



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.
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

DATE: July 6, 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, APRIL 2000 (STUDY 183)

SUMMARY OF RED IMPORTED FIRE ANT (RIFA) COMPOUNDS

During April 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 0.467 and 0.673 parts per billion (ppb) at two nursery sites. There was one detection of chlorpyrifos with a concentration of 0.062 ppb. Four sites had significant mortality (100%) to *Ceriodaphnia dubia* in the water collected. These toxic sites drained two nurseries and two integrated sites. The toxicity could be attributed to diazinon and bifenthrin.

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 RIFA control project. Data included here are from the April 19, 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 multi-residue 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> under Programs and Services then Red Imported Fire Ant Project.

MATERIALS AND METHODS

Sample and Data Collection

On April 19, 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 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°37'25", 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) 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 0.077 to 2.32 ppb. Chlorpyrifos and malathion were detected in one sample each with concentrations of 0.062 and 0.071 ppb, respectively. Dimethoate was detected in two samples with concentrations of 0.132 and 0.197 ppb. Fonofos

John S. Sanders, Ph.D.
July 6, 2000
Page 4

was detected in three samples with concentrations ranging from 0.067 to 0.082 ppb. Bifenthrin was detected in two samples with concentrations of 0.467 and 0.673 ppb. There were no detections of fenoxycarb, hydramethylnon, pyriproxyfen, methidathion, methyl parathion, or phosmet. Bifenthrin and diazinon detections recorded at sites F and G were collected from commercial nursery runoff. Samples collected at an integrated site, site E, in a creek downstream from sites F and G showed detections of chlorpyrifos, diazinon, dimethoate, fonofos, and malathion. Sites A and B, which mainly drain urban areas, had detections of diazinon and fonofos. 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, April 19, 2000, Orange County, California.

Site	Concentration in pbb												% Acute Mortality ¹
	bifenthrin	fenoxycarb	hydramethylnon	pyriproxyfen	chlorpyrifos	diazinon	dimethoate	fonofos	malathion	methidathion	m. parathion	phosmet	<i>C. dubia</i>
A	ND ²	ND	ND	ND	ND	0.377	ND	0.067	ND	ND	ND	ND	100/0 ³
B	ND	ND	ND	ND	ND	0.104	ND	0.082	ND	ND	ND	ND	0/0
C	ND	ND	ND	ND	ND	0.097	ND	ND	ND	ND	ND	ND	5/0
D	ND	ND	ND	ND	ND	0.077	ND	ND	ND	ND	ND	ND	5/0
E	ND	ND	ND	ND	0.062	0.197	0.197	0.073	0.071	ND	ND	ND	100/0 ³
F	0.673	ND	ND	ND	ND	0.323	ND	ND	ND	ND	ND	ND	100/0 ³
G	0.467	ND	ND	ND	ND	2.32	ND	ND	ND	ND	ND	ND	100/0 ³
H	NS ⁴	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS
I	ND	ND	ND	ND	ND	0.191	0.132	ND	ND	ND	ND	ND	0/0
J	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	0/0
RB ⁵	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	NS

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

⁴ NS = not sampled

⁵ RB = rinse blank

Toxicity Data

Samples from sites A, E, F and G were acutely toxic to *C. dubia* causing 100% mortality (Table 2). The five sites (B, C, D, I, and J) that showed non-significant toxicity to *C. dubia* drain both residential areas and integrated sites. Sites F and G drain commercial nurseries and sites A and E drain both residential areas and integrated waters. The toxicities were attributable mostly to bifenthrin and diazinon. All detections of diazinon were below the LC₅₀ for *C. dubia* except

the detection at site G; the detections of bifenthrin at sites F and G were above the LC₅₀ for *D. magna* (Table 3). The detections of chlorpyrifos and malathion at site E were both below the LC₅₀ for *C. dubia* (Table 3).

Table 3. LC₅₀'s of insecticides (ppb) for three aquatic species and U.S. EPA fresh water quality criteria.

Pesticide	Rainbow trout ¹	<i>D. magna</i> ¹	<i>C. dubia</i>	Fresh Water Quality Criteria (Acute)
Bifenthrin	0.15	0.16	ND ²	ND
Chlorpyrifos	3	1.7	0.13 ³	0.083 ⁴
Diazinon	2600	0.96	0.51 ⁵	0.090 ⁶
Dimethoate	6200	4700	ND	ND
Fenoxycarb	1600	400	ND	ND
Fonofos	50	1	ND	ND
Hydramethylnon	160	1140	ND	ND
Malathion	170	1.8	1.14 ⁷ - 2.12 ⁸	ND
Methodathion	10	3	2.2 ⁹	ND
Methyl parathion	2700	7.3	ND	ND
Phosmet	230	8.5	ND	ND
Pyriproxyfen	>325 ¹⁰	400 ¹¹	ND	ND

¹ Data from Tomlin, C.D.S., 1997

² ND= No Data

³ Data from Menconi and Paul, 1994

⁴ Data from U.S. EPA, 1994

⁵ Data from Menconi and Cox, 1994

⁶ Proposed U.S. EPA data

⁷ Data from Nelson and Roline, 1998

⁸ Data from Ankley et al., 1991

⁹ Data from Menconi and Siepmann, 1994

¹⁰ Data from Bowman, Jane H., 1989

¹¹ 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 15.3 to 28.1° C; DO ranged from 5.03 to 9.03 mg/L; pH ranged between 7.5 and 10.2; EC ranged from 439 to 1838 µS/cm; ammonia was between <1 and 3.34 ppb NH₃; alkalinity ranged from 58 to 224 mg/L CaCO₃; and hardness ranged from 58 to 600 mg/L CaCO₃. 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 C and G were above the maximum guideline as were the water temperatures at sites F and G. The one site with ammonia above <1 ppb is in the Santa Ana River Basin.

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

Site	Temperature (°C)	pH	Dissolved Oxygen (mg/L)	Electroconductivity (µS/cm)	Ammonia ppb NH ₃	Alkalinity mg/L CaCO ₃	Hardness mg/L CaCO ₃
A	21.2	8.1	7.96	1149	<1	196	254
B	19.5	7.8	8.33	439	<1	98	124
C	NS	10.2	NS	NS	<1	98	198
D	15.3	8	9.03	1601	<1	224	414
E	17.8	7.7	7.89	1627	<1	146	418
F	25.7	7.5	5.03	1577	3.34	58	524
G	28.1	8.8	8.4	1838	<1	116	600
H	NS	NS	NS	NS	NS	NS	NS
I	17.2	8.2	8.5	1294	<1	60	58
J	17.4	7.8	8.28	760	<1	162	306

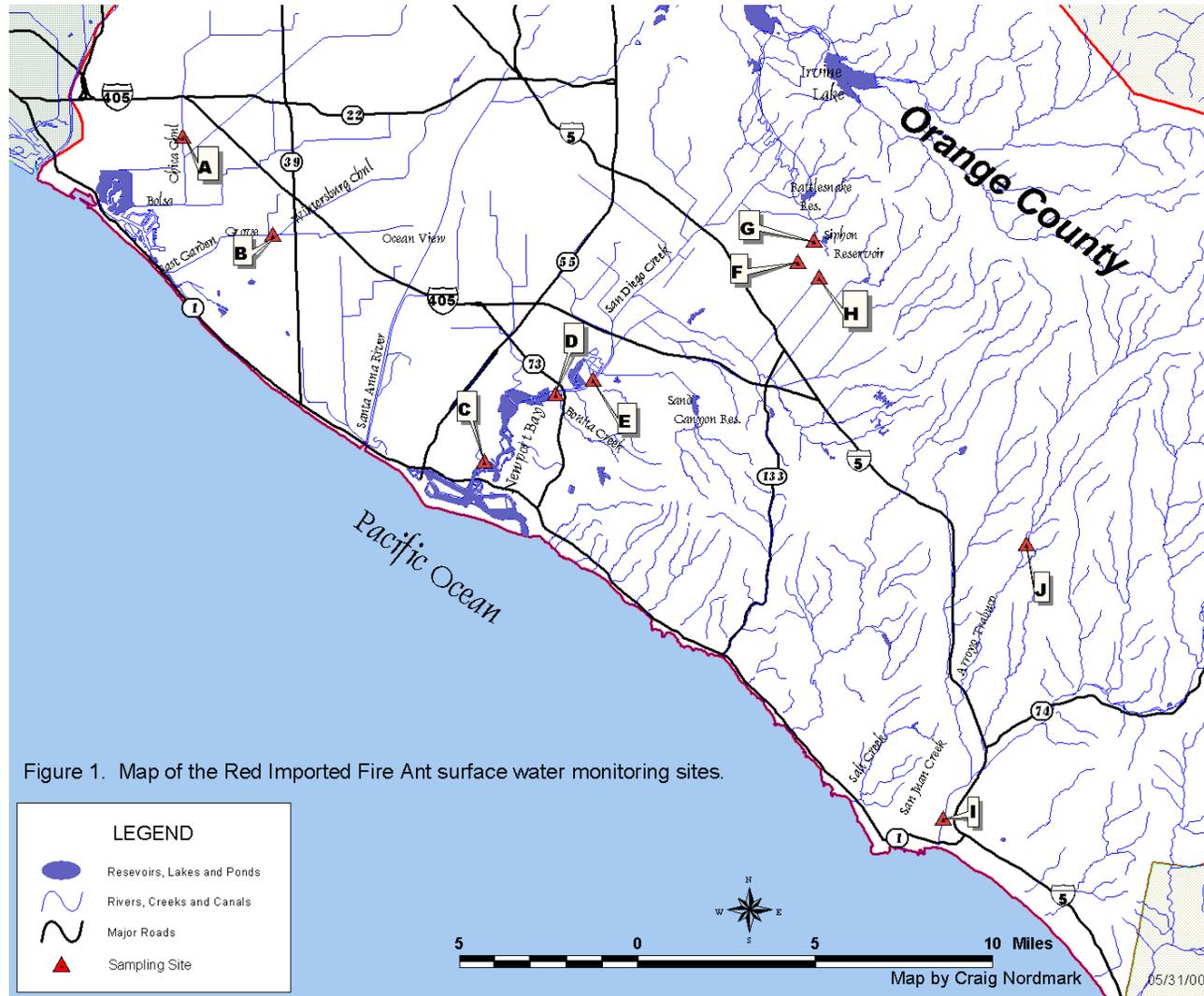


Figure 1. Map of the Red Imported Fire Ant surface water monitoring sites.

References

- Ankley, G.T., J.R. Dierkes, D.A. Jensen, and G.S Peterson. 1991. Piperonyl Butoxide as a Tool in Aquatic Toxicological Research with Organophosphate Insecticides. *Ecotoxicology and Environmental Safety* 21(3): 266-274.
- Bowman, Jane H. 1989. Acute Flow-Through Toxicity of Sumilarv to Rainbow Trout (*Salmo gairdneri*). DPR# 52080-004.
- Burgess, David. 1989. Sumilarv- Acute Flow Through Toxicity of Sumilarv to *Daphnia magna*. DPR# 52080-005
- California Regional Water Quality Control Board. 1995. Water Quality Control Plan (Basin Plan), Region 8, Santa Ana River Basin. Riverside, California.
- California Regional Water Quality Control Board. 1994. Water Quality Control Plan (Basin Plan), Region 9, San Diego Basin. San Diego, California.
- Menconi, Mary, and Angela Paul. 1994. Hazard Assessment of the Insecticide Chlorpyrifos to Aquatic Organisms in the Sacramento-San Joaquin River System. California Department of Fish and Game, Environmental Services Division, Administrative Report 94-1.
- Menconi, Mary, and Cara Cox. 1994. Hazard Assessment of the Insecticide Diazinon to Aquatic Organisms in the Sacramento-San Joaquin River System. California Department of Fish and Game, Environmental Services Division, Administrative Report 94-2.
- Menconi, M and S. Siepmann. 1996. Hazard Assessment of the Insecticide Methidation to Aquatic Organisms in the Sacramento-San Joaquin Drainage. California Department of Fish and Game, Environmental Services Division, Administrative Report 96-1.
- Nelson, S.M. and R.A. Roline. 1998. Evaluation of the Sensitivity of Rapid Toxicity Tests Relative to Daphnid Acute Lethality Tests. *Bulletine of Environmental Contamination and Toxicology* 60: 292-299.
- Tomlin, C.D.S. 1997. *The Pesticide Manual*. 11th edition. British Crop Protection Council, Farnham, Surrey GU9 7PH, UK.
- U.S. Environmental Protection Agency. 1993. Methods for measuring the acute toxicity of effluents and receiving waters to freshwater and marine organisms. 4th ed. EPA/600/4-90/027F. August 1993.
- U.S. Environmental Protection Agency. 1994. *Water Quality Standards Handbook*. 2nd ed. August 1994.

John S. Sanders, Ph.D.
July 6, 2000
Page 10

Precipitation data obtained from The University of California Statewide Integrated Pest Management Project, California Weather Databases. www.ipm.ucdavis.edu/WEATHER/