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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, DECEMBER 1999 (STUDY 183)

SCOPE OF THIS MEMORANDUM

This memorandum reports results of monthly 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 December 9, 1999 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 1999 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 fifth in the monthly sampling series. You can request previous sampling results memos by calling the number above or you may download them from DPR's website at <www.cdpr.ca.gov>.



Sample and Data Collection

On December 9, 1999 surface water samples were collected at nine creeks within the Orange County treatment area (Table 1 and Figure 1). There was no water flowing at site H during this sampling event, so no samples were taken. Quality control samples included one field rinse blank. This sampling event did not coincide with any 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	Central Irvine Channel at Bryan St.	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 to 3.5. Because diazinon rapidly degrades under acidic conditions, it was analyzed from a separate, unacidified 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 parts per billion (ppb), 0.1 ppb for fenoxycarb and pyriproxyfen, 0.2 ppb for hydramethylnon, and 0.05 ppb for the other insecticides.

RESULTS

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. Chlorpyrifos was detected in three samples with concentrations ranging from 0.117 to 0.129 ppb. Diazinon was detected in eight of the samples and ranged from 0.05 to 2.25 ppb. Malathion was detected in two samples with concentrations of 0.055 and 0.093 ppb. Dimethoate was detected in two samples with concentrations of 0.092 and 0.597 ppb. Bifenthrin was detected in two samples with concentrations of 0.629 and 3.12 ppb. Fonofos was detected in one sample at a concentration of 0.056 ppb. Methidathion was detected in one sample at a concentration of 0.051 ppb. There were no detections of fenoxycarb, hydramethylnon, pyriproxyfen, methyl parathion, or phosmet. Chlorpyrifos, diazinon, dimethoate, malathion and bifenthrin detections recorded at site F, were collected from commercial nursery runoff, as were the bifenthrin, diazinon, fonofos, and malathion detections recorded at site G. Samples collected at site E in a creek downstream from sites F and G showed no detections of bifenthrin, fonofos, or malathion.

Diazinon was detected in all samples except for the rinse blank and one site that drains both commercial nurseries and residential areas. Methidathion was detected at one site that drains residential areas. 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, December 9, 1999 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	0.21	ND	ND	ND	ND	ND	ND	75/0
B	ND	ND	ND	ND	ND	0.115	ND	ND	ND	ND	ND	ND	40/0
C	ND	ND	ND	ND	0.129	2.25	ND	ND	ND	0.051	ND	ND	100/0 ⁶
D	ND	ND	ND	ND	ND	0.259	ND	ND	ND	ND	ND	ND	100/0 ⁶
E	ND	ND	ND	ND	0.124	0.189	0.092	ND	ND	ND	ND	ND	100/0 ⁶
F	0.629	ND	ND	ND	0.117	0.57	0.597	ND	0.093	ND	ND	ND	100/0 ⁶
G	3.12	ND	ND	ND	ND	0.338	ND	0.056	0.055	ND	ND	ND	100/0 ⁶
H	NS ³	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS
I	ND	ND	ND	ND	ND	0.05	ND	ND	ND	ND	ND	ND	60/0 ⁶
J	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	20/0
RB ⁴	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	NT ⁵

¹ Two numbers are reported for each toxicity test. The first number is the result from the sample; the second from the corresponding control. These data are preliminary at this point.

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

³ NS = no sample collected.

⁴ RB = rinse blank.

⁵ NT= not tested.

⁶ The difference in mortality between the sample and the corresponding control are significant using Wilcoxon two-sample test.

Toxicity Data

During the December 1999 sampling event, all samples showed some mortality. Samples from sites C, D, E, F and G were acutely toxic to *C. dubia* causing 100% mortality (Table 2). All of these sites contained detectable levels of diazinon. Site C contained additional residues of chlorpyrifos and methidathion. Diazinon was the only chemical detected at site D and was below the LC₅₀ for *C. dubia* (Table 3). Site E, which drains sites F and G, contained additional residues of chlorpyrifos and dimethoate. Site F contained residues of bifenthrin, chlorpyrifos, diazinon, dimethoate, and malathion. Site G contained residues of bifenthrin, diazinon, fonofos, and malathion. Site F is downstream from site G and both drain commercial nurseries. Sites I and A had 60 and 75 percent mortality, respectively. The detection of 0.05 ppb of diazinon at site I is below the LC₅₀ for *C. dubia* and below the proposed U.S. EPA Water Quality Criteria (Table 3). Table 3 lists LC₅₀ values for rainbow trout, *D. magna*, and *C. dubia* and water quality criteria as comparisons to the concentrations detected.

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>	Acute Fresh Water Quality Criteria (ppb)
Bifenthrin	0.15	0.16	ND ²	ND
Chlorpyrifos	3	1.7	0.13 ³	0.083 ⁷
Diazinon	2600	0.96	0.51 ⁴	0.090 ⁸
Dimethoate	6200	4700	ND	ND
Fenoxycarb	1600	400	ND	ND
Fonofos	50	1	ND	ND
Hydramethylnon	160	1140	ND	ND
Malathion	170	1.8	ND	ND
Methidathion	10	3	ND	ND
Methyl parathion	2700	7.3	ND	ND
Phosmet	230	8.5	ND	ND
Pyriproxyfen	>325 ⁵	400 ⁶	ND	ND

¹ Data from Tomlin, C.D.S., 1997.

² ND= No Data

³ Data from Menconi and Paul, 1994

⁴ Data from Menconi and Cox, 1994

⁵ Data from Bowman, Jane H., 1989

⁶ Data from Burgess, David, 1989

⁷ Data from U.S. EPA, 1994.

⁸ Proposed U.S. EPA data.

Environmental Measurements

Table 4 presents the data for DO, temperature, EC, ammonia, alkalinity and hardness. Water temperature ranged from 9.2 to 15.8°C; DO ranged from 8.89 to 15.07 mg/L; EC ranged from 455 to 3229 µS/cm; ammonia was <1 ppb NH₃ for all samples except at site G where it was 4.25 ppb NH₃; alkalinity ranged from 200 to 1440 mg/L CaCO₃; and hardness ranged from 340 to 1150 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 E were above the maximum guideline pH.

Table 4. Water quality measurements at sampling sites, September 1999, 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	10.0	8.36	9.29	2200	<1	383	472
B	9.5	8.2	9.16	800	<1	420	520
C	13.3	9.12	NT ¹	1088	<1	230	340
D	9.2	8.4	10.36	3229	<1	450	890
E	12.1	8.6	13.9	3105	<1	330	890
F	14.5	8.3	9.05	1581	<1	240	480
G	15.8	7.6	8.89	1902	4.25	200	650
H	NS ²	NS	NS	NS	NS	NS	NS
I	12.4	7.7	15.07	1254	<1	1440	1150
J	13.8	7.6	10.04	455	<1	250	350

¹ NT = Readings not taken.

² NS = No sample collected.

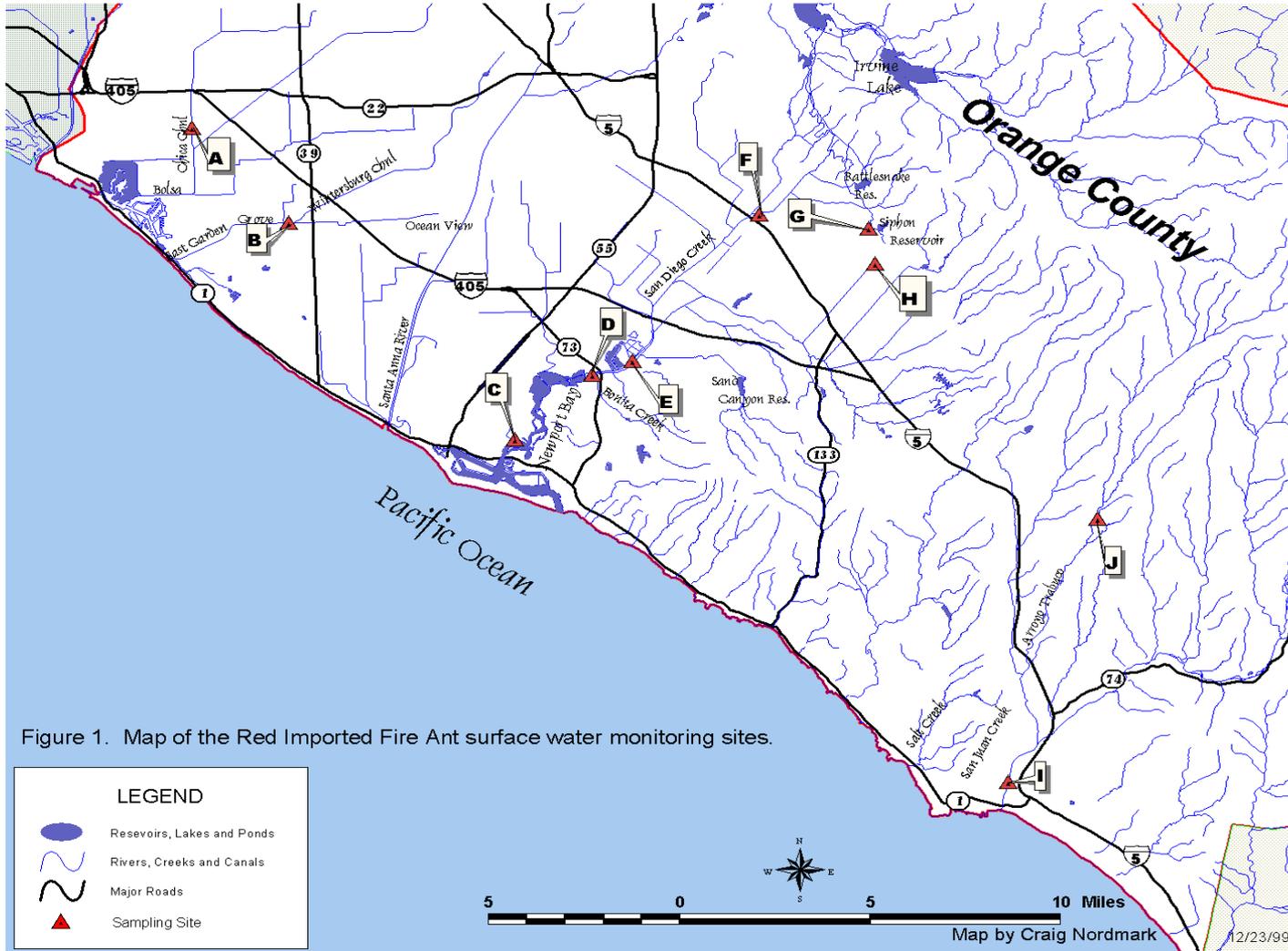


Figure 1. Map of the Red Imported Fire Ant surface water monitoring sites.

References

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