Winston H. Hickox
Secretary for Environmental Protection

Department of Pesticide Regulation

Paul E. Helliker, Director
830 K Street • Sacramento, California 95814-3510 • www.cdpr.ca.gov

Gray Davis
Governor

M E M O R A N D U M

TO: Kean S. Goh, Agriculture Program Supervisor IV
Environmental Monitoring and
Pest Management Branch

FROM: Dave Kim, Associate Environmental Research Scientist
Johanna Walters, Environmental Research Scientist
Roger Sava, Associate Environmental Research Scientist
Environmental Monitoring and
Pest Management Branch
(916) 324-4340

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SUBJECT: PRELIMINARY BACKGROUND RESULTS OF ORGANOPHOSPHATE ANALYSIS AND ACUTE TOXICITY TESTING OF SURFACE WATER MONITORED FOR THE RED IMPORTED FIRE ANT PROJECT IN ORANGE COUNTY, MARCH AND APRIL, 1999

SCOPE OF THIS MEMORANDUM

This memorandum reports results of background water sampling conducted by the Department of Pesticide Regulation (DPR), under 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 period March 25, and April 6 and 8, 1999, and encompass results from chemical analyses conducted by the CDFA Center for Analytical Chemistry and aquatic toxicity testing conducted by the California Department of Fish and Game (DFG). This memorandum summarizes results for eight organophosphorus insecticides: chlorpyrifos, diazinon, dimethoate, fonofos, malathion, methidathion, methyl parathion, and phosmet. Of the eight organophosphates, only chlorpyrifos is used in the RIFA control program. The other seven organophosphates are commonly used for insect control and are included in this report to assist in the interpretation of the toxicity results. Future memoranda will also include chemical and toxicity results for additional pesticides incorporated by CDFA in the RIFA control project.

Sample and Data Collection

On March 25, 1999, samples were collected at two creeks and at three sites draining two commercial nurseries. Samples collected on April 6 and 8, 1999 were collected from four creeks and at the same two nurseries (Table 1 and Figure 1). Rain runoff occurred on all three sampling dates, several sites were sampled multiple times during the rain event. Precipitation on March 25, April 6, and April 8 was recorded as 0.57, 0.54, and 0.10 inches, respectively (UC weather database).

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	San Diego Creek at Coronado St.	N 33°40'32", W 117°49'58"
C	San Juan Creek at Stonehill Dr.	N 33°28'31", W 117°40'43"
D	Arroyo Trabuco at Oso Parkway	N 33°35'06", W 117°38'09"
E	Arroyo Trabuco Canyon west	N 33°39'45", W 117°34'36"
F	Arroyo Trabuco Canyon east	N 33°39'47", W 117°34'24"
G	Storm Drain into Robertson Ranch	N 33°39'25", W 117°34'15"
H	Trabuco Highlands runoff	N 33°39'39", W 117°33'53"

All water samples were collected at center channel using a 10-liter stainless steel bucket or by immersing the one liter amber sample bottles directly into the flow. Samples designated for organophosphate chemical analysis were preserved by acidification with 3N hydrochloric acid to a pH between 3.0 to 3.5. Diazinon rapidly degrades under acidic conditions and 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^{o} C refrigerator until transported to the appropriate laboratory for analysis.

Toxicity Tests

Acute toxicity testing was conducted by the 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 water) (U.S. EPA, 1993). Acute toxicity was determined using a 96-hour, static-renewal bioassay in undiluted sample water. All toxicity tests, except for one, commenced within 36 hours of sample collection. Data were reported as percent mortality.

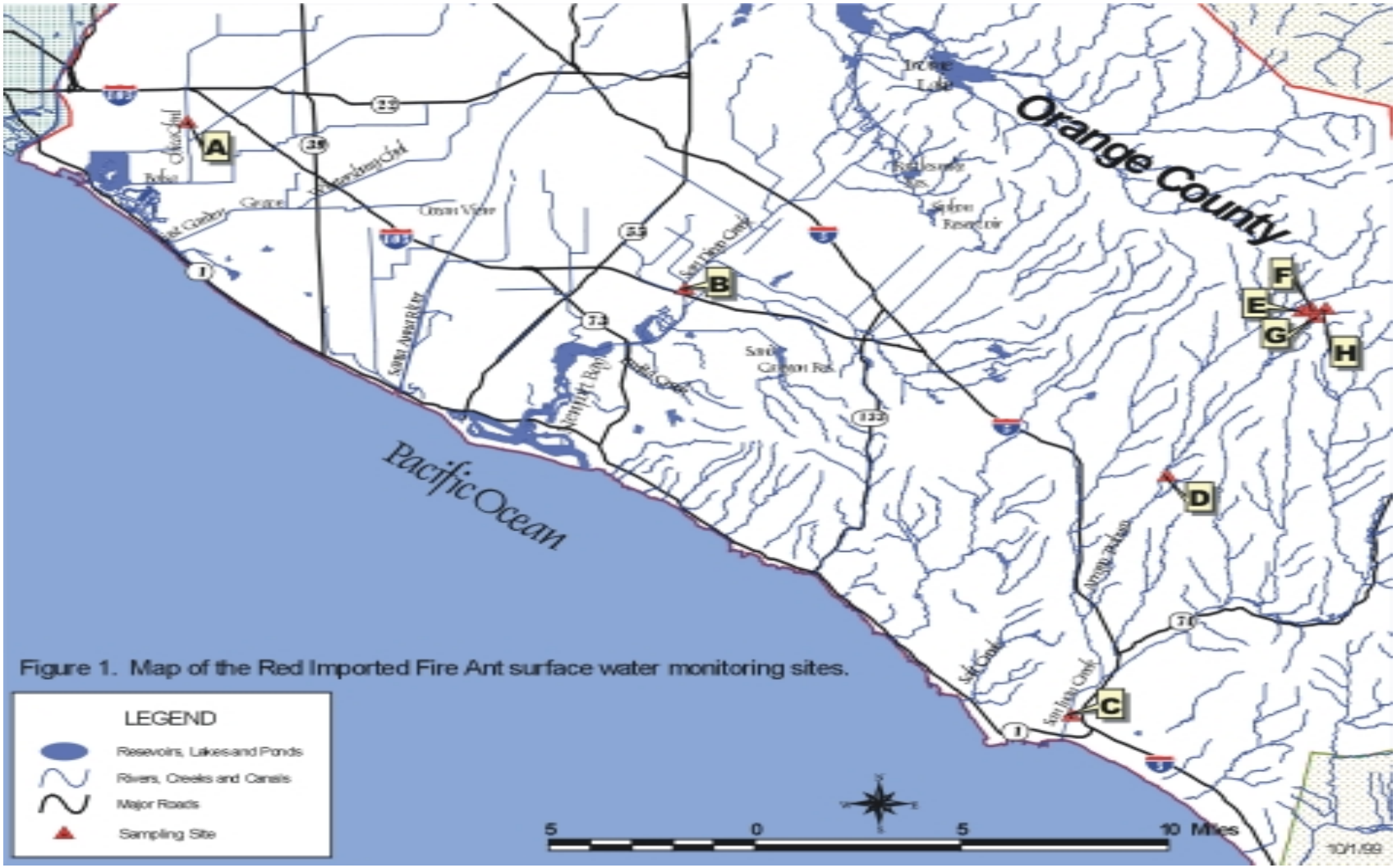

Figure 1. Map of the Red Imported Fire Ant surface water monitoring sites.

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 upon the delivery of the toxicity samples measured alkalinity and hardness. Totals of alkalinity and hardness were measured with a Hach7 titration kit.

Insecticide Analyses

All water samples were analyzed for 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. The reporting limits (reliable detection levels) for chlorpyrifos and diazinon is 0.04 parts per billion (ppb) and 0.05 ppb for the other insecticides.

RESULTS

Insecticide Concentrations

Table 2 shows chemical analysis results. Eighteen samples were analyzed for the 8 organophosphate insecticides. Chlorpyrifos was detected in 13 of the samples and concentrations ranged from 0.118 to 96.8 ppb. Diazinon was detected in 15 of the samples and ranged from 0.048 to 0.561 ppb. Malathion was detected in 14 samples ranging from 0.062 to 1.13 ppb. Methyl parathion was present in 3 samples ranging from 0.055 to 0.125 ppb. Fonophos was detected in 3 samples ranging from 0.063 to 0.14 ppb, and dimethoate was detected in one sample at 0.073 ppb. There were no detections of methidathion or phosmet. Of the eight insecticides tested, only chlorpyrifos was allowed use in nurseries for treatment of fire ants to comply with USDA quarantine requirements. Relatively high concentrations of chlorpyrifos, recorded at sites E, F, and G, were collected from commercial nursery rain runoff. Samples collected at site D in a creek directly downstream from sites E, F, and G showed a 100-fold decrease in chlorpyrifos concentration. The three detections of methyl parathion were associated with commercial nursery rain runoff, concentrations fell below the detectable level at downstream sites C and D. The source and detection of methyl parathion will be further verified. All of the insecticides listed are registered for uses to control insect pests in one or more of the following sites: agriculture, nurseries, golf courses or parks. Malathion, diazinon, and chlorpyrifos are widely available for homeowner use as well, and one or more of these were detected at all sites.

Table 2. Insecticide concentrations and acute toxicity results of surface water samples from Orange County, Calif.

			Organophosphate Concentration (ppb)								Acute Toxicity
Date	Time	Site	chlorpyrifos	diazinon	dimethoate	fonofos	malathion	methidathion	m. parathion	phosmet	Percent mortality[1]
3/25/99	900	B	ND[2]	0.094	ND	0.078	ND	ND	ND	ND	90/30[3,4]
3/25/99	1000	D	ND	ND	ND	ND	ND	ND	ND	ND	5/10
3/25/99	1332	G	62.2	0.109	ND	ND	0.175	ND	ND	ND	NT[5]
3/25/99	1350	F	29.7	0.052	ND	ND	0.604	ND	ND	ND	NT
3/25/99	1550	E	96.8	0.088	ND	ND	1.05	ND	ND	ND	NT
3/25/99	1700	D	0.738	0.561	ND	0.14	0.103	ND	ND	ND	NT
4/6/99	1410	H	0.791	0.425	ND	0.063	0.071	ND	ND	ND	NT
4/6/99	1420	G	42.6	0.298	ND	ND	0.453	ND	ND	ND	NT
4/6/99	1450	F	10.8	ND	ND	ND	0.878	ND	0.055	ND	NT
4/6/99	1540	D	0.166	0.344	ND	ND	1.05	ND	ND	ND	100/0[3]
4/6/99	1630	B	ND	0.365	0.073	ND	0.135	ND	ND	ND	100/0[3]
4/6/99	1715	D	0.701	0.491	ND	ND	0.244	ND	ND	ND	100/0[3]
4/6/99	1740	G	18.5	ND	ND	ND	0.51	ND	0.125	ND	NT
4/6/99	1800	E	19	0.048	ND	ND	1.13	ND	0.084	ND	NT
4/6/99	1850	D	0.118	0.509	ND	ND	0.118	ND	ND	ND	100/0[3]
4/6/99	2035	D	1.12	0.277	ND	ND	0.062	ND	ND	ND	100/0[3]
4/8/99	1330	A	ND	0.156	ND	ND	ND	ND	ND	ND	0/0
4/8/99	1440	C	ND	0.221	ND	ND	ND	ND	ND	ND	NT

[1] Two numbers are reported for all toxicity tests. The first number is the result from the sample. The second is the result from the corresponding control. The numbers reported for percent mortality refers to the mortality at the end of the test. Samples tested using *C. dubia* unless otherwise noted.

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

[3] The differences in survival between the sample and the corresponding control are statistically significant using Fisher's Test ($P<0.05$).

[4] Sample over 33 days old, sample tested using *N. mercedis*.

[5] NT = not tested

Toxicity Data

Five of the eight samples were acutely toxic to *C. dubia* (Table 2). One hundred percent mortality was observed in all five samples. One sample tested with *N. mercedis* had statistically significant mortality. Diazinon was detected in all samples with significant mortality, but was also present in trace amount in one sample that showed no toxicity. Chlorpyrifos was present above the detection level in four of six samples showing significant mortality. Table 3 lists LC_{50} concentrations for rainbow trout, *D. magna,* and *C. dubia* as a comparison to the concentrations detected.

Environmental Measurements

Table 4 presents the data for pH, DO, temperature, EC, hardness, and alkalinity. pH values ranged from 7.0 to 8.0. Water temperature ranged from 11.8 to 22.0°C, DO ranged from 7.54 to 14.25 mg/L and EC ranged from 278 to 2690 µS/cm. Water hardness ranged from 92 to 777 mg/L $CaCO_3$ and alkalinity ranged from 64 to 330 mg/L $CaCO_3$. The California Regional Water Quality Control Board, Water Quality Control Plan, Santa Ana River Basin (1995), and the 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 plans do not provide an acceptable range for EC, hardness, or alkalinity. All measurements were within the acceptable limits set by the guidelines.

Table 3. LC_{50}'s of insecticides (ppb) for three aquatic species

Pesticide	Rainbow trout[1]	*D. magna*[1]	*C. dubia*
Chlorpyrifos	3	1.7	0.13[2]
Diazinon	2600	0.96	0.51[3]
Dimethoate	6200	4700	NA[4]
Fonofos	50	1	NA
Malathion	170	1.8	NA
Methidathion	10	3	NA
Methyl parathion	2700	7.3	NA
Phosmet	230	8.5	NA

[1] Data from Tomlin, C.D.S., 1997
[2] Data from Menconi, Mary and Angela Paul, 1994
[3] Data from Menconi, Mary and Cara Cox, 1994
[4] NA=Data not available

Table 4. Water quality measurement at sampling sites.

Date	Time	Site	Temp. (^{o}C)	pH	Dissolved Oxygen (mg/L)	Electroconductivity (µS/cm)	Hardness mg/L $CaCO_3$	Alkalinity mg/L $CaCO_3$
3/25	0900	B	14.3	7.6	10.68	2690	777	330
3/25	1030	D	15.1	7.4	9.68	890	332	184
4/6	1540	D	14.0	7.0	9.00	581	192	94
4/6	1630	B	15.0	7.9	7.54	608	158	76
4/6	1715	D	13.1	7.9	9.89	425	140	84
4/6	1850	D	12.0	7.5	10.02	278	92	64
4/6	2035	D	11.8	7.5	9.44	470	164	94
4/8	1330	A	20.8	8.0	14.25	1608	366	283
4/8	1440	C	22.0	7.8	8.35	1339	432	180

References

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.

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