



# Department of Pesticide Regulation



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## MEMORANDUM

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SUBJECT: **REVISED-** PRELIMINARY RESULTS OF PESTICIDE ANALYSIS AND  
ACUTE TOXICITY TESTING OF MONTHLY SURFACE WATER  
MONITORING FOR THE RED IMPORTED FIRE ANT PROJECT IN  
ORANGE COUNTY, MAY 2000 (STUDY 183)

### SUMMARY

During May 2000, surface water samples collected from nine sites in Orange County, California, showed no detects of fenoxycarb, hydramethylnon and pyriproxyfen. There were two detections of bifenthrin with concentrations of 0.499 and 0.977 parts per billion (ppb) at two nursery sites. There was one detection of chlorpyrifos with a concentration of 0.057 ppb. Three sites had significant mortality (100%) to *Ceriodaphnia dubia* in the water collected. These toxic sites drained one nursery, one residential site, and one integrated site. The toxicity at the nursery and residential site is due to multiple chemicals. The cause of toxicity at San Juan Creek (integrated site) is unknown. **Backup samples were analyzed for organophosphates at the Hines at weir site. The backup sample had a detection of malathion that was not detected in the original sample. Sample results have been modified in this memo to address this change.**

### 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 May 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 ninth 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 May 24, 2000, surface water samples were collected at nine creeks within the Orange County treatment area (Table 1 and Figure 1) and one rinse blank. Site H was not sampled because of insufficient water. This sampling event did not coincided 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 a 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 six samples and ranged from 0.075 to 0.315 ppb. Chlorpyrifos and methidathion were detected in one sample each with concentrations of 0.057 and 0.087 ppb, respectively. Malathion was detected in two samples with concentrations of 0.112 and 0.192 ppb. Fonofos was detected in four samples with concentrations ranging from 0.05 to 0.218 ppb. Methyl parathion was detected in two samples with concentrations of 0.088 and 0.119 ppb. Bifenthrin was detected in two samples with concentrations of 0.499 and 0.977 ppb. There were no detections of fenoxycarb, hydramethylnon, pyriproxyfen, dimethoate, or phosmet. Site F had a detection of bifenthrin and malathion while site G had detections of bifenthrin, chlorpyrifos, diazinon, and malathion; both samples were collected from commercial nurseries. Samples collected at an integrated site, site E, in a creek downstream from sites F and G showed detections of diazinon and fonofos. Sites C and D, which mainly drain urban areas, had detections of diazinon, fonofos, and methyl parathion; site C 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, May 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	0.19	ND	ND	ND	ND	ND	ND	15/5
B	ND	ND	ND	ND	ND	0.119	ND	ND	ND	ND	ND	ND	20/5
C	ND	ND	ND	ND	ND	0.315	ND	0.218	ND	0.087	0.119	ND	100/5 <sup>3</sup>
D	ND	ND	ND	ND	ND	0.123	ND	0.089	ND	ND	0.088	ND	20/5
E	ND	ND	ND	ND	ND	0.075	ND	0.06	ND	ND	ND	ND	5/5
F	0.499	ND	ND	ND	ND	ND	ND	ND	0.112	ND	ND	ND	10/5
G	0.977	ND	ND	ND	0.057	0.31	ND	ND	0.192	ND	ND	ND	100/5 <sup>3</sup>
H	NS <sup>4</sup>	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS
I	ND	ND	ND	ND	ND	ND	ND	0.05	ND	ND	ND	ND	100/5 <sup>3</sup>
J	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	20/5
RB <sup>5</sup>	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	NS

<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

<sup>5</sup> RB = rinse blank

### Toxicity Data

Samples from sites C, G, and I were acutely toxic to *C. dubia* causing 100% mortality (Table 2). The five sites (A, B, D, E, F, and J) that showed non-significant toxicity to *C. dubia* drain residential areas, integrated sites, and a commercial nursery. Site C drains a residential area and contained residues of diazinon, fonofos, methidathion, and methyl parathion; site G drains a commercial nursery and contained residues of bifenthrin, chlorpyrifos, diazinon, and malathion; and site I drains an integrated area and contained residues of fonofos. The toxicities could not be

attributed to any specific chemical. All detections of diazinon, chlorpyrifos, malathion, 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).

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 18.0 to 23.7° C; DO ranged from 3.45 to 8.87 mg/L; pH ranged between 7.9 to 8.7; EC ranged from 957 to 3103 µS/cm; ammonia was <1 ppb NH<sub>3</sub> for all samples; alkalinity ranged from 96 to 360 mg/L CaCO<sub>3</sub>; and hardness ranged from 300 to 900 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 F was above the maximum guideline and the DO at site B was below the minimum guideline.

Table 4. Water quality measurements at sampling sites, May 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	19.3	8.2	6.9	1922	<1	308	364
B	20.0	7.9	3.45	1587	<1	310	396
C	23.7	8	8.01	1051	<1	140	300
D	18.0	8.2	6.8	3103	<1	360	750
E	22.1	8.5	8.7	2866	<1	224	756
F	21.4	8.7	7.09	1914	<1	232	900
G	20.7	8.4	7.18	1570	<1	150	500
H	NS	NS	NS	NS	NS	NS	NS
I	19.3	8.2	8.87	2657	<1	96	780
J	18.3	8	8.12	957	<1	176	336

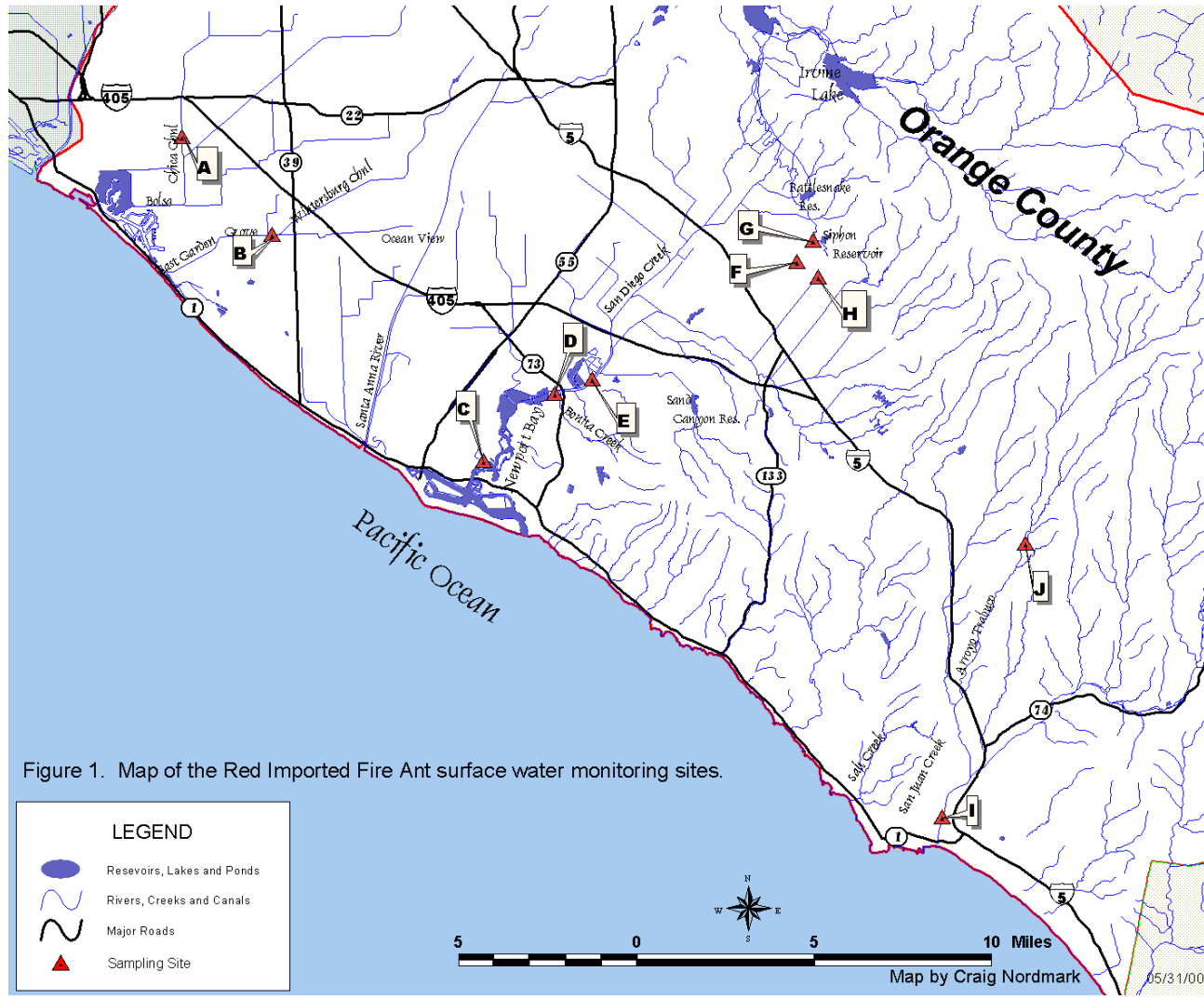


Figure 1. Map of the Red Imported Fire Ant surface water monitoring sites.



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