



# 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,  
JUNE 2000 (STUDY 183)

### SUMMARY

During June 2000, surface water samples were collected from ten sites in Orange County, California. At one site a filter strip was added to the waterway as part of a mitigation study so samples were collected at the entrance and exit to the filter strip. At the time of this sampling, plants had not yet been planted in the filter strip. Samples from all sites showed no detects of fenoxycarb, hydramethylnon, pyriproxyfen, and chlorpyrifos. There were three detections of bifenthrin with concentrations ranging from 0.394 to 0.781 parts per billion (ppb) at three nursery sites, including the filter strip samples. Three sites had significant mortality to *Ceriodaphnia dubia* in the water collected. These toxic sites drained two nurseries and one residential site. The toxicities at the nurseries could be attributed to bifenthrin, while the toxicity at the residential site is attributed to diazinon and other unknown toxins.

### 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 June 13, 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 tenth 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 June 13, 2000, surface water samples were collected at nine creeks within the Orange County treatment area (Table 1 and Figure 1). Site H was not sampled because of insufficient water. Site G was sampled at two different points on the waterway. A 180-foot filter strip was added to the waterway as part of a mitigation study at a commercial nursery so samples were collected at the entrance (site G1) and exit (site G2) to the filter strip. At the time of this sampling, plants had not yet been planted in the filter strip. 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	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.

### **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) 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.

## **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. Diazinon was detected in eight samples and ranged from 0.072 to 0.215 ppb. Methidathion was detected in two samples with concentrations of 0.074 and 0.087 ppb, respectively. Bifenthrin was detected in three samples with concentrations ranging from 0.394 to 0.781 ppb. There were no detections of fenoxycarb, hydramethylnon, pyriproxyfen, chlorpyrifos, dimethoate, fonofos, malathion, methyl parathion, or phosmet. Site G1 had detections of bifenthrin and diazinon while site G2, water exiting 180-foot filter strip, had detections of bifenthrin, diazinon, and methidathion. The G2 sample contained a small amount of street runoff. The street runoff comes from a broken pipe by a landfill above the nursery. The additional runoff from the pipe may have contributed the methidathion to the sample. The bifenthrin detection recorded at site F and the bifenthrin, diazinon, and methidathion detections at site G were both collected at commercial nurseries. Samples collected at integrated site E, in a creek downstream from sites F and G, showed a detection of diazinon. Sites C and D, which mainly drain urban areas, both had detections of diazinon; site D had an additional detection of methidathion. 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.

Table 2. Insecticide concentrations and acute toxicity in surface water samples, June 13, 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	0.076	ND	ND	ND	ND	ND	ND	ND	0/0
B	ND	ND	ND	ND	ND	0.072	ND	ND	ND	ND	ND	ND	ND	0/0
C	ND	ND	ND	ND	ND	0.144	ND	ND	ND	ND	ND	ND	ND	25/0 <sup>3</sup>
D	ND	ND	ND	ND	ND	0.095	ND	ND	ND	0.074	ND	ND	ND	0/0
E	ND	ND	ND	ND	ND	0.074	ND	ND	ND	ND	ND	ND	ND	20/0
F	0.394	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	100/0 <sup>3</sup>
G1	0.781	ND	ND	ND	ND	0.215	ND	ND	ND	ND	ND	ND	ND	NS
G2	0.448	ND	ND	ND	ND	0.086	ND	ND	ND	0.087	ND	ND	ND	100/0 <sup>3</sup>
H	NS <sup>4</sup>	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS
I	ND	ND	ND	ND	ND	ND	ND	0.041	ND	ND	ND	ND	ND	0/0
J	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	0/0

<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.

<sup>4</sup> NS = not sampled

## Toxicity Data

Samples from sites C, F, and G2 were acutely toxic to *C. dubia* causing 25, 100, and 100% mortality, respectively (Table 2). The one site (E) that showed non-significant toxicity to *C. dubia* drains an integrated area. Site C drains a residential area and contained residues of diazinon; Site F drains a commercial nursery and contained residues of bifenthrin; Site G drains a commercial nursery and contained residues of bifenthrin, diazinon, and methidathion. All detections of diazinon and methidathion were below the LC<sub>50</sub> for *C. dubia*; the detections of bifenthrin at sites F and G were above the LC<sub>50</sub> for *D. magna* (Table 3). The toxicities at sites F and G could be attributed to bifenthrin, while the toxicity at site C could be attributed to diazinon.

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	NA <sup>2</sup>	NA
Chlorpyrifos	3	1.7	0.13 <sup>3</sup>	0.083 <sup>4</sup>
Diazinon	2600	0.96	0.51 <sup>5</sup>	0.090 <sup>6</sup>
Dimethoate	6200	4700	NA	NA
Fenoxycarb	1600	400	NA	NA
Fonofos	50	1	NA	NA
Hydramethylnon	160	1140	NA	NA
Malathion	170	1.8	1.14 <sup>7</sup> - 2.12 <sup>8</sup>	NA
Methidathion	10	3	2.2 <sup>9</sup>	NA
Methyl parathion	2700	7.3	NA	NA
Phosmet	230	8.5	NA	NA
Pyriproxyfen	>325 <sup>10</sup>	400 <sup>11</sup>	NA	NA

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

<sup>2</sup> NA= Not Available

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

<sup>4</sup> Data from U.S. EPA, 1994

<sup>5</sup> Data from Menconi and Cox, 1994

<sup>6</sup> Proposed U.S. EPA data

<sup>7</sup> Data from Nelson and Roline, 1998.

<sup>8</sup> Data from Ankley et al., 1991

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

<sup>10</sup> Data from Bowman, Jane H., 1989

<sup>11</sup> Data from Burgess, David, 1989

**Environmental Measurements**

Table 4 presents the data for DO, temperature, pH, EC, ammonia, alkalinity, and hardness. Water temperature ranged from 19.9 to 34.1° C; DO ranged from 6.11 to 17.75 mg/L; pH ranged between 7.8 to 10.1; EC ranged from 496 to 3160 µS/cm; ammonia was <1 ppb NH<sub>3</sub> for all samples read; alkalinity ranged from 178 to 292 mg/L CaCO<sub>3</sub>; and hardness ranged from 140 to 388 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 sites A, C, and E were above the maximum guideline as were the water temperatures at sites A, B, C, E, F, G1, and G2.

Table 4. Water quality measurements at sampling sites, June 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	32.2	9.0	17.71	2200	<1	188	254
B	31.3	8.6	13.13	1567	<1	232	292
C	29.9	10.1	NT	496	<1	222	280
D	19.9	8.1	6.85	3034	<1	292	388
E	26.3	8.7	13.38	3081	<1	178	138
F	32.5	8.1	6.65	3160	NR	258	140
G1	34.1	7.9	NT	2524	NS	NS	NS
G2	31.2	7.8	6.11	2566	NR	186	142
H	NS	NS	NS	NS	NS	NS	NS
I	25.1	8.0	10.5	2662	<1	208	140
J	20.3	8.0	8.92	955	<1	180	136

NT= Not taken

NR= No reading available



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