



# Department of Pesticide Regulation



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## MEMORANDUM

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SUBJECT: PRELIMINARY RESULTS OF PESTICIDE ANALYSIS AND ACUTE  
TOXICITY TESTING OF MONTHLY SURFACE WATER MONITORING  
FOR THE RED IMPORTED FIRE ANT PROJECT IN ORANGE COUNTY,  
AUGUST 2001 (STUDY 183)

### SUMMARY

During August 2001, monthly surface water samples were collected from five sites in Orange County, California. Water samples showed no detects of fenoxycarb, hydramethylnon, pyriproxyfen, chlorpyrifos, dimethoate, malathion, and methidathion. Bifenthrin was detected in two samples at 0.385 and 0.686 parts per billion (ppb) at the two nursery sites. Diazinon was detected in three samples ranging from 0.197 to 0.109 ppb at two urban and an integrated site. Toxicity was tested at San Diego Creek at Campus Drive, an integrated site. This site was not toxic (0% mortality) to *Ceriodaphnia dubia* in the water collected. Water samples collected from a mitigation filter strip planted with *Canna* showed no reduction of bifenthrin concentrations. Additional water samples collected during a polyacrylamide trial showed similar decreases in insecticide concentrations through the mitigation filter strip as the background samples.

### SCOPE OF THIS MEMORANDUM

This memorandum reports results of water sampling conducted by the Department of Pesticide Regulation (DPR), under interagency agreement with the California Department of Food and Agriculture (CDFA), for the Red Imported Fire Ant (RIFA) control project. Data included here are from the August 22, 2001 monthly monitoring, and encompass results from both chemical analyses and aquatic biotoxicity testing. Additional data was collected on August 1, 2001 for a trial introduction of polyacrylamide into the mitigation filter strip. This memorandum summarizes results for bifenthrin, fenoxycarb, hydramethylnon, pyriproxyfen, and five organophosphorus insecticides: chlorpyrifos, diazinon, dimethoate, malathion, and methidathion. Only bifenthrin, fenoxycarb, hydramethylnon, pyriproxyfen, and chlorpyrifos are used in the RIFA control program. The other four organophosphates are in our multiresidue analytical



method and are included in this report to assist in the interpretation of the toxicity results. Acute toxicity results using *Ceriodaphnia dubia* are also included. An in-depth interpretation of data is not included here, but will be provided in the final report when the 2001 pesticide use report becomes available.

Reports of the monthly surface water sampling events will continue through the conclusion of the study. This memo is the twenty-third in the monthly sampling series. You can request previous sampling results memos by calling the number above or you may view or download them from DPR's website at <[www.cdpr.ca.gov/docs/rifa](http://www.cdpr.ca.gov/docs/rifa)>.

## MATERIALS AND METHODS

### Sample and Data Collection

On August 22, 2001, surface water samples were collected at five sites, C, D, E, F, and G within the Orange County treatment area (Table 1 and Figure 1) including one rinse blank. Toxicity sample was collected at site E. Sample at site G was collected at the outflow of the vegetative filter strip (see mitigation sampling). No sample was collected at site H due to lack of water. This sampling event did not coincide with measurable rainfall.

Table 1. Sampling site descriptions in Orange County, California

Site #	Description	Coordinates
A	Bolsa Chica Channel at Westminster Ave.	N 33°45'35", W 118°02'36"
B	East Garden Grove Channel at Gothard St.	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 Dr.	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 Blvd.	N 33°41'45", W 117°44'02"
I	San Juan Creek at Stonehill Dr.	N 33°28'31", W 117°40'43"
J	Arroyo Trabuco at Oso Parkway	N 33°35'06", W 117°38'09"

All water samples were collected at center channel using a 10-liter stainless steel bucket and divided into one-liter amber sample bottles using a Geotech® 10-port splitter. Samples designated for organophosphate chemical analysis were preserved by acidification with 3N hydrochloric acid to a pH between 3.0 and 3.5. Because diazinon rapidly degrades under acidic conditions, it was analyzed from a separate, un-acidified sample. Samples designated for toxicity testing were delivered to the testing laboratory within 36 hours of collection. All

samples were stored on wet ice or in a 4°C refrigerator until transported to the appropriate laboratory for analysis.

### **Mitigation Sampling**

In addition to the monthly surface water samples being collected at sites throughout Orange County, mitigation samples are being collected at El Modeno Gardens (site G) from a concrete lined ditch approximately 160 yards long, three and a half feet deep, and four to six feet wide. The filter strip consists of nine successive settling basins planted with *Canna x 'Tropicana'*. Water samples are collected at the inlet and outlet of the filter strip. Rodamine dye is added to water at the inflow of the filter strip immediately after sampling. The purpose of the dye is to ensure that the same parcel of water is sampled at the inflow and the outflow of the filter strip. Water at the outflow is then sampled just prior to the dye exiting the filter strip. At the time of this sampling *Canna* had been planted in six of the settling basins; the three settling basins closest to the outflow had been harvested. Sediment was collected from the edge of an area where roses are grown to determine if any insecticide inputs are from this source. Irrigation water from the roses enters the filter strip from a pipe that runs under a road into the filter strip at the midway point.

Additional water samples were collected on August 1, 2001 from the filter strip as part of a trial introduction of polyacrylamide (PAM). PAM was introduced into the water of the filter strip to enhance sedimentation. Water samples were collected to determine if the increased sedimentation would have any effect on insecticide concentrations. Six sets of samples were taken from the inflow and outflow of the filter strip, including a background collected prior to PAM introduction. PAM was applied in tablet form in a wire cage at 8:45 AM with the first sample collected approximately 30 minutes later. Samples were not analyzed for fenoxycarb, hydramethylnon, or pyriproxyfen.

Water samples were collected and transported using the technique described previously. Sediment sample was collected by compositing 10 scoops of sediment from a drainage ditch into a 500-mL polycarbonate container and storing on wet ice until delivery to the laboratory for analysis.

### **Toxicity Tests**

Acute toxicity testing was conducted by the Department of Fish and Game (DFG) Aquatic Toxicity Laboratory following current U.S. Environmental Protection Agency (U.S. EPA) procedures using a cladoceran, *Ceriodaphnia dubia*, (U.S. EPA, 1993). Acute toxicity was determined using a 96-hour, static-renewal bioassay in undiluted sample water. Data were reported as percent mortality.

## **Environmental Measurements**

Water quality parameters measured *in situ* included temperature, pH, electrical conductivity (EC), and dissolved oxygen (DO). Water pH was measured using an IQ Scientific Instruments® (model IQ 150) pH meter. EC, water temperature, and DO were measured using an YSI® multi parameter meter (model 85). Additionally, the DFG Aquatic Toxicity Laboratory measured alkalinity, hardness, and ammonia on the samples to be tested for toxicity. Totals of alkalinity and hardness were measured with a Hach7 titration kit. Ammonia was determined using an Orion® 95-12 ammonia selective electrode attached to an Orion® specific ion meter (model 290A).

## **Insecticide Analyses**

All water samples were analyzed for bifenthrin, fenoxycarb, hydramethylnon, pyriproxyfen, chlorpyrifos, diazinon, dimethoate, malathion, and methidathion. The CDFA Center for Analytical Chemistry performed all analyses using gas chromatography and a flame photometric detector for the five organophosphorus insecticides; a high performance liquid chromatography and a ultra violet detector for fenoxycarb, hydramethylnon, and pyriproxyfen; and gas chromatography with an electron capture detector confirmed with a mass selective detector for bifenthrin. The reporting limit (reliable detection levels) for chlorpyrifos and diazinon is 0.04 ppb, 0.1 ppb for fenoxycarb and pyriproxyfen, 0.2 ppb for hydramethylnon, and 0.05 ppb for the other insecticides.

Sediment sample was analyzed for bifenthrin, chlorpyrifos, and diazinon. The Department of Fish and Game Water Pollution Control Laboratory conducted all analyses. Sediment samples were extracted using a 50/50 mixture of acetone/dichloromethane (DCM) using heat and pressure and were analyzed using gas chromatography and two <sup>63</sup>Ni micro-electron capture detectors for bifenthrin and a Thermionic Specific Detector (TSD) for chlorpyrifos and diazinon. The reporting limit for all analyses is 10 ppb based on dry weight.

## **RESULTS and DISCUSSIONS**

### **Insecticide Concentrations**

Of the nine insecticides analyzed, only chlorpyrifos, bifenthrin, fenoxycarb, hydramethylnon, and pyriproxyfen were allowed use in nurseries for treatment of fire ants to comply with the U.S. Department of Agriculture's quarantine requirements. All of the organophosphorus insecticides listed are registered for uses in commercial agriculture, nurseries, golf courses or

parks for the control of other insect pests. Malathion and diazinon are widely available for homeowner use.

The Bonita Creek site, an urban drain, had the highest concentration of diazinon (0.109 ppb). Bifenthrin was only detected at the two nursery sites and did not contribute to residue in water at San Diego Creek.

The *Canna* vegetative filter strip showed no reduction of bifenthrin residues. There were reductions in chlorpyrifos (100%) and malathion (100%) residues. Sediment sample had detections of bifenthrin, chlorpyrifos, and diazinon indicating that there may be some input of these chemicals into the filter strip from this source.

Water samples from the PAM trial had average reductions of 45%, 40%, and 35% for bifenthrin, chlorpyrifos, and malathion respectively. The background samples showed reductions of 51%, 33%, and 100% for the same chemicals.

Table 2. Insecticide concentrations and acute toxicity in monthly surface water samples, August 2001, Orange County, California.

Site	Concentration (ppb)									% Acute Mortality <sup>1</sup>
	bifenthrin	fenoxycarb	hydamethylnon	pyriproxyfen	chlorpyrifos	diazinon	dimethoate	malathion	methidathion	<i>C. dubia</i>
C	ND <sup>2</sup>	ND	ND	ND	ND	0.104	ND	ND	ND	NS <sup>3</sup>
D	ND	ND	ND	ND	ND	0.109	ND	ND	ND	NS
E	ND	ND	ND	ND	ND	0.097	ND	ND	ND	0/0
F	0.385	ND	ND	ND	ND	ND	ND	ND	ND	NS
G	0.686	ND	ND	ND	ND	ND	ND	ND	ND	NS
RB <sup>4</sup>	ND	ND	ND	ND	ND	ND	ND	ND	ND	NS

<sup>1</sup> Two numbers are reported for the toxicity test. The first number is the result from the sample; the second from the corresponding control.

<sup>2</sup> ND = none detected at the reporting limit for that chemical.

<sup>3</sup> NS = no sample collected

<sup>4</sup> RB = rinse blank

Table 3. Insecticide concentrations at mitigation site, August 2001, Orange County, California.

Location	Concentration (ppb)								
	bifenthrin	fenoxycarb	hydramethylnon	pyriproxyfen	chlorpyrifos	diazinon	dimethoate	malathion	methidathion
<u>Surface Water Samples</u>									
Filter strip inflow	0.56	ND <sup>1</sup>	ND	ND	0.057	ND	ND	0.063	ND
Filter strip outflow	0.686	ND	ND	ND	ND	ND	ND	ND	ND
Sediment Sample	1860				54.7	76.1			

<sup>1</sup> ND = none detected at the reporting limit for that chemical.

Table 4. Insecticide concentrations and water quality at filter strip mitigation site (PAM application), August 1, 2001, Orange County, California.

Location	Concentration (ppb)						Water Quality			
	bifenthrin	chlorpyrifos	diazinon	dimethoate	malathion	methidathion	Temperature (°C)	pH	Dissolved Oxygen (mg/L)	Electroconductivity (µS/cm)
Inflow <sup>1</sup>	1.0	0.064	ND <sup>2</sup>	ND	0.068	ND	20.7	7.8	6.8	2638
Outflow <sup>1</sup>	0.492	0.043	ND	ND	ND	ND	21.1	7.2	4.65	2648
Inflow I	1.05	0.055	ND	ND	0.126	ND	NT <sup>3</sup>	7.6	NT	NT
Outflow I	0.526	0.041	ND	ND	0.052	ND	22.5	6.9	4.68	2610
Inflow II	1.26	0.145	ND	ND	0.306	ND	23.1	7.8	7.18	2609
Outflow II	0.541	0.046	ND	ND	0.113	ND	23.2	7.3	4.79	2655
Inflow III	0.728	0.081	ND	ND	0.166	ND	26.5	8.0	7.03	2633
Outflow III	0.597	0.075	ND	ND	0.237	ND	26.8	7.5	5.30	2694
Inflow IV	1.13	0.071	0.203	ND	0.348	ND	30.6	7.8	7.54	2658
Outflow IV	0.405	ND	ND	ND	0.158	ND	31.7	7.7	7.34	2645
Inflow V	0.836	0.056	ND	ND	0.171	ND	33.4	7.9	6.86	2801
Outflow V	0.66	0.644	ND	0.057	0.194	ND	32.5	7.8	4.80	2861

<sup>1</sup> Samples taken prior to PAM treatment; additional inflow sampling intervals started 30 minutes after PAM introduction and were collected at approximately one hour intervals except for interval V which was collected three hours after interval IV.

<sup>2</sup> ND = none detected at the reporting limit for that chemical.

<sup>3</sup> NT = not taken

### Toxicity Data

Toxicity samples were taken from one integrated site within the treatment area. Sample from site E was not acutely toxic to *C. dubia* causing 0% mortality (Table 2). Site E drains an integrated site and had a detection of diazinon below the LC<sub>50</sub> for *C. dubia*. Table 5 gives LC<sub>50</sub> values for some aquatic organisms.

Table 5. 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
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
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

### Environmental Measurements

Table 6 presents the data for DO, temperature, pH, and EC. Ammonia, alkalinity, and hardness are only reported for site E since these measurements are taken with the toxicity tests. 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: water temperature no higher than 78°F (25.5°C), pH between 6.5 and 8.5, and DO above 5.0 mg/L. 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 temperatures at sites E, F, and G were above the maximum guideline and the pH at site C was above the maximum guideline.

Table 6. Water quality measurements at sampling sites, August 2001, Orange County, California.

Site	Temperature (°C)	pH	Dissolved Oxygen (mg/L)	Electroconductivity (µS/cm)	Ammonia mg/L	Alkalinity mg/L CaCO <sub>3</sub>	Hardness mg/L CaCO <sub>3</sub>
C	21.3	8.7	14.33	938	NT	NT	NT
D	19.5	8.0	7.03	1732	NT	NT	NT
E	25.8	7.4	8.02	3132	NR	84	146
F	29.1	7.8	8.59	1551	NT	NT	NT
G	26.9	7.1	5.75	2854	NT	NT	NT
Filter strip inflow	24.7	7.5	10.01	2663	NT	NT	NT
Filter strip outflow	26.9	7.1	5.75	2854	NT	NT	NT

NT= Not taken

NR= No reading available

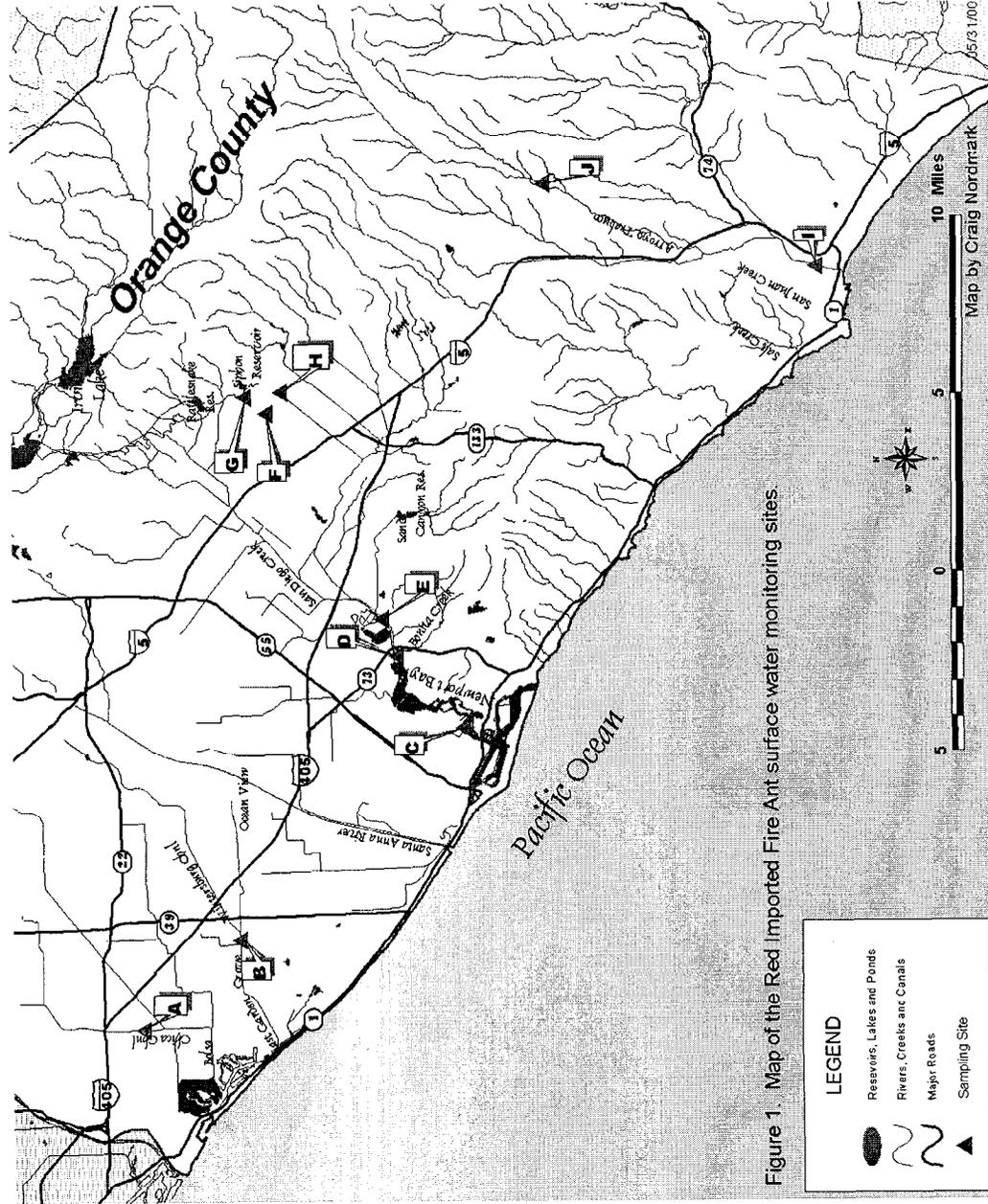


Figure 1. Map of the Red imported Fire Ant surface water monitoring sites.

## References

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