



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, MARCH 2001 (STUDY 183)

SUMMARY

During March 2001, surface water samples were collected from three sites in Orange County, California. Water samples showed no detects of fenoxycarb, hydramethylnon, pyriproxyfen, dimethoate, and methidathion. Bifenthrin was detected in two samples at 0.495 and 0.778 parts per billion (ppb) at nursery sites F and G, respectively. Chlorpyrifos was detected in one sample at 0.06 ppb. Diazinon was detected in two samples at 0.059 and 0.06 ppb at sites F and E, respectively. Malathion was detected in one sample of nursery runoff at 0.07 ppb. Toxicity was tested at San Diego Creek at Campus Drive, an integrated site. This site was not significantly toxic (5% mortality) to *Ceriodaphnia dubia* in the water collected. Additional water and sediment samples were collected from a mitigation filter strip planted with *Canna* to mitigate offsite movement of insecticides and nitrates. Bifenthrin and chlorpyrifos were detected in all water samples with a general trend of declining concentrations as the water passed through the filter strip. Sediment samples were positive for bifenthrin and chlorpyrifos with detections ranging from 776 to 1470 ppb and 27 to 80 ppb, respectively.

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 March 20, 2001 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 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 nineteenth 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>.

MATERIALS AND METHODS

Sample and Data Collection

On March 21, 2001, surface water samples were collected at three sites, 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. Site G was sampled 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. During the March 20 sampling, two water samples were split from the same water. At the time of this sampling *Canna* had been planted in seven of the settling basins; the two settling basins closest to the outflow had been harvested. Sediment samples were taken from two of the filter strip basins approximately 10 feet from the outlet of the basin.

Water samples are collected and transported using the technique described previously. Sediment samples are collected by submerging a 500-mL polycarbonate container and scooping up the sediment and stored 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 CDFR 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 ⁶³Ni 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 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.

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

Site	Concentration (pbb)									% Acute Mortality ¹
	bifenthrin	fenoxycarb	hydramethylnon	pyriproxyfen	chlorpyrifos	diazinon	dimethoate	malathion	methidathion	<i>C. dubia</i>
E	ND ²	ND	ND	ND	ND	0.06	ND	ND	ND	5/0
F	0.495	ND	ND	ND	ND	0.059	ND	0.07	ND	NS ³
G	0.778	ND	ND	ND	0.06	ND	ND	ND	ND	NS
RB	ND	ND	ND	ND	ND	ND	ND	ND	ND	NS

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

² ND = none detected at the reporting limit for that chemical.

³ NS = no sample collected

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

Location	Concentration (ppb)								
	bifenthrin	fenoxycarb	hydramethylnon	pyriproxyfen	chlorpyrifos	diazinon	dimethoate	malathion	methidathion
<u>Surface Water Samples</u>									
Filter strip inflow I ¹	2.89	ND ²	ND	ND	0.436	ND	ND	ND	ND
Filter strip outflow I	0.778	ND	ND	ND	0.06	ND	ND	ND	ND
Filter strip inflow II	2.88	ND	ND	ND	0.402	ND	ND	ND	ND
Filter strip outflow II	0.833	ND	ND	ND	0.066	ND	ND	ND	ND
<u>Sediment Samples</u>									
Basin #2	776				49	ND			
Basin #2	927				27	ND			
Basin #7	1470				80	ND			
Basin #7	1110				43	ND			

¹ Two sets of filter strip samples were taken; first set of data is from first sampling.

² ND = none detected at the reporting limit for that chemical.

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 5% mortality (Table 2). Site E drains an integrated site and had a detection of diazinon below the LC₅₀ for *C. dubia* (Table 4).

Table 4. LC₅₀'s of insecticides (ppb) for three aquatic species.¹

Pesticide	Rainbow trout	<i>D. magna</i>	<i>C. dubia</i>
Bifenthrin	0.15	1.6	0.078 ²
Chlorpyrifos	10	0.1	0.13 ³
Diazinon	3200	0.96	0.51 ⁴
Dimethoate	8500	2500	NA
Fenoxycarb	1600	400	NA
Hydramethylnon	160	1140	NA
Malathion	68	1.0	1.14 ⁵ - 2.12 ⁶
Methidathion	10.5	7.2	2.2
Pyriproxyfen	>325	400	NA

¹ Data from CDPR, 2000.

² Data from CDFG, 2000.

³ Data from Menconi and Paul, 1994

⁴ Data from Menconi and Cox, 1994

⁵ Data from Nelson and Roline, 1998

⁶ Data from Ankley et al., 1991

Environmental Measurements

Table 5 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 temperature at site F was above the maximum guideline.

Table 5. Water quality measurements at sampling sites, March 2001, Orange County, California.

Site	Temperature (°C)	pH	Dissolved Oxygen (mg/L)	Electroconductivity (µS/cm)	Ammonia mg/L	Alkalinity mg/L CaCO ₃	Hardness mg/L CaCO ₃
E	19.6	7.8	11.13	3168	NR	214	788
F	28.4	7.6	2878	5.48	NT	NT	NT
G	22.6	7.6	9.69	2618	NT	NT	NT
Filter strip inflow	18.2	7.6	9.71	2064	NT	NT	NT
Filter strip outflow	22.6	7.6	9.69	2618	NT	NT	NT

NT= Not taken

NR= No reading available

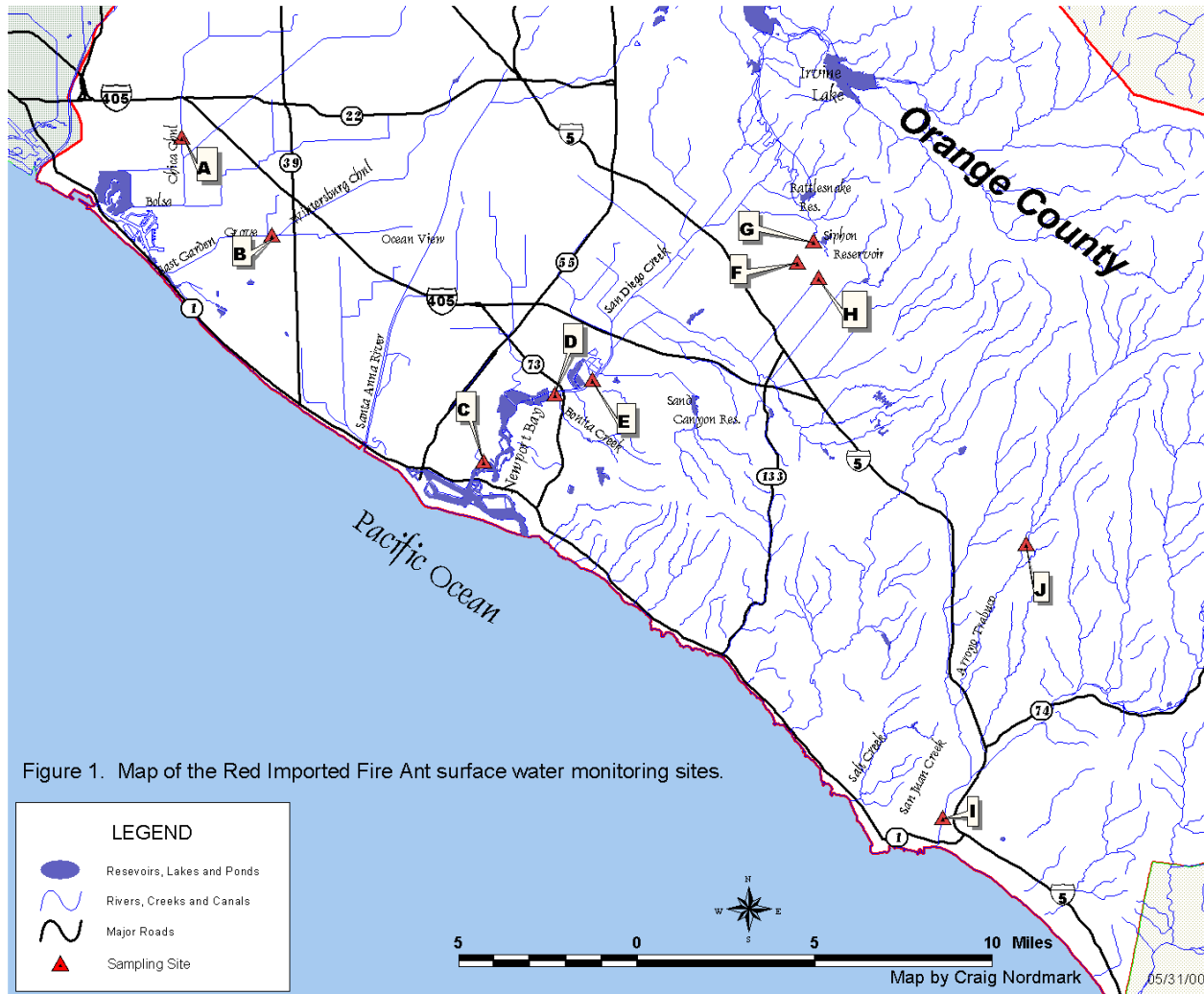


Figure 1. Map of the Red Imported Fire Ant surface water monitoring sites.

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