



# Department of Pesticide Regulation



Paul E. Helliker  
Director

## MEMORANDUM

Gray Davis  
Governor  
Winston H. Hickox  
Secretary, California  
Environmental  
Protection Agency

TO: John S. Sanders, Ph.D.  
Branch Chief  
Environmental Monitoring and  
Pest Management Branch

FROM: Johanna Walters, Environmental Research Scientist  
Dave Kim, Associate Environmental Research Scientist  
Roger Sava, Associate Environmental Research Scientist  
Kean S. Goh, Agriculture Program Supervisor IV  
Environmental Monitoring and  
Pest Management Branch  
(916) 324-4340

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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, FEBRUARY 2000 (STUDY 183)

### SUMMARY

During February 2000, surface water samples collected from ten sites in Orange County, California, showed no detects of fenoxycarb, hydramethylnon, and pyriproxyfen. There were four detections of bifenthrin ranging from 0.0952 to 7.94 parts per billion (ppb) at the three nursery sites, and at one site that drains both residential and nursery areas. There were five detections of chlorpyrifos ranging from 0.053 to 0.172 ppb, one at a nursery site and the others from creeks that drain residential areas. Seven sites had significant mortality (above 80%) to *Ceriodaphnia dubia* in the water collected. These toxic sites drained three nurseries, two residential, and two integrated sites. The toxicity was attributed mostly to diazinon, chlorpyrifos, bifenthrin and malathion.

### 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 February 23 and 24, 2000 monitoring, and encompass results from both chemical analyses and aquatic biotoxicity testing. This memorandum summarizes results for bifenthrin, fenoxycarb, hydramethylnon, pyriproxyfen, and eight organophosphorus insecticides: chlorpyrifos, diazinon, dimethoate, fonofos, malathion, methidathion, methyl parathion, and phosmet. Only bifenthrin, fenoxycarb, hydramethylnon, pyriproxyfen, and chlorpyrifos are used in the RIFA control program. The other seven 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 2000 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 seventh 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](http://www.cdpr.ca.gov)> under Programs and Services then Red Imported Fire Ant Project.

## MATERIALS AND METHODS

### Sample and Data Collection

On February 23 and 24, 2000, surface water samples were collected at ten creeks within the Orange County treatment area (Table 1 and Figure 1). Sites A, B, I, and J were sampled on February 23; the rest of the sites were sampled on February 24. This sampling event coincided with measurable rainfall. In the three days previous to sampling, 3.28 inches of rain was measured in San Juan Canyon (southern sites) and 1.43 inches of rain was measured in Santa Ana. On the days of sampling, 1.28 inches of rain was measured in San Juan Canyon between the hours of 1000 on February 23 and 1000 on February 24 and 0.51 inches in Santa Ana on February 23. There was no measurable rainfall on February 24.

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°37'25", W 117°54'02"
D	Bonita Creek at San Diego Creek	N 33°39'00", W 117°51'48"
E	San Diego Creek at Campus Dr.	N 33°39'23", W 117°50'43"
F	Hines Channel	N 33°42'04", W 117°45'24"
G	Drain at Bee Canyon and Portola Parkway	N 33°42'37", W 117°44'13"
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.

### **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, fonofos, malathion, methidathion, methyl parathion, and phosmet. The CDFA Center for Analytical Chemistry performed all analysis using gas chromatography and a flame photometric detector for the eight 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) is 0.04 ppb for chlorpyrifos and diazinon, 0.1 ppb for fenoxycarb and pyriproxyfen, 0.2 ppb for hydramethylnon, and 0.05 ppb for the other insecticides.

## RESULTS and DISCUSSIONS

### Insecticide Concentrations

Table 2 shows chemical analysis results. A total of ten samples were analyzed for the eight organophosphorus insecticides, bifenthrin and the three RIFA insecticide baits. Chlorpyrifos was detected in five samples with concentrations ranging from 0.053 to 0.41 ppb. Diazinon was detected in all ten samples and ranged from 0.069 to 7.99 ppb. Dimethoate was detected in one sample at a concentration of 0.138 ppb. Malathion was detected in six samples with concentrations ranging from 0.07 to 2.44 ppb. Methyl parathion was detected in one sample at a concentration of 0.168 ppb. Bifenthrin was detected in four samples with concentrations ranging from 0.0952 to 1.94 ppb. There were no detections of fenoxycarb, hydramethylnon, pyriproxyfen, fonofos, methidathion, or phosmet. Bifenthrin and diazinon detections recorded at site F were collected from commercial nursery runoff, as were the bifenthrin, diazinon, and methyl parathion detections recorded at site G and the bifenthrin, chlorpyrifos, diazinon, and malathion detections at site H. Samples collected at site E in a creek downstream from sites F, G, and H showed detections of chlorpyrifos, diazinon, dimethoate, and malathion. Of the twelve insecticides tested, only chlorpyrifos, bifenthrin, fenoxycarb, hydramethylnon, and pyriproxyfen were allowed use in nurseries for treatment of fire ants to comply with U.S. Department of Agriculture 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, diazinon, and chlorpyrifos are widely available for homeowner use.

### Toxicity Data

Samples from sites A, E, F, G, H, and J were acutely toxic to *C. dubia* causing 100% mortality, and sample from site C caused 80% mortality (Table 2). All three sites (B, D, and I) that showed non-significant toxicity to *C. dubia* drain residential areas. Three of the toxic sites (F, G, and H) drain commercial nurseries; two (E and J) drain both nursery and residential, and two (A and C) drain mostly residential areas. The toxicities were attributable mostly to bifenthrin, chlorpyrifos, diazinon, and malathion. The detections of diazinon at sites F and G were above the LC<sub>50</sub> for *C. dubia* as were the detections of chlorpyrifos at sites B and J (Table 3).

Table 2. Insecticide concentrations and acute toxicity in surface water samples, February 23 and 24, 2000, Orange County, California.

Site	Concentration in pbb												% Acute Mortality <sup>1</sup>
	bifenthrin	fenoxycarb	hydramethylnon	pyriproxyfen	chlorpyrifos	diazinon	dimethoate	fonofos	malathion	methidathion	m. parathion	phosmet	<i>C. dubia</i>
A	ND <sup>2</sup>	ND	ND	ND	ND	0.293	ND	ND	0.088	ND	ND	ND	100/5 <sup>3</sup>
B	ND	ND	ND	ND	0.41	0.137	ND	ND	0.082	ND	ND	ND	30/5
C	ND	ND	ND	ND	ND	0.174	ND	ND	0.153	ND	ND	ND	80/10 <sup>3</sup>
D	ND	ND	ND	ND	ND	0.069	ND	ND	ND	ND	ND	ND	15/10
E	ND	ND	ND	ND	0.101	0.135	0.138	ND	0.07	ND	ND	ND	100/10 <sup>3</sup>
F	1.08	ND	ND	ND	ND	0.792	ND	ND	ND	ND	ND	ND	100/10 <sup>3</sup>
G	1.94	ND	ND	ND	ND	7.99	ND	ND	ND	ND	0.168	ND	100/10 <sup>3</sup>
H	0.365	ND	ND	ND	0.056	0.291	ND	ND	2.44	ND	ND	ND	100/10 <sup>3</sup>
I	ND	ND	ND	ND	0.053	0.13	ND	ND	0.073	ND	ND	ND	10/5
J	0.0952	ND	ND	ND	0.172	0.185	ND	ND	ND	ND	ND	ND	100/5 <sup>3</sup>

<sup>1</sup> Two numbers are reported for each 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> The difference in mortality between the sample and the corresponding control are significant using Wilcoxon two-sample test.

Table 3. LC<sub>50</sub>'s of insecticides (ppb) for three aquatic species and U.S. EPA fresh water quality criteria.

Pesticide	Rainbow trout <sup>1</sup>	<i>D. magna</i> <sup>1</sup>	<i>C. dubia</i>	Fresh Water Quality Criteria (Acute)
Bifenthrin	0.15	0.16	ND <sup>2</sup>	ND
Chlorpyrifos	3	1.7	0.13 <sup>3</sup>	0.083 <sup>7</sup>
Diazinon	2600	0.96	0.51 <sup>4</sup>	0.090 <sup>8</sup>
Dimethoate	6200	4700	ND	ND
Fenoxycarb	1600	400	ND	ND
Fonofos	50	1	ND	ND
Hydramethylnon	160	1140	ND	ND
Malathion	170	1.8	ND	ND
Methidathion	10	3	2.2 <sup>9</sup>	ND
Methyl parathion	2700	7.3	ND	ND
Phosmet	230	8.5	ND	ND
Pyriproxyfen	>325 <sup>5</sup>	400 <sup>6</sup>	ND	ND

<sup>1</sup> Data from Tomlin, C.D.S., 1997

<sup>2</sup> ND= No Data

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

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

<sup>5</sup> Data from Bowman, Jane H., 1989

<sup>6</sup> Data from Burgess, David, 1989

<sup>7</sup> Data from U.S. EPA, 1994

<sup>8</sup> Proposed U.S. EPA data

<sup>9</sup> Data from Menconi and Siepmann, 1994

### Environmental Measurements

Table 4 presents the data for DO, temperature, EC, ammonia, alkalinity, and hardness. Water temperature ranged from 10.1 to 18.0° C; DO ranged from 9.20 to 13.48 mg/L; EC ranged from 92 to 1599 µS/cm; ammonia was between <1 and 13 ppb NH<sub>3</sub>; alkalinity ranged from 26 to 148 mg/L CaCO<sub>3</sub>; and hardness ranged from 30 to 550 mg/L CaCO<sub>3</sub>. 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, and water temperature no higher than 78°F (25.5°C). 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 pH at site C was above the maximum guideline pH. The three sites with ammonia above <1 ppb are in the Santa Ana River Basin.

Table 4. Water quality measurements at sampling sites, February 2000, Orange County, California.

Site	Temperature (°C)	pH	Dissolved Oxygen (mg/L)	Electroconductivity (µS/cm)	Ammonia ppb NH <sub>3</sub>	Alkalinity mg/L CaCO <sub>3</sub>	Hardness mg/L CaCO <sub>3</sub>
A	14.0	8.22	9.60	145	<1	38	40
B	14.3	7.97	9.20	92	<1	26	30
C	14.2	9.10	13.48	1260	<1	100	320
D	10.1	7.84	9.37	1412	<1	148	360
E	11.1	7.78	9.83	879	<1	96	230
F	12.6	7.35	9.82	1036	3.53	80	350
G	18.0	8.09	9.47	1467	13	124	510
H	12.9	7.50	10.58	1599	5.96	40	550
I	13.1	8.18	10.45	980	<1	80	276
J	12.3	8.04	10.27	226	<1	44	82





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Precipitation data obtained from The University of California Statewide Integrated Pest Management Project, California Weather Databases. [www.ipm.ucdavis.edu/WEATHER/](http://www.ipm.ucdavis.edu/WEATHER/)