



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,
SEPTEMBER 1999 (STUDY 183)

SCOPE OF THIS MEMORANDUM

This memorandum reports results of water sampling conducted by the Department of Pesticide Regulation (DPR), under the interagency agreement with the Department of Food and Agriculture (CDFA), for the Red Imported Fire Ant (RIFA) control project. Data included here are from the September 23, 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* and *Neomysis mercedis* 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.



Sample and Data Collection

On September 23, 1999, surface water samples were collected at eight creeks within the Orange County treatment area including one rinse blank (Table 1 and Figure 1). There was no runoff at site C or H, so no samples were taken. No rain runoff occurred during this sampling date.

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*, and/or a mysid, *Neomysis mercedis* (depending on the conductivity of the sample) (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 a Sentron® (model 1001) pH meter. EC was measured using an Orion® conductivity-salinity meter (model 140). Water temperature and DO were measured using an YSI® dissolved oxygen meter (model 57). 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 8 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 nine samples were analyzed for the eight organophosphorus insecticides, bifenthrin and the three RIFA insecticide baits. Chlorpyrifos was detected in one of the samples with a concentration of 0.315 ppb. Diazinon was detected in seven of the samples and ranged from 0.059 to 0.637 ppb. Malathion was detected in two samples with concentrations of 0.061 and 1.24 ppb. Dimethoate was detected in one sample at 2.82 ppb. Bifenthrin was detected in two samples with concentrations of 0.242 and 1.12 ppb. There were no detections of fenoxycarb, hydramethylnon, pyriproxyfen, fonofos, methidathion methyl parathion, or phosmet. Chlorpyrifos, diazinon, dimethoate and bifenthrin detections, recorded at site F, were collected from commercial nursery runoff, as were the bifenthrin, diazinon, 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 chlorpyrifos, dimethoate, bifenthrin, or malathion. Diazinon was detected in all samples except for the rinse blank and one site that drains both commercial nurseries and 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 USDA 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, September 1999, Orange County, California.

Site	Chemical Concentrations (ppb)												% Acute Mortality ¹	
	bifenthrin	fenoxycarb	hydramethylnon	pyriproxyfen	chlorpyrifos	diazinon	dimethoate	fonofos	malathion	methidathion	m. parathion	phosmet	<i>C. dubia</i>	<i>N. mercedis</i>
A	ND ²	ND	ND	ND	ND	0.222	ND	ND	ND	ND	ND	ND	15/0	35/45
B	ND	ND	ND	ND	ND	0.107	ND	ND	ND	ND	ND	ND	0/0	NT ⁵
C	NS ³	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS
D	ND	ND	ND	ND	ND	0.242	ND	ND	0.061	ND	ND	ND	20/0	45/45
E	ND	ND	ND	ND	ND	0.134	ND	ND	ND	ND	ND	ND	30/0	50/45
RB ⁴	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	NT	NT
F	0.242	ND	ND	ND	0.315	0.191	2.82	ND	ND	ND	ND	ND	100/0 ⁶	100/45 ⁶
G	1.12	ND	ND	ND	ND	0.637	ND	ND	1.24	ND	ND	ND	100/0 ⁶	100/45 ⁶
H	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS
I	ND	ND	ND	ND	ND	0.059	ND	ND	ND	ND	ND	ND	100/0 ⁶	35/45
J	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	0/0	NT

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 NS = no runoff at this site and 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

Samples from sites F and G were acutely toxic to *C. dubia* and *N. mercedis* and site I was acutely toxic to *C. dubia* causing 100% mortality (Table 2). Site I lacked significant pesticide residues, the detection of 0.059 ppb of diazinon is below the LC₅₀ for *C. dubia* and below the proposed U.S. EPA Water Quality Criteria (Table 3). Site F contained residues of bifenthrin, chlorpyrifos, diazinon, and dimethoate. Site G contained residues of bifenthrin, diazinon, and malathion. Site F is downstream from site G and both drain commercial nurseries. Site E (San Diego Creek), downstream from site F, had 30% mortality to *C. dubia*, 50% mortality to *N. mercedis* and detectible residues of diazinon. Sample from site D containing residues of diazinon and malathion had 20% toxicity to *C. dubia* and 45% toxicity to *N. mercedis*. Site B, containing residues of diazinon, showed no mortality. 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>	Fresh Water Quality Criteria (Acute)
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	NT	ND
Methyl parathion	2700	7.3	NT	NT
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 20.2 to 26.8°C; DO ranged from 6.79 to 19.5 mg/L; EC ranged from 914 to 3150 µS/cm; ammonia was <1 ppb NH₃ for all samples; alkalinity ranged from 146 to 386 mg/L CaCO₃; and hardness ranged from 330 to 1050 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. Sites A and G were above the maximum guideline temperature of 25.5°C.

Table 4. Water quality measurements at sampling sites, September 1999, Orange County, Calif.

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	26.8	NT ¹	19.5	2060	<1	146	400
B	24	NT	16.65	1420	<1	300	360
C	NS ²	NS	NS	NS	NS	NS	NS
D	NT	NT	NT	3150	<1	250	1050
E	23	NT	10.65	2600	<1	234	700
F	23.5	NT	6.79	2250	<1	162	860
G	26.4	NT	9.05	1675	<1	148	520
H	NS	NS	NS	NS	NS	NS	NS
I	20.3	NT	8.13	2940	<1	368	805
J	20.2	NT	8.17	914	<1	200	330

¹ NT = Readings not taken.

² NS = No sample collected.

References

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