



# Department of Pesticide Regulation



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Director

## MEMORANDUM

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DATE: December 22, 2000

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, SEPTEMBER 2000 (STUDY 183)

### SUMMARY

During September 2000, surface water samples were collected from eight sites in Orange County, California. At one site a filter strip and settling pond were added to the waterway as part of a mitigation study, samples were collected twice at the inflow and outflow of the filter strip and once at the two inflow and one outflow of the settling pond. At the time of this sampling, Canna had been planted in approximately one half of the filter strip. Monthly surface water samples showed no detects of fenoxycarb, hydramethylnon, pyriproxyfen, chlorpyrifos, and dimethoate. There were two detections of bifenthrin with concentrations of 0.224 and 0.574 parts per billion (ppb) at the two commercial nursery sites. Toxicity was tested at one integrated site. This site was not significantly toxic to *Ceriodaphnia dubia* in the water collected. Mitigation samples consisted of water samples and sediment samples taken from the filter strip and settling pond. Surface water samples showed no detects of fenoxycarb, hydramethylnon, pyriproxyfen, dimethoate, and methidathion. Bifenthrin was detected in all mitigation study samples. Four toxicity samples were taken at the inflow and outflow of the filter strip. Significant toxicity to *Ceriodaphnia dubia* in three samples can be attributed to bifenthrin and diazinon. Bifenthrin and chlorpyrifos were detected in all sediment 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 September 6 and 7, 2000 monitoring, and encompass results from both chemical



analyses and aquatic biotoxicity testing. 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 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 thirteenth 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 September 6 and 7, 2000, surface water samples were collected at eight sites 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 the outflow of the vegetative buffer strip (see mitigation sampling). Toxicity samples were collected at sites E and G. 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.

### **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). A concrete lined ditch approximately 160 yards long and three and a half feet deep was split down the middle with sandbags running the length to create a vegetative filter strip and an overflow channel. The filter strip consists of three successive settling basins planted with *Canna x 'Tropicana'*. Water and toxicity samples are collected at the inlet and outlet of the filter strip and sediment samples are collected from the three sediment basins. During the September 7 sampling, water and toxicity samples were taken twice approximately four hours apart. At the time of this sampling *Canna* had been planted in approximately half of the buffer strip. Sediment samples were collected in each of the three sediment basins approximately 10 feet from the outlet of each basin. A settling pond has also been installed at el modeno Gardens. The settling pond has two inflows, west and north, and one outflow that drain into the concrete ditch of the vegetative buffer strip. Samples collected at the settling pond consist of two inflow and one outflow water samples as well as one sediment sample from the eastern edge of the pond outlet.

Water samples are collected using the technique described previously. Sediment samples are collected by submerging a 500-mL polycarbonate container and scooping up the sediment. 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, 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 samples were 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**

A total of fifteen water samples were analyzed for the five organophosphorus insecticides, bifenthrin and the three RIFA insecticide baits. Monthly surface water samples (Table 2) had no detectable residues of fenoxycarb, hydramethylnon, pyriproxyfen, chlorpyrifos, and dimethoate. Bifenthrin was detected in two samples taken from commercial nurseries at 0.574 and 0.224 ppb. Diazinon was detected in six samples and ranged from 0.087 to 0.215 ppb. Malathion and methidathion were detected in one sample each at 0.102 and 0.168 ppb, respectively. Site F drains a commercial nursery and had a detection of bifenthrin. Site G also drains a commercial nursery had detections of bifenthrin, diazinon, and malathion. Samples collected at integrated site E, in a creek downstream from sites F and G, showed a detection of diazinon and

dimethoate. 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'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, diazinon, and chlorpyrifos are widely available for homeowner use.

Seven surface water samples (Table 3) were taken as part of a mitigation study at site G. Bifenthrin was detected in all samples ranging from 0.196 to 3.38 ppb. Chlorpyrifos was detected in three samples ranging from 0.044 to 0.075 ppb. Diazinon was detected in five samples ranging from 0.066 to 0.106 ppb. Malathion was detected in six samples ranging from 0.102 to 0.608 ppb. There were no detects of fenoxycarb, hydramethylnon, pyriproxyfen, dimethoate, and methidathion. There was a general trend of declining concentrations of bifenthrin, chlorpyrifos and malathion as the water and sediment passed through the filter strip. Sediment samples were also taken from the three sediment basins of the buffer strip and from the sediment pond. Diazinon was not detected in any samples. Bifenthrin was detected in all samples ranging from 28 ppb in the sediment pond to 277 ppb in basin 3 at the outflow of the buffer strip. Chlorpyrifos was also detected in all samples ranging from 16 to 25 ppb.

Table 2. Insecticide concentrations and acute toxicity in monthly surface water samples, September 2000, Orange County, California.

Site	Concentration in pbb									% Acute Mortality <sup>1</sup>
	bifenthrin	fenoxycarb	hydramethylnon	pyriproxyfen	chlorpyrifos	diazinon	dimethoate	malathion	methidathion	<i>C. dubia</i>
A	ND <sup>2</sup>	ND	ND	ND	ND	0.095	ND	ND	ND	NS <sup>3</sup>
B	ND	ND	ND	ND	ND	0.118	ND	ND	ND	NS
C	ND	ND	ND	ND	ND	0.215	ND	ND	ND	NS
D	ND	ND	ND	ND	ND	0.104	ND	ND	0.168	NS
E	ND	ND	ND	ND	ND	0.102	ND	ND	ND	10/5
F	0.574	ND	ND	ND	ND	ND	ND	ND	ND	NS
G	0.224	ND	ND	ND	ND	0.087	ND	0.102	ND	30/5
H	NW <sup>4</sup>	NW	NW	NW	NW	NW	NW	NW	NW	NS
I	ND	ND	ND	ND	ND	ND	ND	ND	ND	NS
J	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> NS = not sampled

<sup>4</sup> NW= no water discharged

Table 3. Insecticide concentrations and acute toxicity in mitigation samples, September 2000, Orange County, California.

Location	Concentration in ppb									% Acute Mortality <sup>1</sup>
	bifenthrin	fenoxycarb	hydramethylnon	pyriproxyfen	chlorpyrifos	diazinon	dimethoate	malathion	methidathion	
<u>Surface Water Samples</u>										
Filter strip inflow I <sup>2</sup>	0.196	ND <sup>3</sup>	ND	ND	ND	0.076	ND	0.119	ND	70/5 <sup>4</sup>
Filter strip inflow II	0.438	ND	ND	ND	0.075	0.066	ND	0.608	ND	100/5 <sup>4</sup>
Filter strip outflow I	0.224	ND	ND	ND	ND	0.087	ND	0.102	ND	30/5
Filter strip outflow II	0.199	ND	ND	ND	ND	0.106	ND	0.434	ND	100/5 <sup>4</sup>
Pond inflow-west	0.367	ND	ND	ND	ND	ND	ND	ND	ND	NS <sup>5</sup>
Pond inflow-north	3.38	ND	ND	ND	0.108	ND	ND	0.441	ND	NS
Pond outflow	0.683	ND	ND	ND	0.044	0.084	ND	0.417	ND	NS
<u>Sediment samples</u>										
Basin 1	187				17	ND				
Basin 2	168				16	ND				
Basin 3	277				18	ND				
Sediment pond	28				25	ND				

<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> Two sets of filter strip samples were taken; first set of data is from first sampling.

<sup>3</sup> ND = none detected at the reporting limit for that chemical.

<sup>4</sup> The difference in mortality between the sample and the corresponding control are significant using Wilcoxon two-sample test.

<sup>5</sup> NS = not sampled

### 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 10 % 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 4). Toxicity samples were also taken from the filter strip inflow and outflow at both of the sampling intervals. Three of the samples were acutely toxic to *C. dubia* with 70 and 100% toxicity from the two inflow

samples and 30 and 100% toxicity from the outflow samples. The bifenthrin detections were above the LC<sub>50</sub> for *D. magna* for all samples as were the diazinon detections for *C. dubia*.

Table 4. 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
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
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 5 presents the data for DO, temperature, pH, and EC. Ammonia, alkalinity, and hardness are only reported for sites E, G, and the inflow and outflow of the filter strip since these measurements are taken with the toxicity tests. Water temperature ranged from 17.1 to 33.1° C; pH ranged between 7.8 to 9.7; DO ranged from 6.27 to 14.86 mg/L; EC ranged from 688 to 3510 µS/cm; ammonia ranged between 0.11 and 4.68 mg/L NH<sub>3</sub>; alkalinity ranged between 144 and 236 mg/L CaCO<sub>3</sub>; and hardness ranged between 84 and 128 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: 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 temperature at sites C, F, filter strip inflow, outflow, and pond inflow-north were above the maximum guideline as were the pH at site C.

Table 5. Water quality measurements at sampling sites, September 2000, 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>
A	24.9	8.5	12.02	1905	NR	NR	NR
B	23.8	8.2	10.12	1393	NR	NR	NR
C	33.1	9.7	14.86	688	NR	NR	NR
D	19.2	8.1	7.45	3019	NR	NR	NR
E	21.2	8.1	7.68	3085	0.11	236	84
F	27.1	8.4	6.27	3510	NR	NR	NR
G	17.1	8.1	6.36	2025	1.36	158	128
H	NW	NW	NW	NW	NW	NW	NW
I	22.0	8.2	13.26	2660	NR	NR	NR
J	20.1	8.2	10.06	817	NR	NR	NR
Filter strip inflow I	17.4	8.4	6.85	2019	4.68	154	120
Filter strip outflow II	17.1	8.1	6.36	2025	1.36	158	128
Filter strip inflow I	26.6	7.9	7.08	1707	2.46	146	112
Filter strip outflow II	27.5	7.8	7.95	1972	2.16	144	122
Pond inflow-north	26.6	8.0	NT	2447	NR	NR	NR
Pond inflow-west	25.1	8.2	NT	2293	NR	NR	NR
Pond outflow	24.2	8.2	NT	2225	NR	NR	NR

NW= No water discharged; NT= Not taken

NR= No reading available

## References

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December 22, 2000  
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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/)

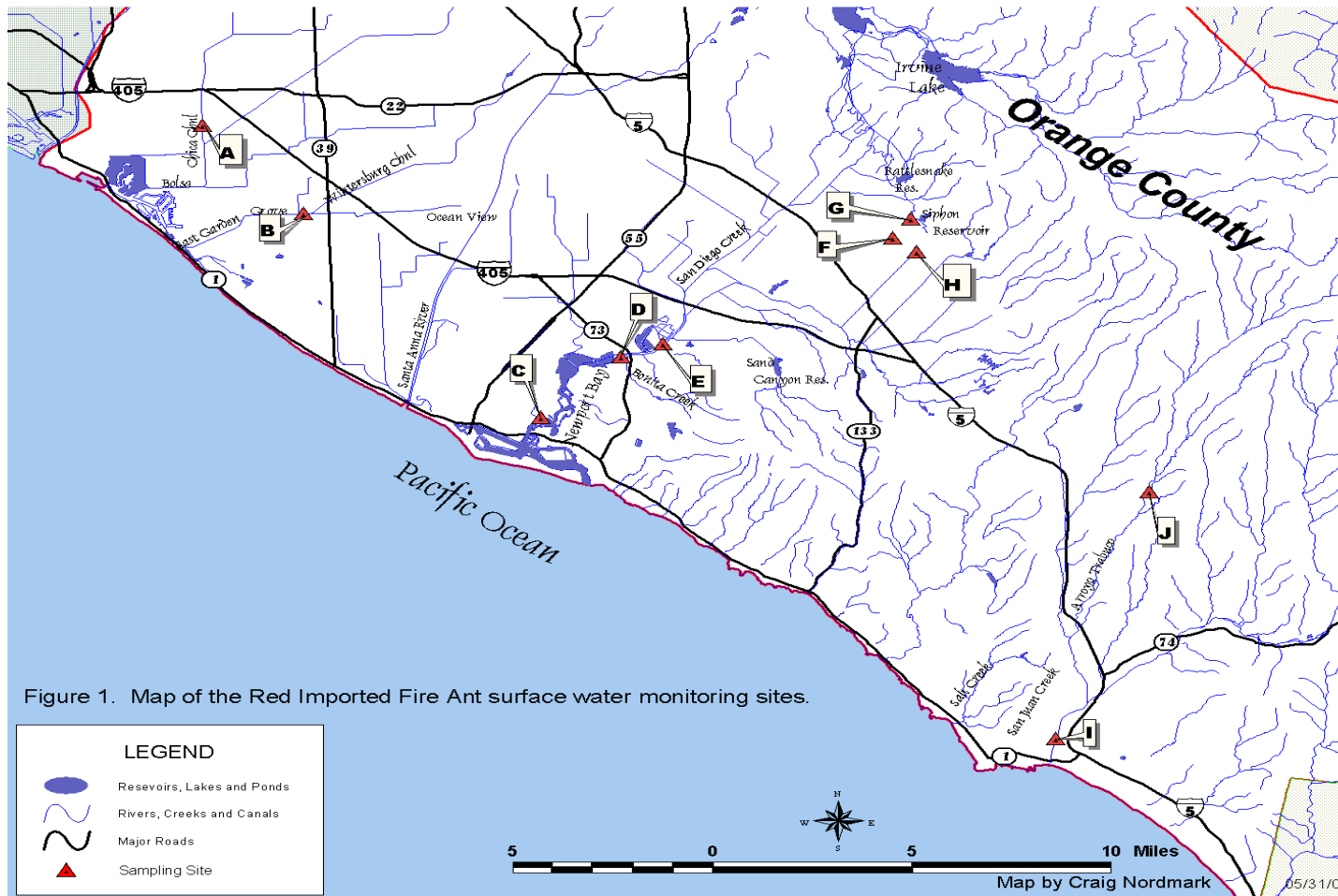


Figure 1. Map of the Red Imported Fire Ant surface water monitoring sites.