursery stock is free of RIFA prior to exiting the quarantine area. These protocols include application of either chlorpyrifos, bifenthrin, or diazinon to the soil of all nursery stock moving out of the quarantine area (CDFA, 1999). In addition, a fenoxycarb insecticidal bait is used as a treatment for their growing sites (CDFA, 1999). Orange County, with CDFA funding, has set up the Orange County Fire Ant Authority (OCFAA) with the purpose of better treating nonagricultural areas. To date more than 20,000 RIFA sites have been located and treated (OCFAA, 2004). RIFA applications sites can range from individual fire ant mounds to entire parks, schools, or neighborhoods within the treatment area. When a site is identified as having a RIFA infestation, field staff return to the location and treat the ground with two different types of fire ant baits: hydramethylnon is used to directly treat the mound and pyriproxyfen is broadcast in a large area around the mound or positioned in forage location of RIFA.

In 1999, DPR entered into an interagency agreement with CDFA to monitor water samples for the presence of pesticides used in RIFA treatments. The objective was to provide information on the concentrations of these chemicals in surface water. Surface waterways collecting runoff water from residential and agricultural irrigation runoff were monitored on a monthly basis for the presence of RIFA insecticides and their toxicity to *Ceriodaphnia*

*dubia* (*C. dubia*). In addition, samples were collected during the first significant storm events of the 1999–2000 and 2000–2001 rainy seasons. Lastly, ground water samples were collected in high infestation areas.

## **Materials and Methods**

### **Irrigation Surface Water Sampling**

#### Sampling Sites

Sampling sites were selected throughout Orange County in areas where RIFA applications were known to take place (Table 1 and Figure 1). Sites were selected based on their proximity to treatment areas, which included sites that differentiated commercial nursery and urban applications according to the guidelines set forth in the study protocol (Kim, 1999). Sites A, B, C, D, I, and J were sites that represented urban waterways; sites F, G, and H were located near commercial nurseries; and site E represented an integrated site with both urban and commercial nursery inputs.

The exact sampling location for site F was changed three times in order to better isolate the runoff water generated from nurseries. Coordinates for site F in Table 1 are the location of the final sampling site. Sampling on May 21, 1999 and June 25, 1999, occurred at the Hines Nursery channel at Irvine Boulevard. Sampling from September 23, 1999 to April 4, 2000, took place on the Central Irvine Channel at the intersection of Jeffrey Road and Bryan Avenue. From May 24, 2000, till the end of sampling, samples were collected from Hines Nursery channel located on nursery property at the v-notch weir to avoid additional water input from other agricultural fields next to the nursery. The sampling site location for site G was also relocated during the study to better isolate nursery inputs. Samples collected from June 25, 1999 to April 19, 2000, were collected southwest of El Modeno nursery as the waterway flowed under Portola Parkway and into Hines Nursery. Samples collected from May 24, 2000, until the end of the study were collected from the v-notch weir at El Modeno Nursery. Coordinates in Table 1 are for the final sampling location.

Table 1. Surface water sampling sites in Orange County, California

Site	Description	Coordinates
A	Bolsa Chica Channel at Westminster Avenue	N 33°45'35", W 118°02'36"
B	East Garden Grove Channel at Gothard Street	N 33°43'03", W 117°59'59"
C	Westcliff Park	N 33°37'24", W 117°54'02"
D	Bonita Creek at San Diego Creek	N 33°39'03", W 117°51'49"
E	San Diego Creek at Campus Drive	N 33°39'18", W 117°50'44"
F	Hines at Weir	N 33°42'30", W 117°44'19"
G	El Modeno Gardens	N 33°42'43", W 117°44'16"
H	Marshburn Slough at Irvine Boulevard	N 33°41'45", W 117°44'02"
I	San Juan Creek at Stonehill Drive	N 33°28'31", W 117°40'43"
J	Arroyo Trabuco at Oso Parkway	N 33°35'06", W 117°38'09"

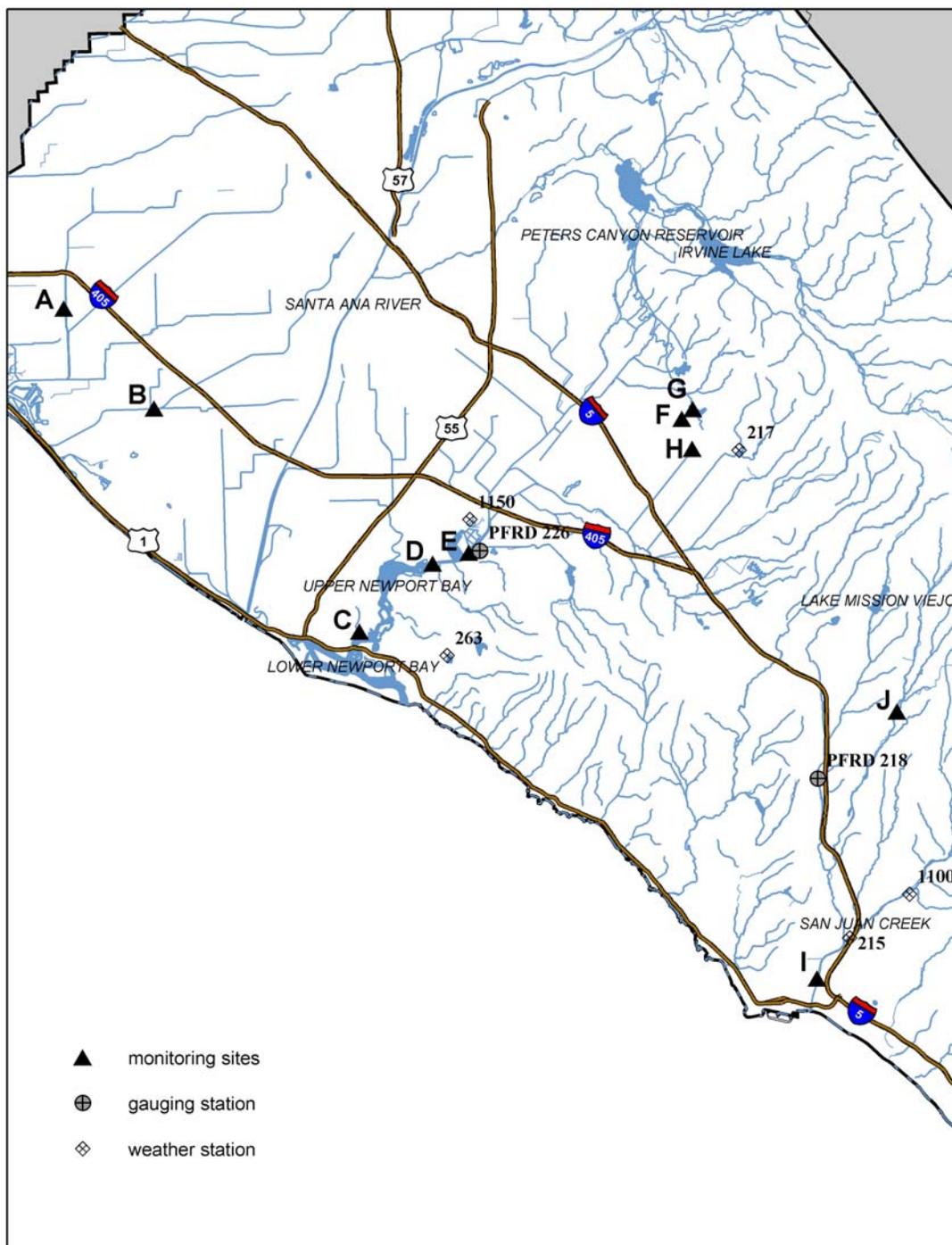


Figure 1. Surface water sampling sites, gauging stations, and weather stations

## Irrigation Runoff Sampling Frequency and Methods

Monthly sampling commenced in May 1999. Sampling was initiated for sites A, E, F, I, and J starting in May 1999, for sites B and G starting June 1999, and for sites C and D starting December and September 1999, respectively. Sampling at site H was initiated in February 2000, due to lack of water; this site was sampled only five times.

All water samples were collected as close as possible to the center of the water channel as possible. Samples were collected using a ten-liter stainless steel bucket and then split into one-liter amber glass bottles using a ten-port Dekaport Teflon® Sample Splitter (Geotech Environmental Equipment, Inc., Denver, Colorado) according to EM SOP FSWA004 (Ganapathy, 1998). Each sample was split into six bottles numbered and designated for these separate analyses:

- bifenthrin
- fenoxycarb, hydramethylnon, and pyriproxyfen,
- organophosphates, excluding diazinon
- diazinon
- back-up un-acidified
- back-up acidified

For four sampling events at site C, in January, February, April, and June of 2000, water was pumped into a one-liter glass amber bottle using a Mityvac hand pump (Lincoln Industrial Corp., St. Louis, Michigan) and then poured into the stainless steel bucket until enough water was collected to split using the ten-port splitter. Samples were collected in this fashion due to low water flows. Samples designated for organophosphate chemical analysis were preserved by acidification with 3N hydrochloric acid to a pH between 3.0 and 3.5 according to EM SOP FSWA007.00 (Bradley/Ganapathy, 1998). Diazinon was analyzed from a separate, un-acidified sample because its degradation is known to increase in acidic conditions (Ross et. al., 1996). All samples were stored on wet ice or in a 4°C refrigerator until transported to the appropriate laboratory for analysis.

Surface waterways draining residential/urban and agricultural/nursery runoff sites were monitored with an attempt to separate these two land uses. Other distinctions include the amount and frequency of water discharge at the sites. For example, site C, a residential site, required a different sampling procedure for four samplings due to a small volume of water available for sampling, while site H, a nursery site, had no water to sample except for during five sampling events. A total of 236 samples were taken from 10 sites over 3 years. Seventy-three from sites representing nursery runoff (sites F, G, and H), 127 from sites representing urban waterways (sites A, B, C, D, I, and J), and 36 from an integrated site combining inputs from nursery and urban runoff (site E). Bifenthrin, fenoxycarb, hydramethylnon, pyriproxyfen, chlorpyrifos, diazinon, malathion, and methidathion were analyzed in all 236 samples; fonophos, methyl parathion, and phosmet were analyzed in 103 of those samples. Rainfall was associated with sampling in February 2000, April 2000, May 2000, (sites F and G), September 2000, and February 2001.

## Physical and Chemical Measurements of Water Quality

Physical and chemical water quality measurements were recorded during each sampling interval at all sites. Physical water quality measurements included temperature and pH measured *in situ*. Chemical water quality measurements included electrical conductivity and dissolved oxygen (DO) measured *in situ* and alkalinity, hardness, and ammonia measured by the California Department of Fish and Game (CDFG) Aquatic Toxicity Laboratory on water samples that were tested for toxicity. Water pH was measured using a model IQ 150 pH meter (IQ Scientific Instruments®, Inc. Carlsbad, California). Water temperature, EC, and DO were measured using a model 85 YSI® multi parameter meter (Yellow Springs Instrument Company, Yellow Springs, Ohio). Totals of alkalinity and hardness were measured with a Hach7 titration kit (Hach Company, Loveland, Colorado). Ammonia was determined using an Orion® 95-12 ammonia selective electrode attached to a model 290A Orion® specific ion meter (Thermo Electron Corporation, Waltham, Massachusetts).

## Pesticide Analysis and Toxicity Testing

The analyzing laboratory was the CDFA, Center for Analytical Chemistry in Sacramento, California. Water samples were analyzed for bifenthrin, fenoxycarb, hydramethylnon, pyriproxyfen, and eight organophosphorus insecticides: chlorpyrifos, diazinon, dimethoate, fonofos, malathion, methidathion, methyl parathion, and phosmet. Only bifenthrin, fenoxycarb, hydramethylnon, pyriproxyfen, chlorpyrifos, and diazinon were used in the RIFA control program (Table 2). The other six organophosphates were part of the multiresidue analytical method and were included for informational purposes and to assist in the interpretation of the toxicity results.

Analysis was performed using gas chromatography and a flame photometric detector (GC-FPD) for the eight organophosphorus (OP) insecticides; a high performance liquid chromatography and a ultra violet detector (HPLC-UV) for fenoxycarb, hydramethylnon, and pyriproxyfen; and gas chromatography with an electron capture detector (GC-ECD) confirmed with a mass selective detector for bifenthrin. Appendix A contains method validation results (percent insecticide recovery) for the active ingredients. The reporting limit for each active ingredient is presented in Table 3. Samples collected from September 6, 2000, until the termination of sampling were not analyzed for fonofos, methyl parathion, or phosmet for several reasons:

1. these chemicals were not used specifically in the RIFA eradication program
2. lack of significant detections
3. workload reduction for the chemistry laboratory

Table 2. Pesticide active ingredients, common product names, and mode of action of chemicals used in the RIFA control program

Active ingredient	Product name	Mode of Action
bifenthrin	Talstar Fire Ant-X Ortho Fire Ant Killer	Pyrethroid affecting the central and peripheral nervous system causing paralysis (Fecko, 1999a).
fenoxycarb (bait)	Award	Nonneurotoxic carbamate insect growth regulator mimics the action of the juvenile hormones during molting and reproduction (Sullivan, 2000a).
hydramethylnon (bait)	Amdro Fire Ant Bait SiegePro Fire Ant Bait	Slow acting stomach irritant toxic to insects with chewing or sponging mouthparts (Bacey, 2000).
pyriproxyfen (bait)	Distance Nylar	Fenoxycarb derivative that mimics the action of juvenile hormone inhibiting embryogenesis, metamorphosis, and adult formation (Sullivan, 2000b).
chlorpyrifos	Dursban Lorsban	Organophosphate that functions as a cholinesterase inhibitor, contact or ingested poison (NPTN, 1999).
diazinon	Hot Shot Fire Ant Killer KGRO Fire Ant Killer Ortho Fire Ant Killer Granules	Organophosphate that functions as a cholinesterase inhibitor, contact or ingested poison (NPTN, 1998).

Table 3. Minimum detection limit (ppb) for the insecticide active ingredients

Chemical Active Ingredient	Reporting Limit (ppb)
bifenthrin, dimethoate, fonofos, malathion, methidathion, methyl parathion, and phosmet	0.05
fenoxycarb and pyriproxyfen	0.1
hydramethylnon	0.2
chlorpyrifos and diazinon	0.04

Water samples used for toxicity testing were collected from all sites sampled between May 1999 and June 2000. Samples for toxicity testing were collected from site E only between July 2000 and August 2001. Toxicity testing was not conducted after August 2001. Toxicity testing was conducted by the CDFG Aquatic Toxicity Laboratory following current U.S. Environmental Protection Agency (EPA) procedures using a cladoceran, *Ceriodaphnia dubia* (*C. dubia*) (U.S. EPA, 1993). Acute toxicity was determined using a 96-hour, static-renewal bioassay in undiluted sample water (CDFG, 1997). Data was reported as percent mortality.

## **Rain Runoff Surface Water Monitoring**

### Sampling Sites

Storm runoff samples were collected during the first significant storm event of two winter rain seasons in January 2000 and October 2000. Samples from the January 2000 storm event were collected from sites within the Upper Newport Bay watershed and included sites C, D, E, F, G, and H (Table 1, Figure 1). Samples from the October 2000 storm event were collected from sites I and J, which were downstream of some of the most heavily infested areas.

### Sampling Frequency and Methods

Runoff water samples from the January 2000 storm event were collected approximately every 1.5 hours from each site over a ten-hour period. Samples from site F were collected on Hines Nursery channel at Irvine Boulevard. Samples from the October 2000 storm event were collected approximately every two hours over an eight-hour period.

Samples were collected and water quality measurements were recorded as described in the monthly surface water sampling section. Stream flow discharge data was collected during this monitoring. During the January 2000 monitoring, stream velocity and width/depth measurements were collected in accordance with EM SOP FSWA009.00 (Fecko, 1999b) at sites F, G, and H. Discharge data was provided by the Orange County Public Facilities and Resources Department (OCPFRD) gauging station 226 at San Diego Creek at Campus Drive for site E. No discharge information was collected at sites C and D. Precipitation was recorded hourly at Alert weather stations 263, 1150, and 217 (OCPFRD, 2000a). During the October 2000 monitoring, discharge information was provided by the OCPFRD gauging station 218 at Oso Creek at Crown Valley Parkway, approximately four miles from the confluence with San Juan Creek. Precipitation data was obtained from Alert stations 215 and 1100 (OCPFRD, 2000b). Figure 1 displays the locations of the gauging and weather stations.

### Chemical Analysis and Toxicity Sampling

Samples were analyzed for the same chemicals and in the same manner as described for the monthly surface water monitoring. Samples from the October 2000 sampling were not analyzed for fonofos, methyl parathion, and phosmet. Toxicity samples were collected during the January 2000 but not during the October 2000 sampling.

## **Ground Water Monitoring**

### Sampling Sites

Ground water samples were collected in two counties with large RIFA infestations and RIFA insecticide treatments. Samples in Riverside County were collected in the Palm Springs area of the Coachella Valley on November 14, 2000 and June 11, 2002 from

private wells located on golf courses and nurseries that were under a compliance agreement with CDFA for treatment if RIFA was found on the property (Table 4, and Figure 2). Samples in Orange County were collected on February 27 (sites 8, 9, and 10) and July 25, 2001 (sites 6 and 7) near nurseries required to treat for RIFA (Table 4, and Figure 3). The El Toro wells and the Tosco wells were monitoring wells and the Rose Canyon well was a municipal well owned by the Trabuco Canyon Water District.

Of the nine insecticides analyzed, only chlorpyrifos, bifenthrin, fenoxycarb, hydramethylnon, and pyriproxyfen were approved for use in treatment of fire ants to comply with the U.S. Department of Agriculture’s nursery quarantine requirements and on golf courses under the compliance agreement. All of OP insecticides listed are registered for uses in commercial agriculture, nurseries, golf courses, or parks for the control of other insect pests. At the time of the monitoring malathion and diazinon were widely available for homeowner use.

Table 4. Ground water sampling sites in Riverside and Orange Counties, California

Site	Description	Coordinates
<b>Riverside County</b>		
1	Canyon Country Club	N 33°47’09”, W 116°32’06”
2	Bel Aire Greens	N 33°48’31”, W 116°30’48”
3	Seven Lakes Country Club	N 33°47’53”, W 116°30’00”
4	Tamarisk County Club	N 33°46’29”, W 116°26’42”
5	California Desert Nursery	N 33°44’07”, W 116°17’35”
<b>Orange County</b>		
6	El Toro #1	N 33°39’59”, W 117°46’03”
7	El Toro #2	N 33°41’05”, W 117°44’38”
8	Tosco #1	N 33°42’49”, W 117°46’36”
9	Tosco #2	N 33°42’50”, W 117°46’36”
10	Rose Canyon	N 33°39’36”, W 117°35’07”

#### Sampling Frequency and Methods

Samples were collected by obtaining ground water from wells prior to the storage tank. All wells in Riverside County had a sample port at which water was collected. The El Toro and Tosco wells in Orange County were monitoring wells without submersible pumps. At these sites, sampling was coordinated so that samples were collected alongside county contracted well monitoring personnel using their equipment. The El Toro wells were collected by submersing a pump into the well and sampling from a ball check valve. The Tosco wells were sampled by submersing a plastic bailer and directly filling the sample bottles, new bailers were used at each well. Samples designated for

organophosphate chemical analysis were preserved by acidification with 3N hydrochloric acid to a pH between 3.0 and 3.5. Diazinon rapidly degrades under acidic conditions, so it was analyzed from a separate, un-acidified sample. All samples were stored on wet ice or in a 4°C refrigerator until transported to the appropriate laboratory for analysis. Water pH was measured using a model IQ 150 pH meter (IQ Scientific Instruments®, Inc. Carlsbad, California).

### Chemical Analyses

All ground water samples were analyzed for bifenthrin, fenoxycarb, hydramethylnon, pyriproxyfen, chlorpyrifos, diazinon, dimethoate, malathion, and methidathion. CDFA Center for Analytical Chemistry performed all analyses using GC-FPD for the five organophosphorus insecticides; a HPLC-UV for fenoxycarb, hydramethylnon, and pyriproxyfen; and GC-ECD confirmed with a mass selective detector for bifenthrin. The reporting limits for each active ingredient is presented in Table 3.

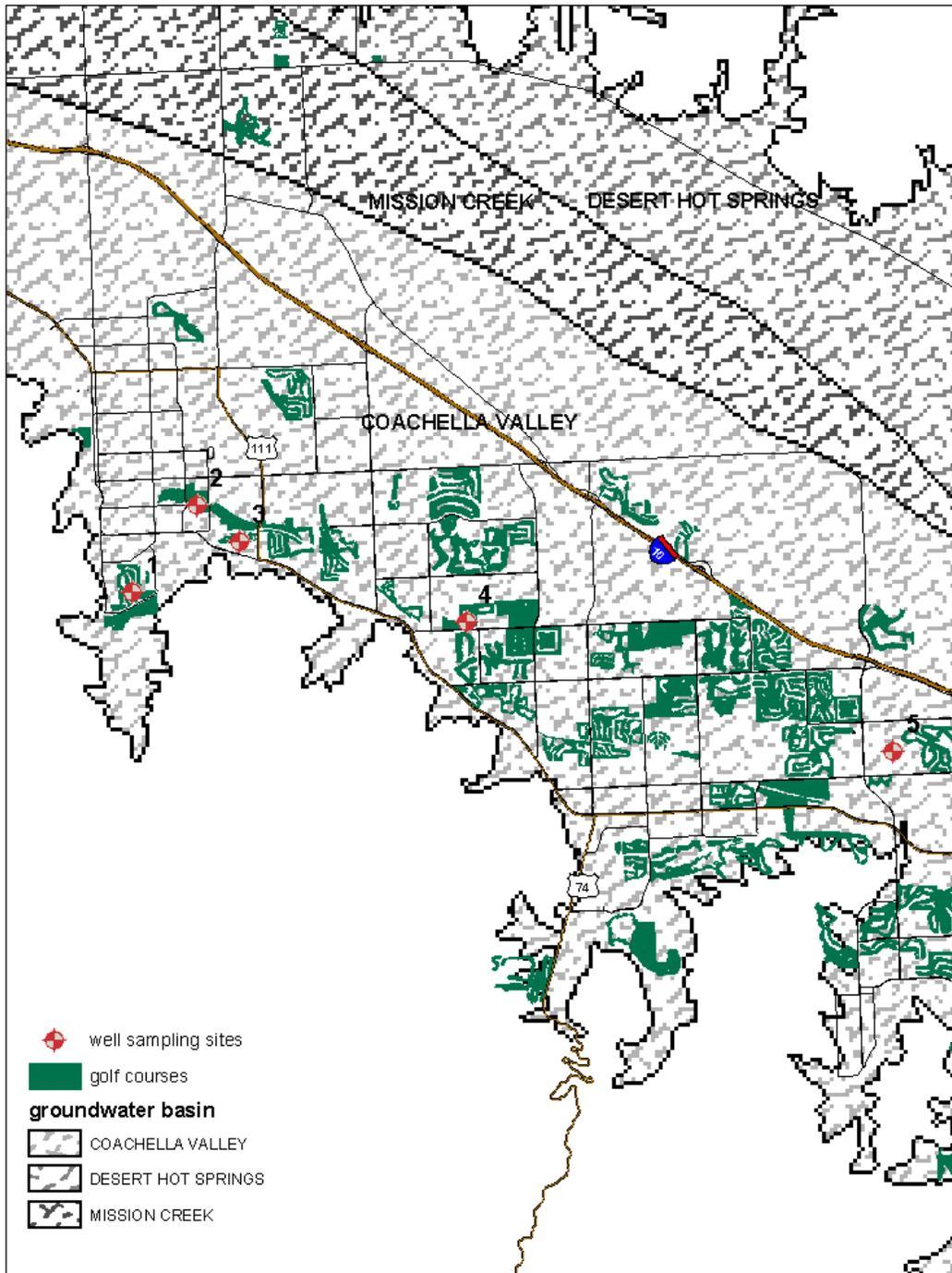


Figure 2. Riverside County well sampling sites.

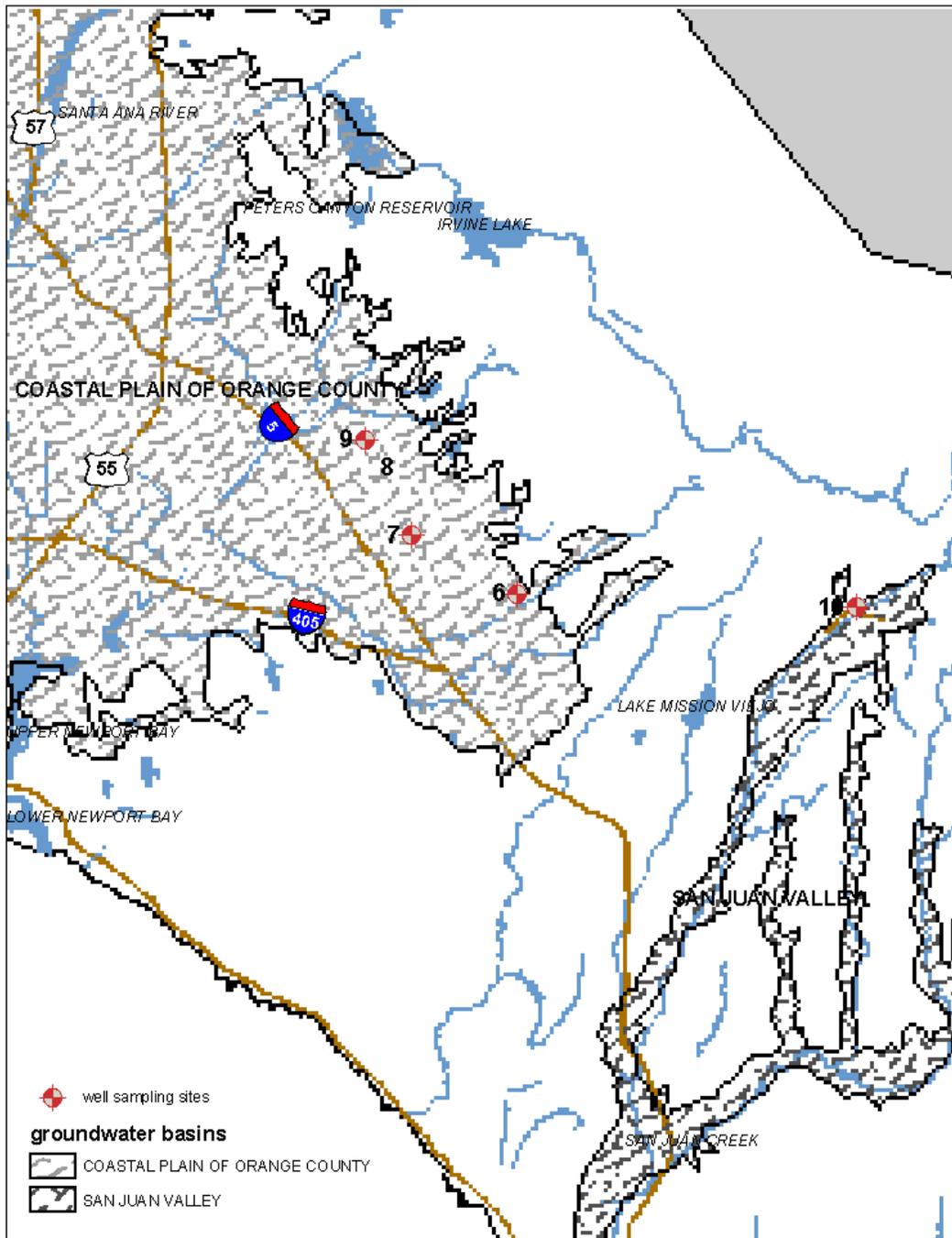


Figure 3. Orange County well sampling sites.

## Quality Control

The quality control (QC) program consists of assessing all study results using data generated during method validation. The methods for this study were developed and validated according to EM SOP QAQC001.00 (Segawa, 1995) and can be found in Appendix A. Storage stability was conducted for all analytes in surface water, explanation and results are available in Appendix A. The method validation data was used to establish warning and control limits. A warning limit is the mean  $\pm$  2 standard deviation, where the mean is the average percent recovery found in method validation. The upper control limit (UCL) and lower control limit (LCL) is the mean  $\pm$  3 standard deviation. Continuing QC samples generally consist of a blank matrix and a blank matrix spiked with the analyte that is analyzed with each extraction set. For this study, blank matrix for surface water samples was either North Fork or Middle Fork American River Water and the ground water blank matrix was well water from Auburn, California. All continuing QC samples are spiked the day samples are to be extracted.

For chemical analyses, one set of rinse blanks were taken during every monthly sampling event to equal 10% of samples submitted to the lab. Rinse blanks were transported and stored with other water samples and analyzed for the same chemicals as the monthly sampling. In addition, blind spikes were submitted to lab in numbers that equaled approximately 10% of all samples submitted. A blind spike sample is a matrix spiked with analyte by a chemist other than the chemist extracting and analyzing that matrix. The blind spike is then given field staff to relabel and disguised as an actual field sample. A total of 98 blind spike samples were made for the surface water study. The blind spike samples were spiked at a range of 0.10 ppb to 2.0 ppb, with greater than 95% of samples spiked at 0.40 or less.

Owing to an expectation of higher bifenthrin concentrations than for the other chemicals, QC samples were spiked at two levels at 0.1 and at 1.0 ppb for each of the 47 sets of samples analyzed. Forty-five sets of fenoxycarb, hydramethylnon, and pyriproxyfen samples were extracted and analyzed (two spikes were run for three extraction sets; see Appendix A). QC samples were spiked at 1.0 ppb of each of the 3 analytes in each sample.

Two methods were used to analyze for OP's; the older method (method #163) was used from extraction date March 29, 1999 through October 10, 2001, and the new method (method #262) was used for samples in sets extracted from November 11, 2001, to the end of the study. The analytes were spiked at two times their reporting limits, ranging from 0.08 to 0.10 ppb except for phosmet which was spiked at 0.50 ppb. Forty-one QC spikes were analyzed using the old OP method. After the August 7, 2000, extraction set, fonofos, methyl parathion, and phosmet were dropped from the screen. Nine extraction sets were analyzed using the new OP method. Forty seven diazinon QC samples were spiked at 0.08 ppb and extracted and analyzed following the same method used for the OP analytes.

## Results and Discussion

### Pesticide Use

Annual total pounds used for each the chemicals used specifically for RIFA treatments ranged from 1 to 71, 937 throughout the study area for 1999, 2000, and 2001 (Table 5). Use data included all agricultural applications even those that were nonRIFA, but it does not include applications by homeowners. Generally, use of three RIFA insecticides, bifenthrin, fenoxycarb, and hydramethylnon increased in Riverside County by 140%, 100%, and 237%, respectively whereas use of chlorpyrifos, diazinon, and pyriproxyfen decreased by 21%, 20%, and 65%, respectively. In Orange County, bifenthrin, chlorpyrifos, and fenoxycarb uses decreased by 4%, 67%, and 12%, respectively, whereas uses of diazinon, hydramethylnon, and pyriproxyfen increased by 11%, 45%, and 1250%, respectively. Figures 4-6 illustrate the relationship of use patterns in Orange County to the monitoring sites in 1999–2001. Figures 7 thru 9 illustrate the relationship of use patterns in Riverside County to the monitoring sites in 1999–2001. These figures include chemical use that was reported to the Department of Pesticide Regulation with meridian/township/range/section location. The Figures exclude applications made to golf courses and by landscape services and pest control companies.

Table 5. Pesticide use (pounds active ingredient) in Riverside and Orange Counties 1999–2001

Chemical	Riverside County			Orange County		
	1999	2000	2001	1999	2000	2001
bifenthrin	677	1,263	1,630	5,365	6,839	5,128
chlorpyrifos	54,697	64,127	43,339	71,937	34,311	23,484
diazinon	18,182	18,917	14,604	24,535	29,903	27,319
fenoxycarb	4	1	8	48	47	42
hydramethylnon	75	105	253	134	164	195
pyriproxyfen	247	482	87	10	42	135

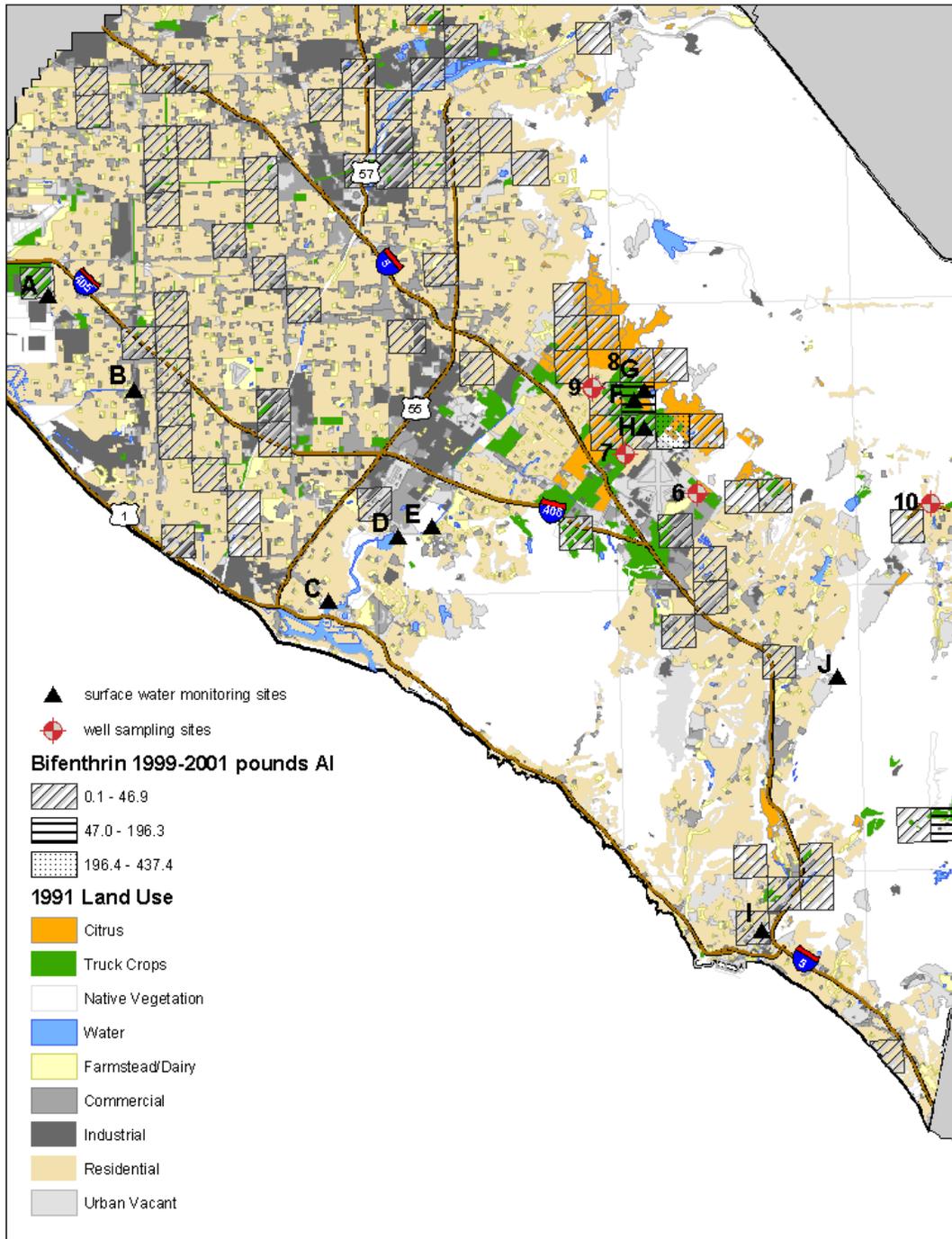


Figure 4. Bifenthrin pesticide use for 1999–2001 in Orange County.

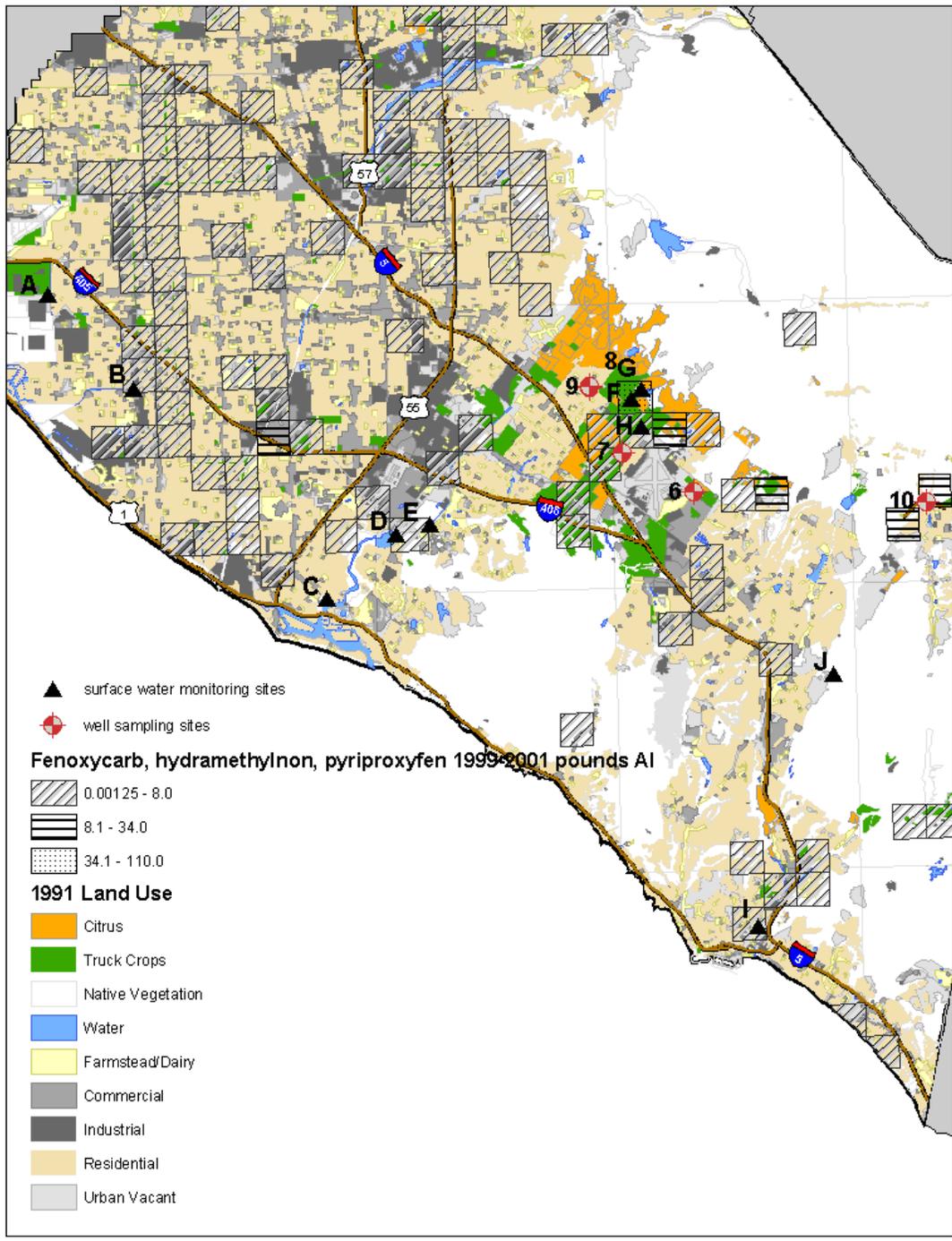


Figure 5. Fenoxycarb, hydramethylnon, and pyriproxyfen use for 1999-2001 in Orange County.

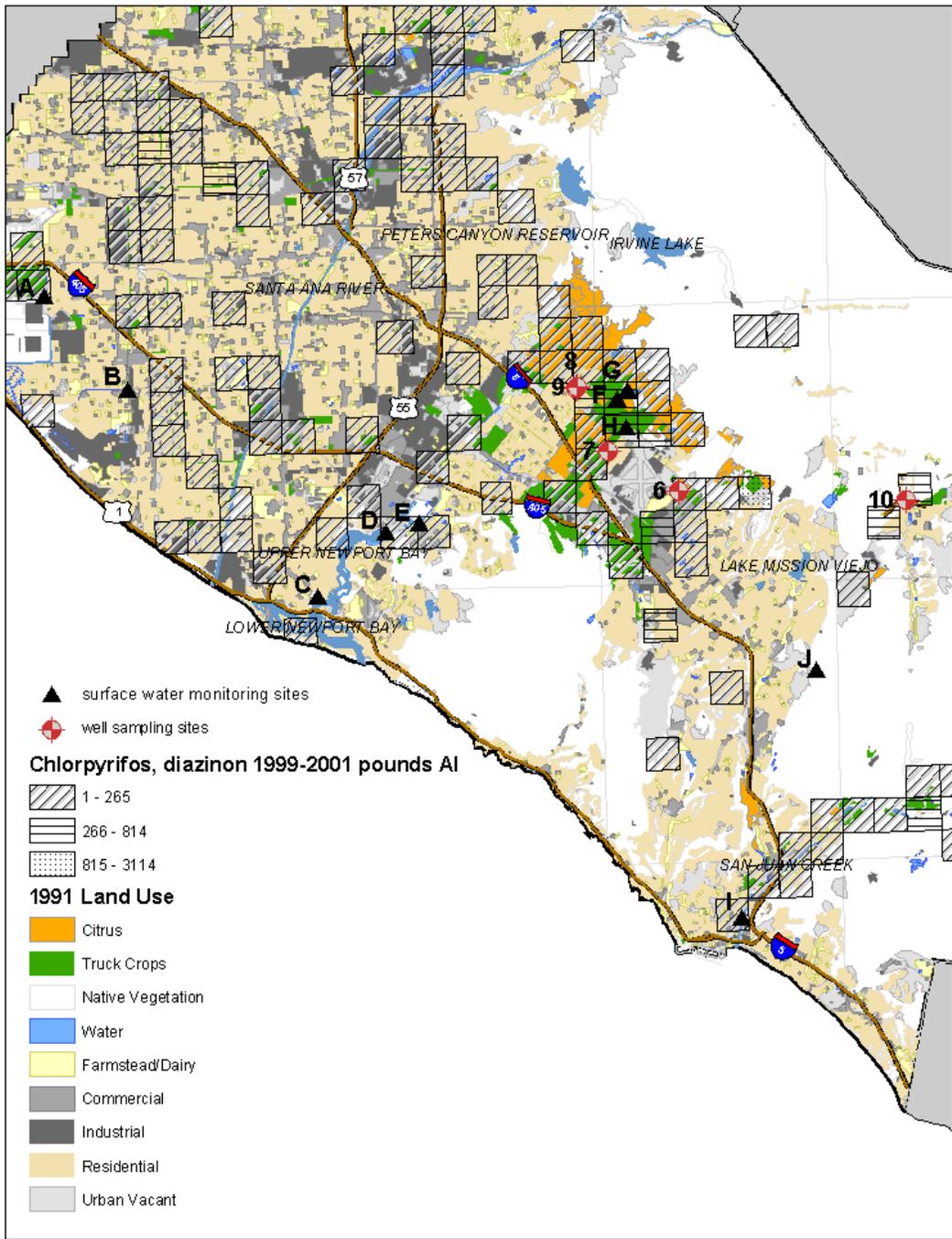


Figure 6. Chlorpyrifos use for 1999–2001 in Orange County.

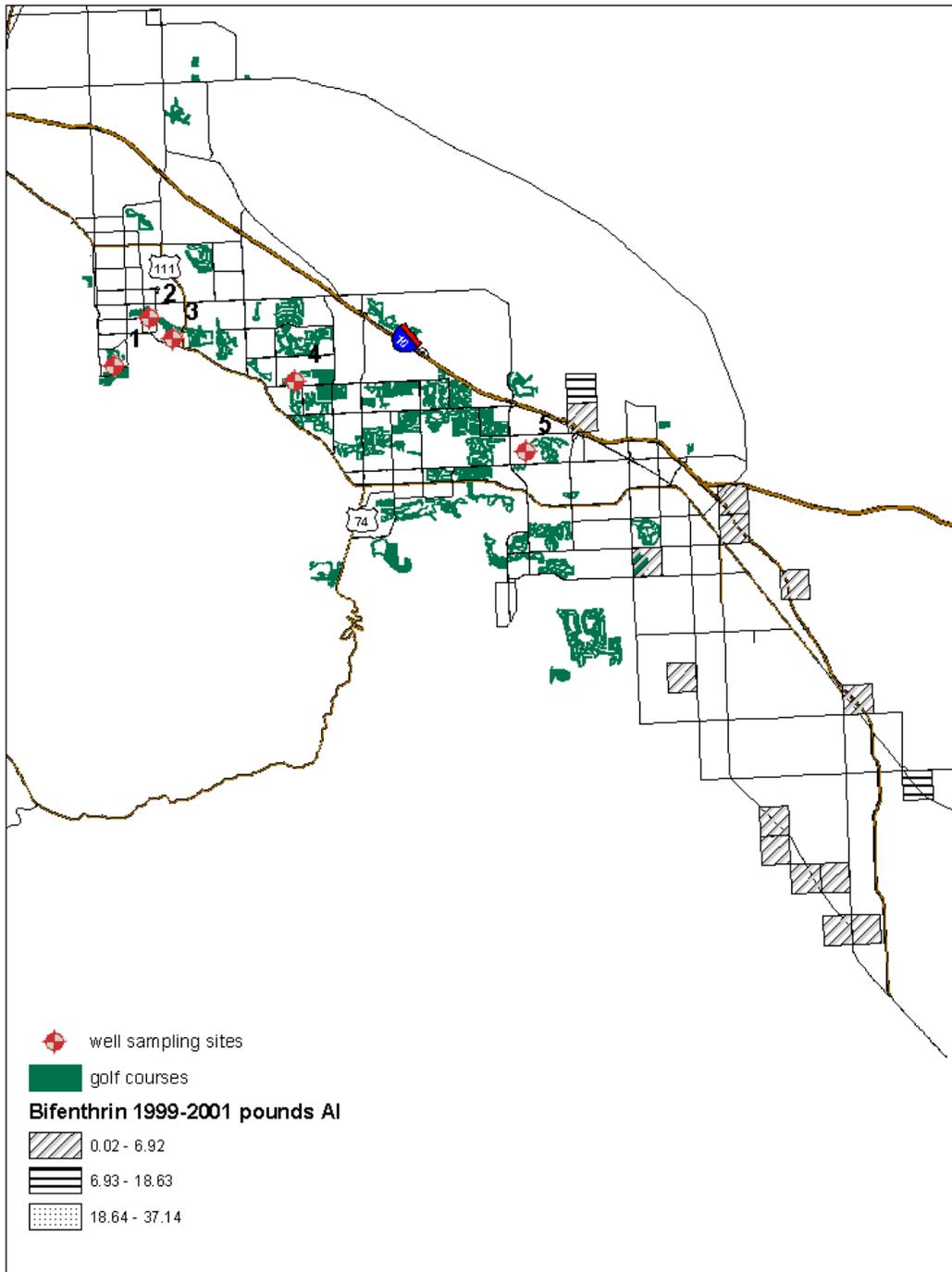


Figure 7. Bifenthrin use for 1999–2001 in the Coachella Valley, Riverside County.

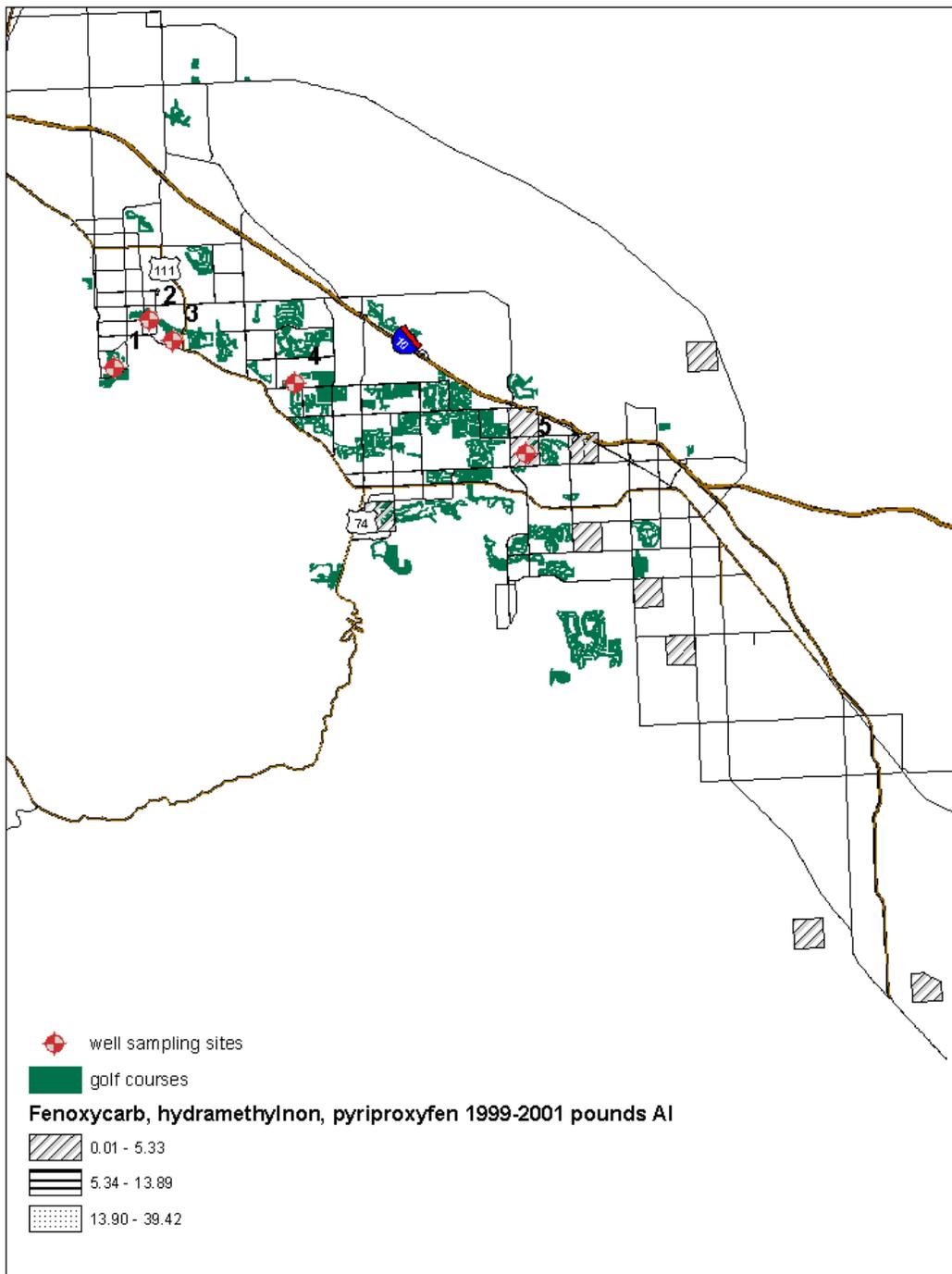


Figure 8. Fenoxycarb, hydramethylnon, and pyriproxyfen use for 1999–2001 in the Coachella Valley, Riverside County.

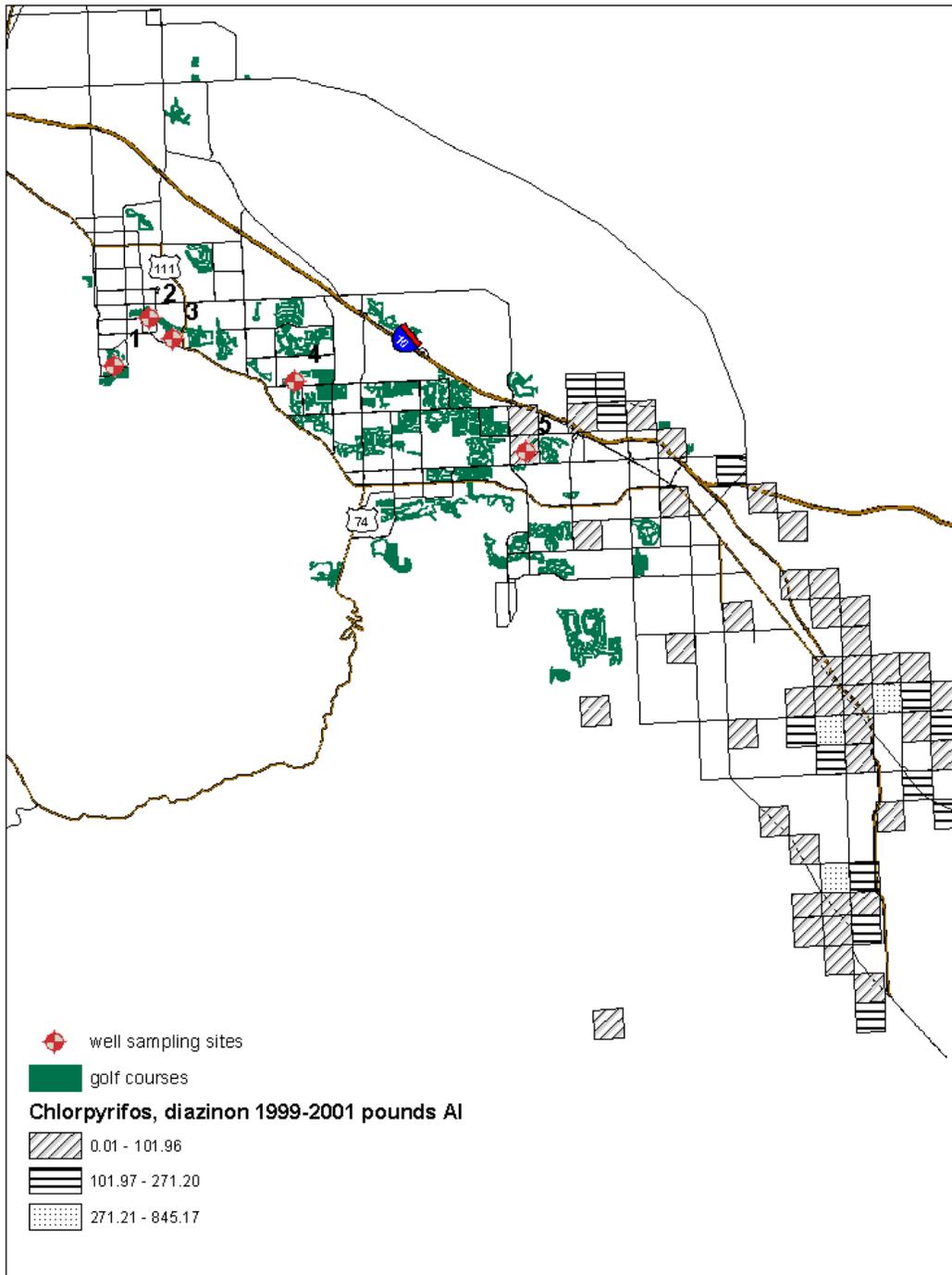


Figure 9. Chlorpyrifos and diazinon use for 1999–2001 in the Coachella Valley, Riverside County.

## Monthly Surface Water Sampling

### Continuing Quality Control

Results for all continuing QC can be found in Appendix A. The average percent recovery for each chemical ranged from 83.1 for hydramethylnon to 104 for methidathion (Table 6). Eight of the bifenthrin QC samples were beyond the warning limits, but no samples were beyond the control limits. Two fenoxycarb recoveries were above the UCL (May 1999 and May 2002) and one was below the LCL (September 2000). An additional four QC samples were beyond the warning limits. Three pyriproxyfen QC samples were above the UCL (May 1999, March 2000, and April 2000) and one was below the LCL (January 2002). An additional nine were beyond the warning limits. Hydramethylnon QC samples were never beyond control limits and were beyond the upper warning limit once. The variation in the validation of the method created wider control limits.

Using the old OP method, chlorpyrifos QC samples were never beyond the warning limits, dimethoate QC was beyond warning limits in ten samples, malathion QC samples were beyond the upper warning limit five times, and methidathion QC samples were above warning limits three times and below the warning limit once. In the 22 extraction sets for fonofos, methyl parathion, and phosmet, one fonofos and one methyl parathion QC sample was beyond the lower warning limit and phosmet QC recoveries were beyond the upper and lower warning limits twice. Using the new OP method, recoveries of dimethoate, malathion, chlorpyrifos, and methidathion were not beyond any of the control or warning limits. Recoveries for diazinon QC samples were beyond the UCL two times (January 2000 and October 2001) and beyond the LCL one time (May 1999).

Table 6. Average continuing QC recoveries in surface water.

	Percent Recovery
bifenthrin	93.7 (at 0.1 ppb); 98.8 (at 1.0 ppb)
fenoxycarb	98.2
hydramethylnon	83.1
pyriproxyfen	98.1
dimethoate	100
malathion	98.8
chlorpyrifos	92.2
methidathion	104
fonofos	89.3
methyl parathion	97.4
phosmet	96.8
diazinon	91.2 (method 163); 93.7 (method 262)

*No blind spike recoveries were above the upper control limit, five samples were below the lower control limit (5.10%), and 19 samples were beyond the lower and upper warning limits (19.4%) (Appendix A). Physical and Chemical Measurements of Water Quality*

Data for physical and chemical water quality measurements are included in Appendix B along with the chemistry results. The California Regional Water Quality Control Board, Water Quality Control Plan, Santa Ana River Basin (1995), and the Water Quality Control Plan, San Diego Basin, (1994), list the following water quality guidelines as acceptable:

- DO above 5.0 mg/L
- pH between 6.5 and 8.5
- water temperature no higher than 25.5°C (78°F)

The Santa Ana River Basin plan determines ammonia levels to be dependent upon water temperature and pH, while the San Diego Basin plan states that ammonia levels shall not exceed 0.025 mg/L. The plans do not provide an acceptable range for EC, alkalinity, or hardness. The San Diego Basin plan covers water quality at sites I and J; all the other sites are covered under the Santa Ana River Basin plan. Table 7 displays the mean water quality measurements for each site and counts for how many samples exceeded the water quality guidelines. The reporting limit for ammonia is above the water quality criteria so no counts are available.

Table 7. Mean of monthly sampling physical and chemical water quality measurements.

Physical Water Quality Measurements			Chemical Water Quality Measurements				
Site	Temp. °C	pH	DO (mg/L)	EC (µS/cm)	Ammonia (mg/L) NH <sub>3</sub>	Alkalinity (mg/L) CaCO <sub>3</sub>	Hardness (mg/L) CaCO <sub>3</sub>
A	19.3 (3) *	8.1 (3)	10.3 (1)	1916	<1	265.2	347.5
B	18.9 (2)	8.1 (3)	9.7 (3)	1096	2.8	263.2	341.2
C	23.2 (11)	9.2 (23)	14.1 (0)	966	<1	158.3	279.7
D	15.3 (0)	7.9 (0)	8.2 (0)	2955	<1	290.2	649.8
E	19.4 (5)	8.0 (3)	10.3 (0)	2710	<1	214.9	596.8
F	20.1 (11)	8.0 (4)	8.1 (0)	2067	2.4	149.8	600.0
G	20.1 (10)	7.7 (4)	8.4 (2)	2080	2	146.5	502.7
H	15.0 (0)	7.7 (0)	9.9 (0)	1176	5.96	40	550
I	19.5 (1)	8.1 (1)	12.1 (0)	2348	<1	289.7	584.0
J	18.2 (1)	7.9 (1)	9.3 (0)	793.1	<1	172.7	325.8

\* The number in parentheses is the number of measurements collected exceeding water quality guidelines.

## Pesticide Analyses

Pesticide analytical results for all samples are in Appendix B. Figures 10, 11, and 12 display site specific insecticide detections for each of the RIFA chemicals. In general, bifenthrin and the RIFA baits, fenoxycarb, hydramethylnon, and pyriproxyfen, were most frequently detected in runoff water collected from the nursery sites. In contrast, detections of the organophosphates, chlorpyrifos, diazinon, fonophos, and malathion, were most frequent in runoff water collected from the urban and integrated sites with detections of diazinon especially frequent at these sites:

- 73 detections of bifenthrin—2 at site C, 1 at sites E and J, 34 at site F, 32 at site G, and 3 at site H
- detections of fenoxycarb,—1 each at sites F, G, H, and J
- 1 detection of hydramethylnon at site J
- 2 detections of pyriproxyfen at sites F and J
- 29 detection of chlorpyrifos—1 at sites B, I, and J, 4 at site C, 8 at site E, 6 at sites F and G, and 2 at site H
- 165 detections of diazinon—17 at sites A and G, 15 at site B, 28 at site C, 31 at site D, 33 at site E, 11 at site F, 3 at site H, 9 at site I, and 1 at site J
- 12 detections of dimethoate—1 at sites C, G, and I, 5 at site E, and 4 at site F
- 14 detections of fonophos—2 at sites A, E and G, 1 at sites B and D, and 3 at sites C and I
- 45 detections of malathion—1 at sites A and I, 2 at sites B, D, and E, 9 at site C, 10 at site F, 16 at site G, and 3 at site H
- 6 detections of methidathion—3 at site C, 2 at site D, and 1 at site G
- 5 detections of methyl parathion—1 each at sites C, D, and F and 2 at site G
- phosmet was not detected in any of the samples

Table 8 displays the percent of samples for each chemical/site combination with positive detections along with the mean of the positive detections.

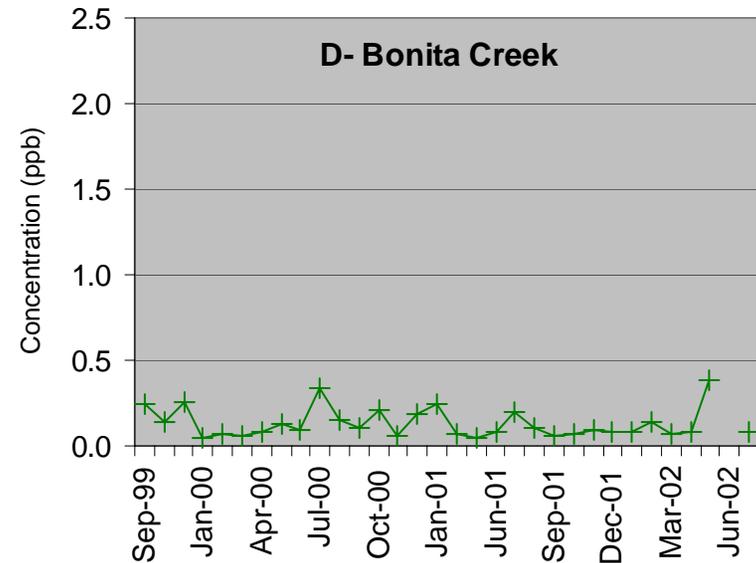
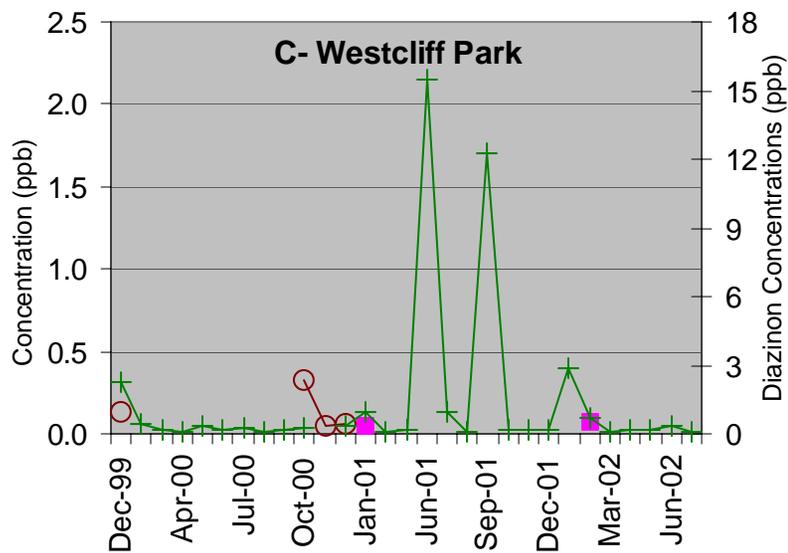
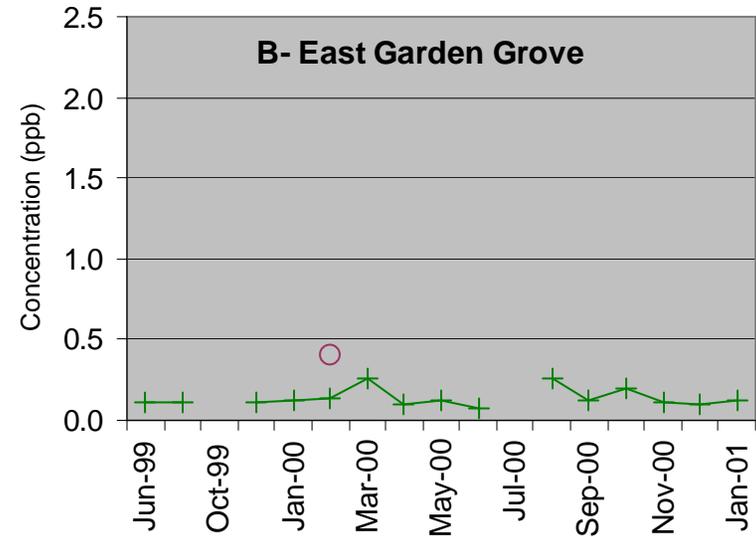
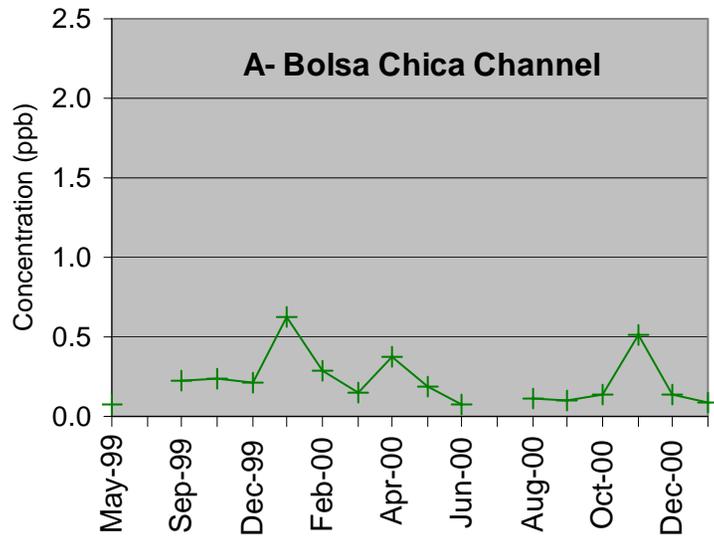
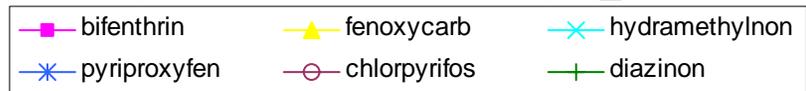


Figure 10. Insecticide concentration for sites A-D.



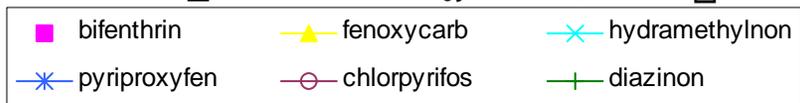
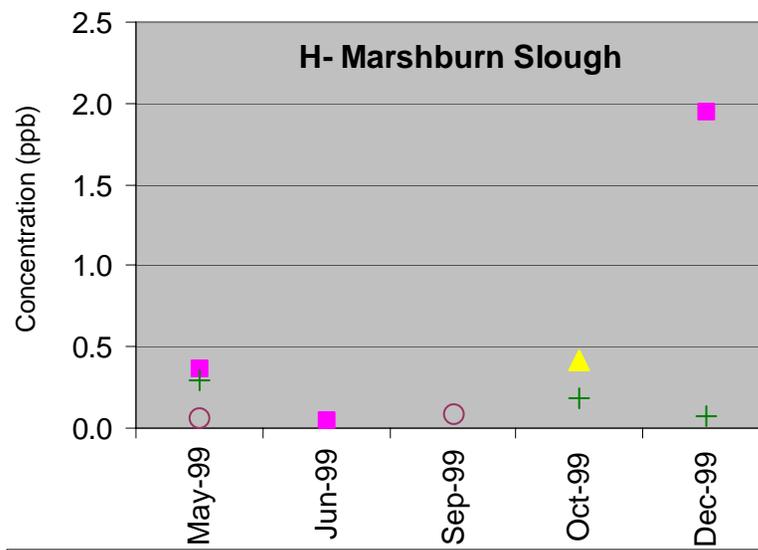
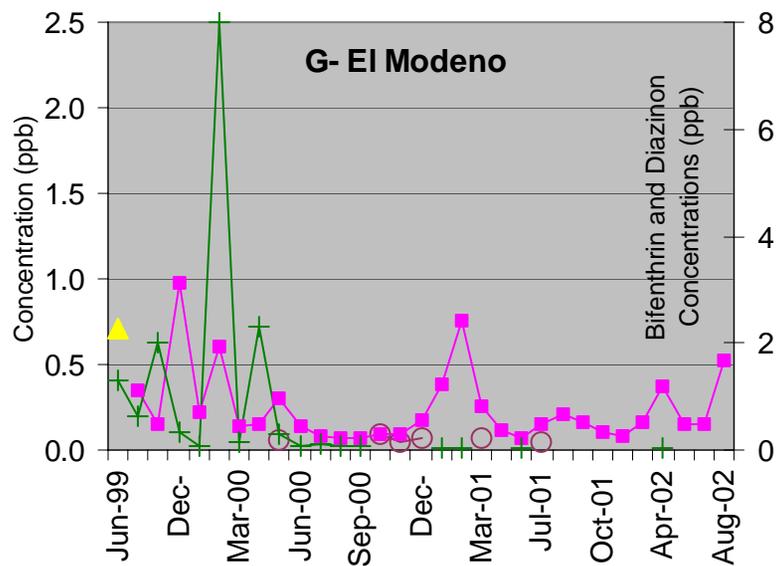
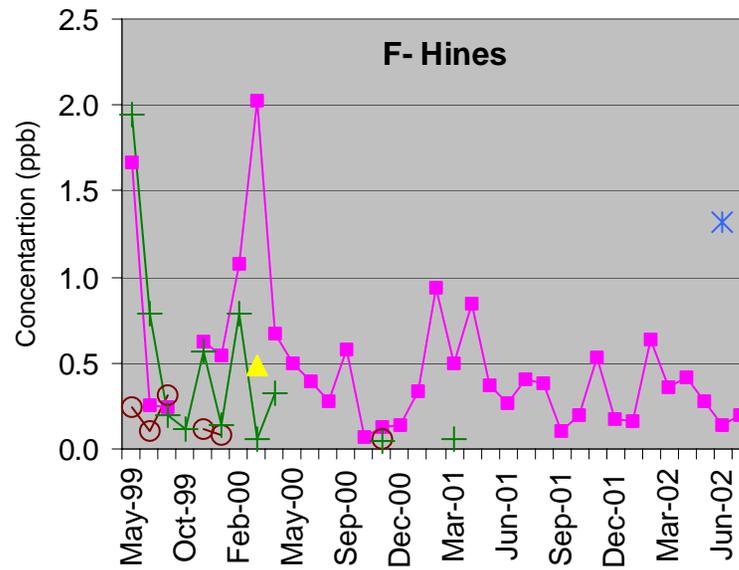
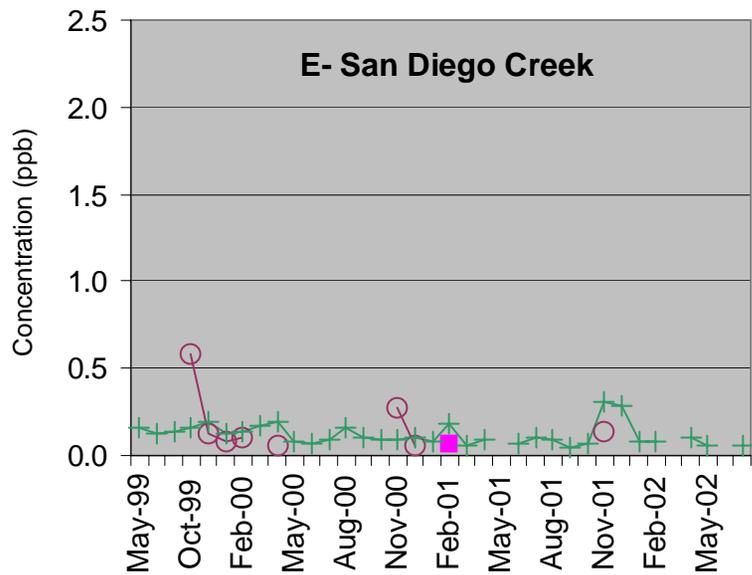


Figure 11. Insecticide concentrations for sites E-H.

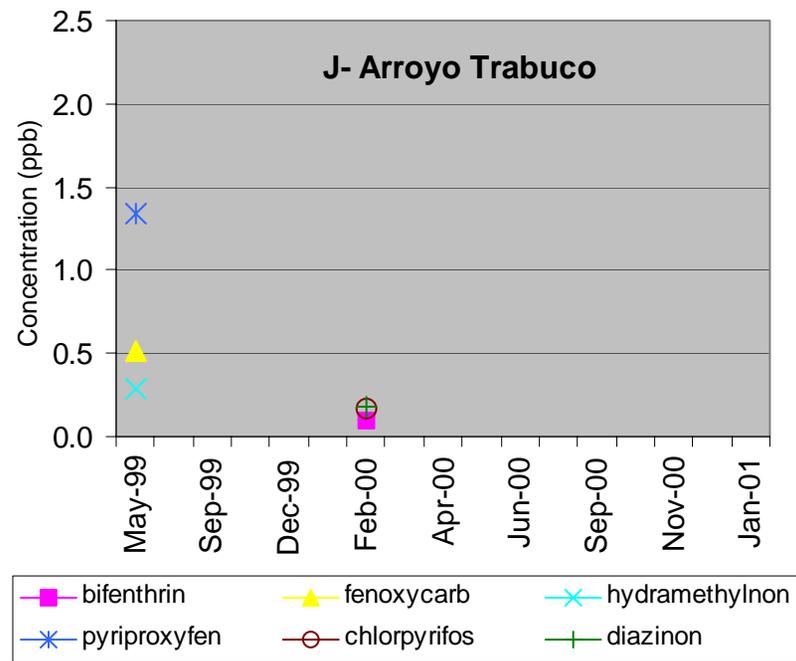
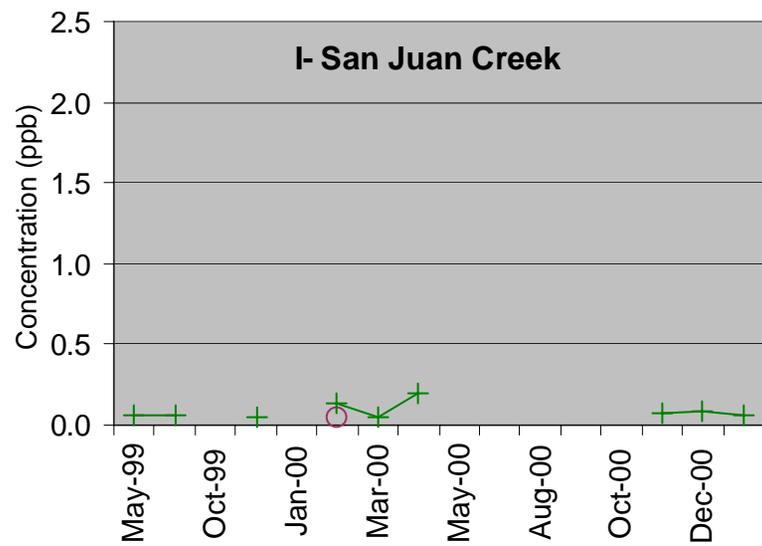


Figure 12. Insecticide concentrations for sites I and J.

Table 8. Percent of samples with positive detections. Numbers in parentheses are the mean of the positive detections.

	bifenthrin	fenoxycarb	hydramethylnon	pyriproxyfen	chlorpyrifos	diazinon	dimethoate	fonophos	malathion	methidathion	methyl parathion	phosmet
A	--	--	--	--	--	100(0.21)	--	17(0.06)	6(0.09*)	--	--	--
B	--	--	--	--	6(0.41*)	94(0.13)	--	9(0.08*)	13(0.25)	--	--	--
C	7(0.06)	--	--	--	14(0.14)	96(1.41)	3(0.28*)	37(0.16)	31(0.78)	10(0.06)	12(0.12*)	--
D	--	--	--	--	--	94(0.13)	--	3(0.09*)	6(0.06)	6(0.12)	3(0.09*)	--
E	3(0.07*)	--	--	--	22(0.18)	92(0.12)	14(0.2)	15(0.07)	6(0.07)	--	--	--
F	97(0.48)	3(0.49*)	--	3(1.32*)	24(0.16)	31(0.46)	11(1.85)	--	29(0.38)	--	8(0.09*)	--
G	97(0.76)	3(0.71*)	--	--	18(0.06)	51(0.92)	3(0.09*)	17(0.07)	48(1.46)	3(0.09*)	17(0.14)	--
H	60(0.79)	20(0.41*)	--	--	40(0.07)	60(0.18)	--	--	60(1.41)	--	--	--
I	--	--	--	--	6(0.05*)	56(0.08)	6(0.13*)	27(0.05)	6(0.07*)	--	--	--
J	6(0.09*)	6(0.51*)	6(0.29*)	6(1.34*)	6(0.17*)	6(0.19*)	--	--	--	--	--	--

\* Number given is the sole detection for that chemical/site combination.

## Toxicity Testing

Toxicity to *C. dubia* was measured at all sites (Table 9) until June, 2000, and until August 2001, at site E, because it was a site of interest to the Regional Water Quality Control Board and was downstream from the nursery inputs. Toxicity was most frequent at the nursery sites with 81%, 90%, and 100% of toxicity samples demonstrating significant mortality at sites F, G, and H, respectively. Toxicity in samples from the residential/urban waterways displayed a wide range with 0% measured at site B to 83% measured at site C. Site E was an integrated site and 44% of samples were determined to be toxic. Table 10 displays LC<sub>50</sub>'s (concentration which is lethal to 50% of a given population in a given time) of insecticides for three aquatic species: Rainbow trout, *D. magna*, *C. dubia*. Table 11 displays LC<sub>50</sub>'s for the water quality measurements ammonia, alkalinity, and hardness for *C. dubia*. The LC<sub>50</sub>'s for *C. dubia* aid in interpretation of chemical analyses results to determine if acute toxicity in samples were due to high levels of any given chemical. These numbers do not, however, give any aid in determining synergistic toxicity factors such as multiple chemicals in a water sample. It is noted that the samples collected in January 2000 may not have accurate toxicity results since the toxicity of some samples did not match up with the chemical concentrations that were detected. Further investigation revealed that the sample EC measured in the field did not match with that measured in the laboratory. Based on this data it can be inferred that site E may have been switched with site J and site F may have been switched with site I. Results in Table 9 have not been corrected for this possible error.

Table 9. Percent mortality of *C. dubia* in water samples collected in Orange County.

Date	Site									
	A	B	C	D	E	F	G	H	I	J
May-99	0	NS	NS	NS	0	100*	NS	NS	0	10
Jun-99	0	0	NS	NS	0	100*	100*	NS	NS	0
Sep-99	15	0	NS	20	30	100*	100*	NS	100*	0
Oct-99	50*	10	NS	60*	100*	100*	100*	NS	5	15
Dec-99	75 <sup>†</sup>	40 <sup>†</sup>	100*	100*	100*	100*	100*	NS	60*	20
Jan-00	100*	5	100*	100*	100*	0	0	NS	100*	100*
Feb-00	100*	30	80*	15	100*	100*	100*	100*	10	100*
Mar-00	20	0	NS	15	95*	100*	100*	NS	5	10
Apr-00	100*	0	5	5	100*	100*	100*	NS	0	0
May-00	15	20	100*	5	20	10	100*	NS	100*	20
Jun-00	0	0	25*	0	20	100*	100*	NS	0	0
Jul-00					30*					
Aug-00					10					
Sep-00					10					
Oct-00					0					
Nov-00					100*					
Dec-00					100*					
Jan-01					55*					
Feb-01					100*					
Mar-01					5					
Apr-01					0					
May-01					5					
Jun-01					0					
Jul-01					10					
Aug-01					0					

\*= survival significantly less than the control group (P< 0.05)

<sup>†</sup>= survival not significantly different from control due to replicate variability

Table 10. LC<sub>50</sub>'s of insecticides (ppb) for three aquatic species. <sup>1</sup>

Pesticide	Rainbow trout	<i>D. magna</i>	<i>C. dubia</i>
bifenthrin	0.15	1.6	0.078 <sup>2</sup>
chlorpyrifos	10	0.1	0.13 <sup>3</sup>
diazinon	3200	0.96	0.51 <sup>4</sup>
dimethoate	8500	2500	NA
fenoxycarb	1600	400	NA
fonofos	50 <sup>7</sup>	1 <sup>7</sup>	NA
hydramethylnon	160	1140	NA
malathion	68	1.0	1.14 <sup>5</sup> - 2.12 <sup>6</sup>
methidathion	10.5	7.2	2.2
methyl parathion	2700 <sup>7</sup>	7.3 <sup>7</sup>	NA
phosmet	230 <sup>7</sup>	8.5 <sup>7</sup>	NA
pyriproxyfen	>325	400	NA

<sup>1</sup> Data from CDPR, 2000

<sup>2</sup> Data from CDFG, 2000

<sup>3</sup> Data from Menconi and Paul, 1994

<sup>4</sup> Data from Menconi and Cox, 1994

<sup>5</sup> Data from Nelson and Roline, 1998

<sup>6</sup> Data from Ankley et al., 1991

<sup>7</sup> Data from Tomlin, C.D.S., 1997.

Table 11. LC<sub>50</sub>'s (mg/L)\* of chemical water quality parameters for *C. dubia*.

Water Quality Parameter	Test Type	LC <sub>50</sub> (mg/L)
Ammonia (NH <sub>3</sub> )	48-hour static acute test	1.18 (Andersen and Buckley, 1998)
Alkalinity (CaCO <sub>3</sub> )	3 brood test	237 (Cowgill and Milazzo, 1991)
Hardness (CaCO <sub>3</sub> )	3 brood test	1031(Cowgill and Milazzo, 1990)

\* LC<sub>50</sub>'s are reported in mg/L to be consistent with chemical water quality data reported from the CDFG Aquatic Toxicity Laboratory. The conversion to ppb is:

1 ppb= .001mg/L.

## Relationship Between Chemical Constituents and Toxicity Testing

The toxic unit (TU) approach was used to determine if the observed toxicity could be attributed to the chemicals used as part of the RIFA program. TU for a single chemical is calculated from a sample's measured analytical concentration and the known LC<sub>50</sub> to *C. dubia* for that chemical. TUs were calculated for each detection of bifenthrin, chlorpyrifos, diazinon, malathion, and methidathion according to the following equation:

$$\text{Toxic Unit} = \text{chemical concentration} / \text{LC}_{50}$$

As the TU approaches 1.0, the sample is theoretically more likely to show toxicity. For chemicals with a common mode of action, such as the OP's, the TU's are additive allowing for the joint acute toxicity for the OP's to be determined (Bailey et al. 1997; Spurlock, 2002). Appendix 3 contains TU calculations for 95 monthly samples with a corresponding toxicity sample that displayed significant toxicity. Samples collected on January 17 and 18, 2000 were not used due to samples possibly being switched in the laboratory.

Figures 13 and 14 display the observed versus the predicted toxicity for the organophosphates and bifenthrin, respectively. Spurlock (2002) determined that significant toxicity was consistently observed in samples with calculated TU greater than 0.5 for diazinon and chlorpyrifos. Samples where the TU < 0.5 but have shown significant toxicity in actual tests are considered false negatives with respect to OP or bifenthrin toxicity. The TU's for the OP's and bifenthrin can not be added and must be displayed separately because they do not have similar modes of action and there is no data to suggest that their joint toxicity would be strictly additive. Therefore, samples may be false negatives when analyzing the OP TU but not the bifenthrin TU and vice versa. Eighteen samples (19%) when analyzed for the OP TU were false negatives, whereas twenty-four samples (25%) when analyzed for the BI TU were false negatives. Other factors, in addition to these chemicals where TU's were calculated, may have caused toxicity. These factors include exceeding the water quality guidelines or the LC<sub>50</sub>'s for ammonia, alkalinity, and hardness, other chemicals present in the water, and the occurrence of precipitation in the days prior to sampling. Tables 12 and 13 display the occurrence of these additional factors for those samples that were identified as false negatives with respect to lack of OP and bifenthrin toxic units, respectively.

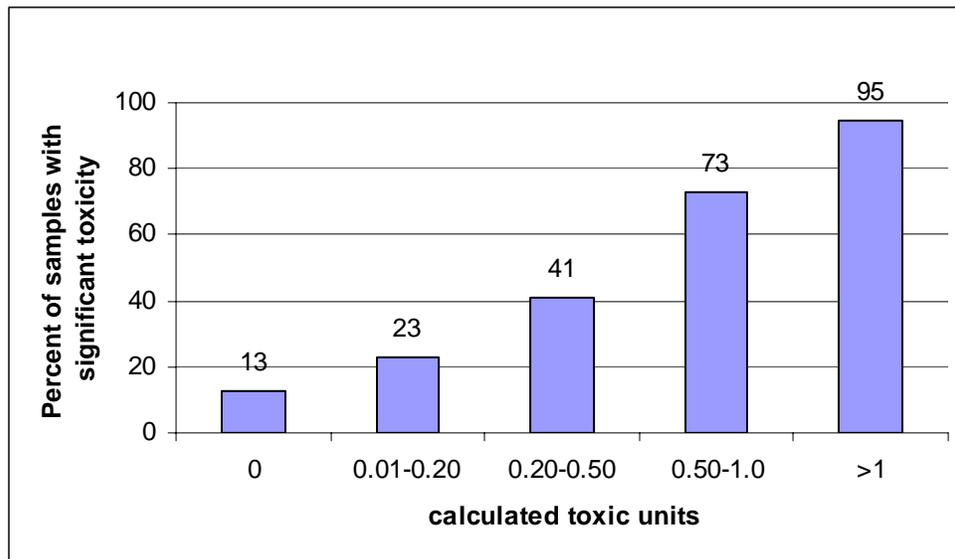


Figure 13. Observed vs. predicted toxicity from analytical concentrations of diazinon, chlorpyrifos, malathion, and methidathion.

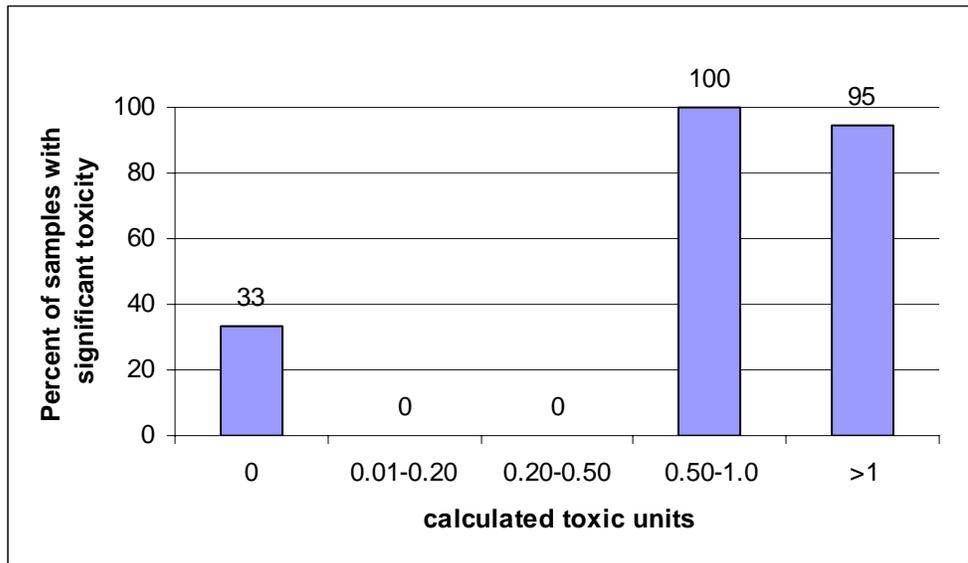


Figure 14. Observed vs. predicted toxicity from analytical concentrations of bifenthrin.

Table 12. Additional constituents and water quality factors that may have caused toxicity to those samples identified as false negatives with respect to lack of organophosphate toxic units.

Site	Date	BI TU > 0.5	additional chemicals detected	associated with precipitation	Exceeded water quality guidelines		Exceeded LC <sub>50</sub>		
					Temp °C	DO pH (mg/L)	Ammonia NH <sub>3</sub>	Alkalinity CaCO <sub>3</sub>	Hardness CaCO <sub>3</sub>
A	Oct-99					yes		yes	
A	Dec-99							yes	
B	Dec-99							yes	
C	Feb-00			yes		yes			
C	Jun-00				yes	yes			
D	Oct-99							yes	
E	Mar-00								
E	Jul-00					yes		yes	
E	Jan-01							yes	
E	Feb-01	yes		yes					
F	Oct-99		dimethoate						
F	Mar-00	yes	fenoxy carb						
F	Jun-00	yes			yes		yes	yes	
G	Mar-00	yes							
G	Jun-00	yes			yes		yes		
I	Sep-99							yes	
I	Dec-99							yes	yes
I	May-00		fonophos	yes					

Table 13. Additional constituents and water quality factors that may have caused toxicity to those samples identified as false negatives with respect to lack of bifenthrin toxic units.

Site	Date	OP TU > 0.5	additional chemicals detected	associated with precipitation	Exceeded water quality guidelines			Exceeded LC <sub>50</sub>		
					Temp °C	pH	DO (mg/L)	Ammonia NH <sub>3</sub>	Alkalinity CaCO <sub>3</sub>	Hardness CaCO <sub>3</sub>
A	Oct-99						yes		yes	
A	Dec-99								yes	
A	Feb-00	yes		yes						
A	Apr-00	yes	fonophos	yes						
A	Dec-99								yes	
C	Dec-99	yes					yes			
C	Feb-00			yes			yes			
C	May-00	yes	fonophos	yes						
C	Jun-00				yes	yes				
D	Oct-99								yes	
D	Dec-99	yes							yes	
E	Oct-99	yes	dimethoate							
E	Dec-99	yes	dimethoate				yes		yes	
E	Feb-00	yes	dimethoate	yes						
E	Mar-00									
E	Apr-00	yes	fonophos	yes						
E	Jul-00						yes	yes		
E	Nov-00	yes							yes	
E	Dec-00	yes							yes	
E	Jan-01								yes	
F	Oct-99		dimethoate fenoxy carb, methyl parathion							
G	Jun-99	yes								
I	Sep-99								yes	
I	Dec-99								yes	yes
I	May-00		fonophos	yes						

## **Rain Event Monitoring**

### Continuing Quality Control

Continuing QC results were discussed in the corresponding section for the monthly surface water sampling results. See Appendix A for complete data.

### Discharge and Rainfall Information

Rain event monitoring occurred on two days, January 25, 2000 and October 27, 2000. Sampling in January 2000 was concentrated on the San Diego Creek watershed, which included sites C, D, E, F, G, and H. Figure 15 displays rainfall data from three precipitation stations within the watershed and discharge from an OCPFRD gauging station at San Diego Creek at Campus Drive (OCPFRD 226). A total of 0.43, 0.31, and 0.39 inches of rain was recorded at Alert stations 217, 263, and 1150, respectively, on January 25, 2000. Figure 1 displays the locations of the discharge and Alert weather stations. Alert stations 217 and 263 represent rainfall for the lower San Diego Creek watershed for sites C, D, and E while Alert station 1150 is representative of rainfall in the upper watershed near sites F, G, and H. Most rain occurred during 9:00 a.m. and 10:00 a.m. on January 25. Sampling did not commence until approximately 2:30 p.m. of that day. A second surge of rainfall occurred after midnight with discharge reaching its highest levels at approximately 1:00 a.m. on January 26. Sampling for this rain event ended at 12:30 a.m.

On October 27, 2000, a total of 0.64 and 0.52 inches of rain was recorded at Alert stations 215 and 1100, respectively. Alert station 215 is a better representation of rainfall around the sampling sites, especially site I, while Alert station 1100 is further inland in the hills of the San Juan Creek watershed. Figure 16 displays rainfall data from two precipitation stations within the San Juan Creek watershed and discharge from an OCPFRD gauging station on Oso Creek at Crown Valley Parkway (OCPFRD 218). Figure 1 displays the locations of the discharge and Alert weather stations. According to the data collected at station 215, most rain fell between 6:00 a.m. and 9:00 a.m. and had stopped by about 12:00 p.m. Sampling for this rain event commenced at 5:50 a.m. and continued until 3:10 p.m.

Figure 15. Hourly precipitation (represented by bars) from three Alert stations and water discharge (solid line) measured at San Diego Creek at Campus Drive for the January 2000 rain event.

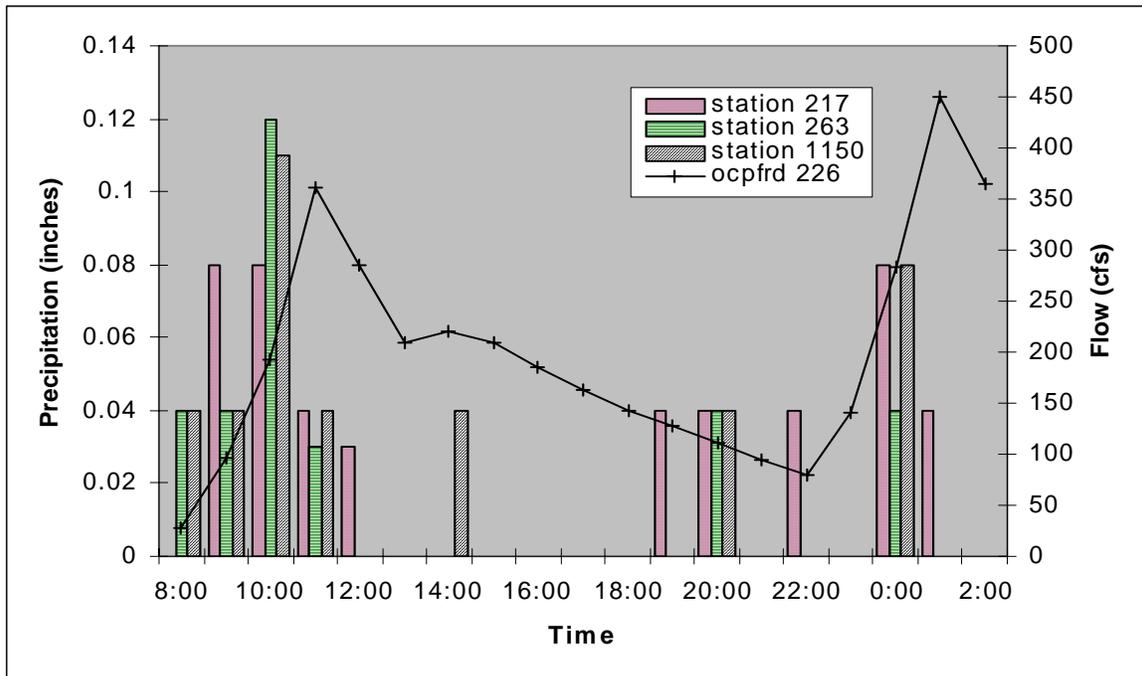
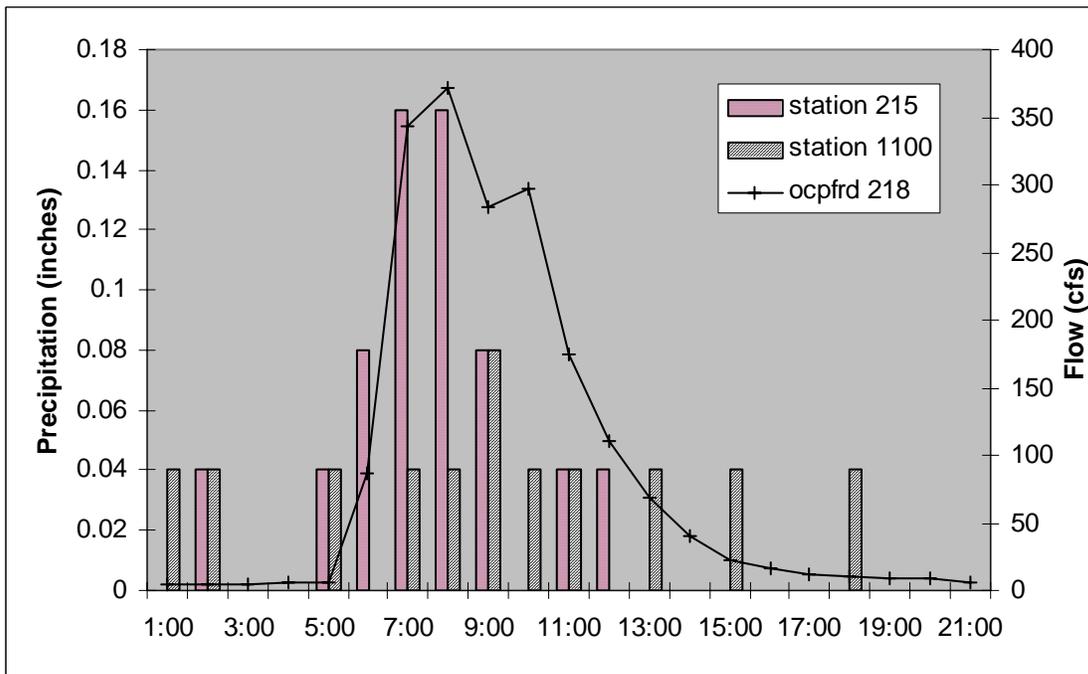


Figure 16. Hourly precipitation (represented by bars) from two Alert stations and water discharge (solid line) measured at Oso Creek at Crown Valley Parkway for the October 2000 rain event.



## Physical and Chemical Measurements of Water Quality

Physical and chemical water quality measurements were collected at all sites. Measurements were collected in the same fashion as the monthly sampling. Water quality guidelines can be found in the water quality section for monthly surface water monitoring. During the January 2000 monitoring, dissolved oxygen was not collected due to time constraints. During the October 2000 monitoring, water quality was collected at site J from a jar so no dissolved oxygen measurements were recorded. Since toxicity samples were not collected during the October 2000 monitoring, there were no measurements for ammonia, alkalinity, or hardness. None of the water quality measurements exceeded the guidelines. Table 14 displays the mean water quality measurements for all sites.

Table 14. Mean physical and chemical water quality measurements for rain runoff sampling.

Physical Water Quality Measurements				Chemical Water Quality Measurements				
Date	Site	Temp. °C	pH	DO (mg/L)	EC (µS/cm)	Ammonia (mg/L) NH <sub>3</sub>	Alkalinity (mg/L) CaCO <sub>3</sub>	Hardness (mg/L) CaCO <sub>3</sub>
1/25/00	C	16.4	7.7		452	22.0	40	68
	D	15.2	7.9		2084	<1	182	453.3
	E	16.4	7.9		878	1.64	79	209
	F	15.8	8.0		1568	1.1	81	505
	G	15.7	8.1		1625	1.7	87	490
	H	15.7	7.6		2800	3.9	69	940
	I*	NA	7.7		1194	1.1	108	270
	J*	NA	7.9		678	<1	100	220
10/27/00	I	16.2	7.9	NA	552			
	J	16.3	7.8	8.4	522			

\*=only one sample was collected from site.

NA=not available

## Pesticide Analysis

Results for all samples are reported in Appendix B. Figures 17 and 18 display insecticide detections for the RIFA chemicals at sites monitored for the duration of the rain events. During the January 2000 rain event, the nursery sites had the only detection of the fenoxycarb, a RIFA bait. Diazinon and malathion were both detected at all sites throughout the rain event. At the three nursery sites (F, G, and H) bifenthrin was detected in all samples collected.

- fenoxycarb was detected at two sites, once at site G and four times at site H
- chlorpyrifos was detected at five of the sites, once at site G, three times at site F five times at sites C and E, and in all samples collected at site H
- diazinon was detected in all samples at all sites
- dimethoate was detected in one samples at site E
- malathion was detected in all samples except for one at site G
- there were no detections of hydramethylnon, pyriproxyfen, fonophos, methidathion, methyl parathion, or phosmet

During the October 2000 sampling, bifenthrin was detected once at each location. Chlorpyrifos was detected once at site I and in every sample at site J. Diazinon was detected in all samples. Dimethoate was detected in two samples at site I. Malathion was detected in all samples at site I and in five samples at site J. There were no detections of fenoxycarb, hydramethylnon, pyriproxyfen, or methidathion.

## Toxicity Testing

Toxicity samples were collected at all sites during the January 2000 sampling, none were collected during the October 2000 sampling. All samples were 100% toxic to *C. daphnia*, see Appendix B. Table 10 displays the LC<sub>50</sub> values for *C. dubia* for bifenthrin, diazinon, chlorpyrifos, methidathion, and malathion: values are not available for the other pesticides. During the January 2000, rain event, only three samples, all collected at site D, were not associated with a chemical detection above an LC<sub>50</sub>. All bifenthrin detections were above the LC<sub>50</sub> (0.078 ppb) for *C. dubia*. Four of the twenty-one chlorpyrifos detections were above the LC<sub>50</sub> of 0.13 ppb. Twenty of the thirty-eight diazinon detections exceeded the LC<sub>50</sub> of 0.51 ppb. One of the thirty-seven malathion detections exceeded the LC<sub>50</sub> of 1.14 ppb.

Although toxicity samples were not collected during the October 2000, rain event, inference that the samples would have been toxic to *C. dubia* can be made based on the previous rain event monitoring and on the pesticide detections that were recorded. All samples except for two had pesticide detections that exceeded the LC<sub>50</sub> for *C. dubia* for a particular chemical. Both bifenthrin detections exceeded the LC<sub>50</sub>. Seven of the eight chlorpyrifos detections exceeded the LC<sub>50</sub> as did 5 of the 12 diazinon detections.

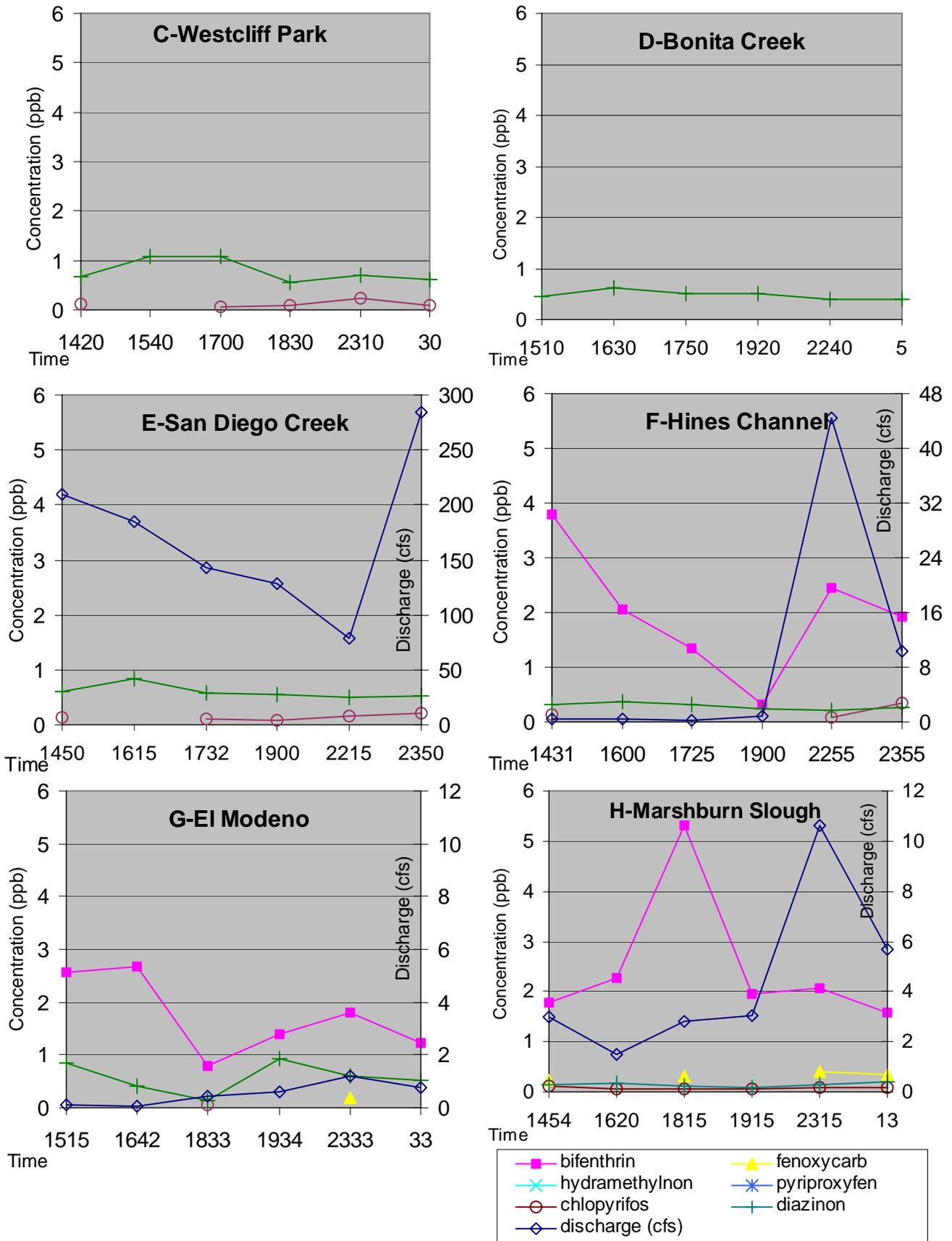


Figure 17. January 2000 rain event concentrations.

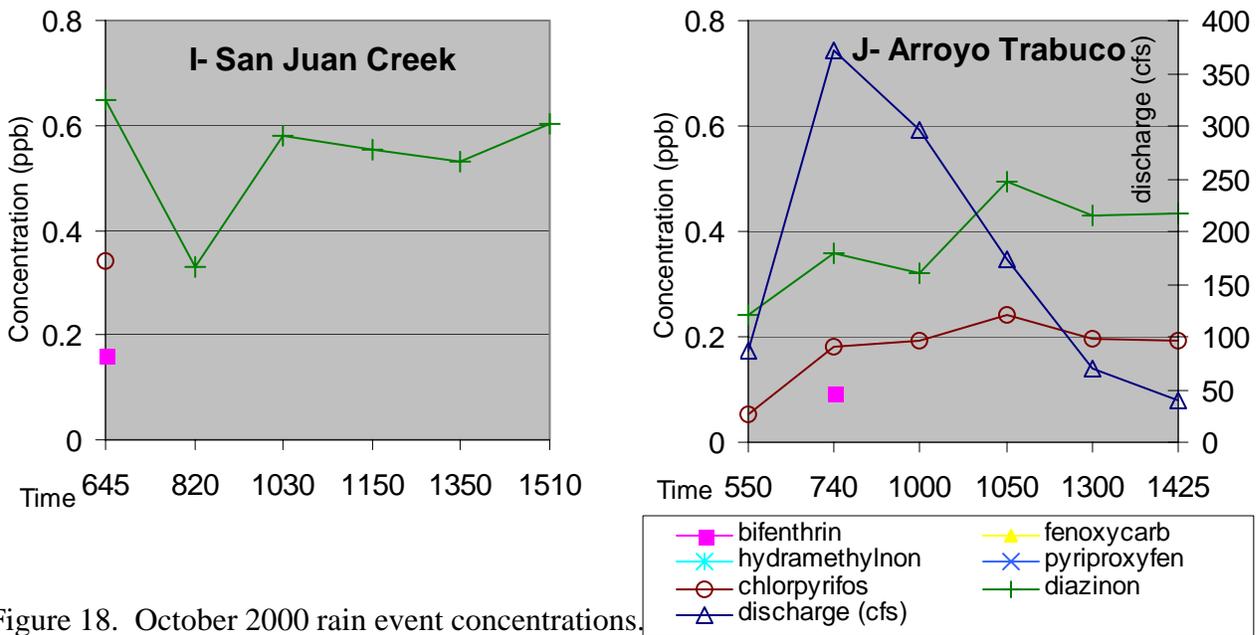


Figure 18. October 2000 rain event concentrations.

### Ground Water Monitoring

Ground water samples were collected from ten wells in Riverside and Orange Counties, California (Figures 2 and 3). Samples were collected in February and July 2001 in Orange County and in November 2000 and June 2002 in Riverside County.

#### Continuing Quality Control

Results for all continuing QC can be found in Appendix A. In total, four sets of samples were submitted for each analytical screen. All four sets of QC analyzed for bifenthrin were out of control. All but one was above UCL and the first 0.10 ppb spiked sample was below LCL. No fenoxycarb, hydramethylnon, or pyriproxyfen QC was beyond the control limits. Fenoxycarb and hydramethylnon samples were beyond the upper and lower warning limit, respectively, once. All QC samples for the organophosphate analytes were within control limits. Malathion was above the warning limit once. Average recoveries are displayed in Table 15. None of the blind spikes exceeded control limits.

Table 15. Average continuing QC recoveries for the RIFA insecticides in ground water.

	Percent Recovery
bifenthrin	94.0 (at 0.1 ppb); 104 (at 1.0 ppb)
fenoxycarb	98.0
hydramethylnon	78.4
pyriproxyfen	96.2
dimethoate	104
malathion	103
chlorpyrifos	97.2
methidathion	106
diazinon	93.0

### Pesticide Analysis

There were no detections above the reporting limits for the nine insecticides in the well water samples. The results probably reflect the low amount of insecticides used for RIFA treatments, application methods, depth to groundwater, and physical and chemical properties of the pesticides affecting their movement in soils.

### Summary

Monthly surface water sampling was conducted at ten sites over approximately three years (1999–2002). Bifenthrin and the RIFA baits (fenoxycarb, hydramethylnon, and pryiproxyfen) were detected mainly at the three nursery sites. In contrast, most organophosphate detections, especially diazinon, were in water sampled that originated from the urban and integrated sites. Toxicity testing, using the cladoceran *Ceriodaphnia dubia*, was conducted at all sites for the first half of the study and then only at site E for the remainder of the time. Only the nursery sites, F, G, and H, displayed toxicity that could be directly linked to RIFA insecticide concentrations found in the water. Toxicity at the urban/ residential and integrated sites' could not be attributed to the chemicals used specifically for the RIFA treatments.

Two rain events were monitored over the course of the study; one in the Upper Newport Bay watershed and the second at the most southern sites in an area that had a high RIFA infestation. Diazinon was detected in all samples collected from all sites for both events whereas bifenthrin was detected in all samples collected from the nursery sites during the first event. All water samples collected during the first rain event exhibited 100% mortality to *C. dubia*. No toxicity samples were collected during the second rain event, but based on the concentrations of detections the samples were theoretically as toxic as those from the first event. It is unlikely that all toxicity was caused by the pesticides monitored, many other factors influence toxicity especially during an urban rain event.

Well monitoring was conducted in ten wells; five in Orange County and five in Riverside County. All samples had no detectable residue of any of the chemicals tested; no toxicity tests were conducted.

bcc: Kim Surname File

## References

- Andersen, H.B. and J.A. Buckley. 1998. Acute Toxicity of Ammonia to *Ceriodaphnia dubia* and a Procedure to Improve Control Survival. *Bulletin of Environmental Contamination and Toxicology* 61(1): 116-122.
- Ankley, G.T., J.R. Dierkes, D.A. Jensen, and G.S Peterson. 1991. Piperonyl Butoxide as a Tool in Aquatic Toxicological Research with Organophosphate Insecticides. *Ecotoxicology and Environmental Safety* 21(3): 266-274.
- Bacey, J. 2000. Environmental Fate of Hydramethylnon.  
<<http://www.cdpr.ca.gov/docs/empm/pubs/fatememo/hydmthn.pdf>>.
- Bailey, H C., J.L. Miller, M.J. Miller, L.C. Wiborg, L. Deanovic, and T. Shed. 1997. Joint Acute Toxicity of Diazinon and Chlorpyrifos to *Ceriodaphnia dubia*. *Environmental Toxicology and Chemistry* 16(11): 2304-2308.
- Bradley, A. and C. Ganapathy 1998. Instructions for Preserving Water Samples Using Hydrochloric Acid (HCL). SOP FSWA007.00.  
<<http://www.cdpr.ca.gov/docs/empm/pubs/sops/fswa007.pdf>>.
- CDFA. 2004. Red Imported Fire Ant Program. <<http://www.cdfa.ca.gov/phpps/pdep/rifa/>>.
- CDFA. 1999. California Action Plan- Red Imported Fire Ant.  
<<http://www.cdfa.ca.gov/phpps/pdep/rifa/html/english/mediaroom/longtermplan.htm>>.
- CDFG. 2000. Pesticide Investigation Unit. Aquatic Toxicology Laboratory Report P-2161-2.
- CDFG. 1997. Acute Toxicity Test Procedures Using *Ceriodaphnia dubia*. SOP-ATL-012.
- CDPR. 2000. CDPR Aquatic Toxicology Registration Database.
- California Regional Water Quality Control Board. 1995. Water Quality Control Plan (Basin Plan), Region 8, Santa Ana River Basin. Riverside, California.
- California Regional Water Quality Control Board. 1994. Water Quality Control Plan (Basin Plan), Region 9, San Diego Basin. San Diego, California.
- Cowgill, U.M. and D.P. Milazzo. 1990. The Sensitivity of Two Cladocerans to Water Quality Variables: Salinity and Hardness. *Archive of Hydrobiology* 120(2): 185-196.
- Cowgill, U.M. and D.P. Milazzo. 1991. The Sensitivity of Two Cladocerans to Water Quality Variables: Alkalinity. *Archives of Environmental Contamination and Toxicology* 21(2): 224-232.

- Fecko, A. 1999a. Environmental Fate of Bifenthrin. <<http://www.cdpr.ca.gov/docs/emppm/pubs/fatememo/bifentn.pdf>>.
- Fecko, A. 1999b. Procedure for Determining Wadable Stream Discharge With Price Current Meters. SOP FSWA009.00. <<http://www.cdpr.ca.gov/docs/emppm/pubs/sops/fswa009.pdf>>.
- Ganapathy, C. 1998. Instructions for Splitting Water and Rinsing the Geotech Dekaport Splitter and Splitting Equipment. SOP FSWA004. <<http://www.cdpr.ca.gov/docs/emppm/pubs/sops/fswa004.pdf>>.
- Kim, D. 1999. Monitoring Surface Water for Selected Insecticides in Red Imported Fire Ant Treatment Areas. <<http://www.cdpr.ca.gov/docs/emppm/pubs/protocol/prot183.pdf>>.
- Menconi, Mary, and Cara Cox. 1994. Hazard Assessment of the Insecticide Diazinon to Aquatic Organisms in the Sacramento-San Joaquin River System. CDFG, Environmental Services Division, Administrative Report 94-2.
- Menconi, Mary, and Angela Paul. 1994. Hazard Assessment of the Insecticide Chlorpyrifos to Aquatic Organisms in the Sacramento-San Joaquin River System. CDFG, Environmental Services Division, Administrative Report 94-1.
- National Pesticide Telecommunications Network (NPTN). 1999. Chlorpyrifos Technical Fact Sheet. <<http://npic.orst.edu/factsheets/chlorpotech.pdf>>.
- NPTN. 1998. Diazinon. <<http://npic.orst.edu/factsheets/diazinon.pdf>>.
- Nelson, S.M. and R.A. Roline. 1998. Evaluation of the Sensitivity of Rapid Toxicity Tests Relative to Daphnid Acute Lethality Tests. Bulletin of Environmental Contamination and Toxicology 60: 292-299.
- OCFAA, 2004. Orange County Fire Ant Authority. <<http://www.ocfireant.com/>>.
- OCPFRD, 2000a. Orange County Public Facilities and Resources Department, Watershed and Coastal Resources Division: gauging station 226 and Alert weather stations 217, 263, and 1150.
- OCPFRD, 2000b. Orange County Public Facilities and Resources Department, Watershed and Coastal Resources Division: gauging station 218 and Alert weather stations 215 and 1100.
- Ross, L. J., R. Stein, J. Hsu, J. White and K. Hefner. 1996. Distribution and Mass Loading of Insecticides in the San Joaquin River, California. Winter 1991-92 and 1992-93. DPR. EH96-02. <<http://www.cdpr.ca.gov/docs/emppm/pubs/ehapreps/eh9602.pdf>>.

Segawa, R. 1995. Chemistry Laboratory Quality Control. SOP QAQC001.00.  
<<http://www.cdpr.ca.gov/docs/empm/pubs/sops/qaqc001.pdf>>.

Sullivan, J. 2000a. Environmental Fate of Fenoxycarb.  
<<http://www.cdpr.ca.gov/docs/empm/pubs/fatememo/fenxycrb.pdf>>.

Sullivan, J. 2000b. Environmental Fate of Pyriproxyfen.  
<<http://www.cdpr.ca.gov/docs/empm/pubs/fatememo/pyrprxfn.pdf>>.

Spurlock, Frank. 2002. Analysis of Diazinon and Chlorpyrifos Surface Water Monitoring and Acute Toxicity Bioassay Data, 1991–2001. DPR EH01-01.  
<<http://www.cdpr.ca.gov/docs/empm/pubs/ehapreps/eh0101.pdf>>.

Tomlin, C.D.S. 1997. The Pesticide Manual. 11th edition. British Crop Protection Council, Farnham, Surrey GU9 7PH, UK.

U.S. Environmental Protection Agency. 1993. Methods for measuring the acute toxicity of effluents and receiving waters to freshwater and marine organisms. 4th ed. EPA/600/4-90/027F. August 1993.