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MEMORANDUM

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SUBJECT: PRELIMINARY RESULTS OF PESTICIDE ANALYSIS AND ACUTE
TOXICITY TESTING OF SURFACE WATER MONITORED FOR THE RED
IMPORTED FIRE ANT PROJECT IN ORANGE COUNTY, MAY AND
JUNE, 1999



SCOPE OF THIS MEMORANDUM

This memorandum reports results of 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 May 21 and June 25, 1999, 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 mercedes* are also included.



Sample and Data Collection

On May 21, 1999, surface water samples were collected at five creeks within the treatment area including one rinse blank. Samples collected on June 25, 1999 were collected from six creeks within the treatment area (Table 1 and Figure 1). There was no runoff at site H, so no samples were taken. No rain runoff occurred during these sampling dates.

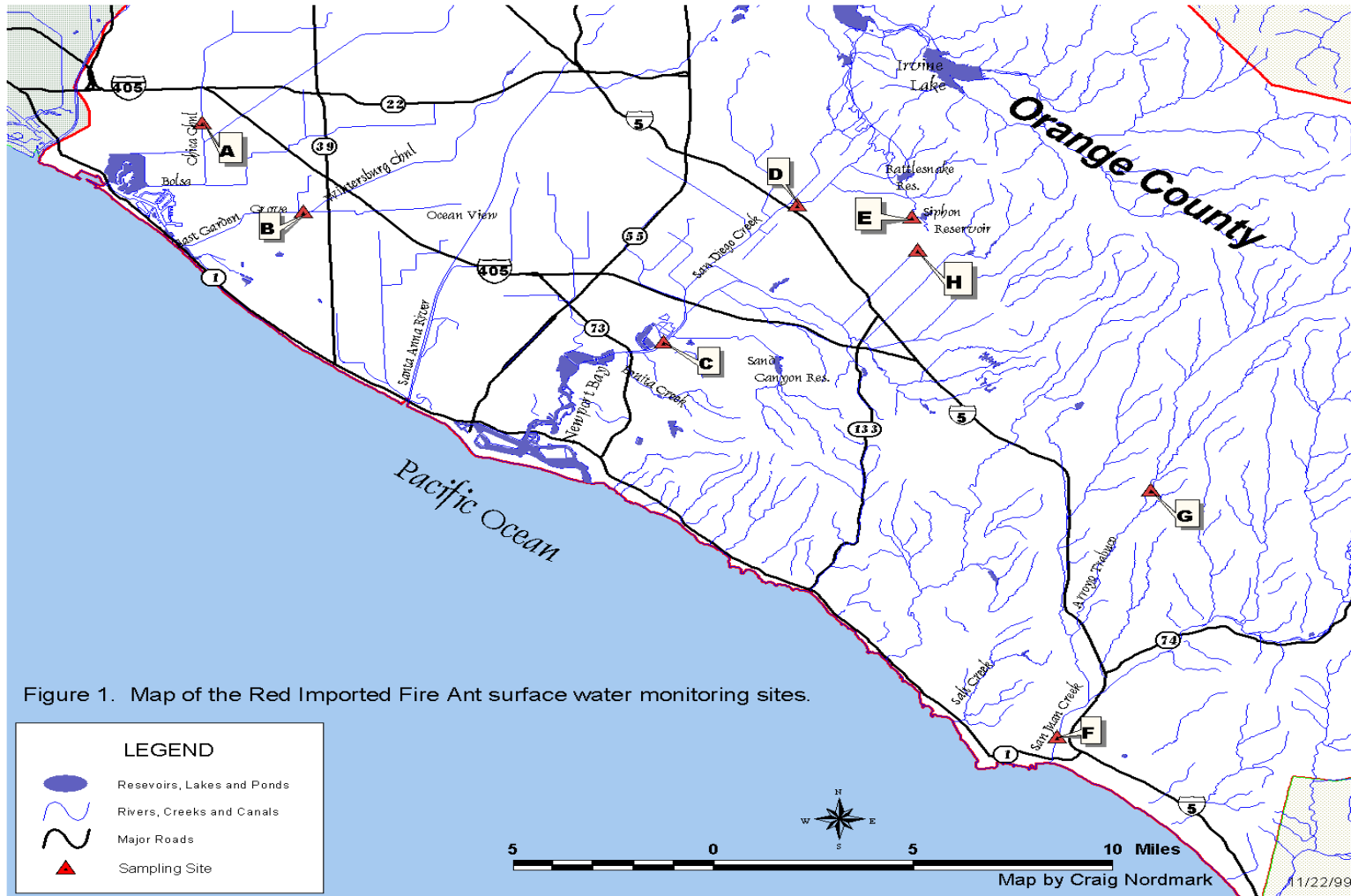
Table 1. Sampling site descriptions in Orange County, California

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	San Diego Creek at Campus Dr.	N 33°39'23", W 117°50'43"
D	Central Irvine Channel at Bryan St.	N 33°42'04", W 117°45'24"
E	Drain at Bee Canyon and Portola Parkway	N 33°42'37", W 117°44'13"
F	San Juan Creek at Stonehill Dr.	N 33°28'31", W 117°40'43"
G	Arroyo Trabuco at Oso Parkway	N 33°35'06", W 117°38'09"
H	Marshburn Slough	N 33°41'45", W 117°44'02"

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. 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° C refrigerator until transported to the appropriate laboratory for analysis.

Toxicity Tests

The Department of Fish and Game Aquatic Toxicity Laboratory (ATL) conducted acute toxicity testing 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 started within 36 hours of sample collection. All samples collected on May 21 were tested using both *C. dubia* and *N. mercedis*. Samples taken on June 25 were tested using only *C. dubia* except for sites A and C that were tested using both species due to high electro-conductivity. 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 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 bifenthrin, fenoxycarb, hydramethylnon, pyriproxyfen, chlorpyrifos, diazinon, dimethoate, fonofos, malathion, methidathion, methyl parathion, and phosmet. The CDFCA 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

A total of 11 field samples were analyzed for the eight organophosphorus insecticides, bifenthrin and the three insecticide baits: fenoxycarb, hydramethylnon, and pyriproxyfen (Table 2). Chlorpyrifos was detected in 2 of the samples with concentrations of 0.103 and 0.246 ppb. Diazinon was detected in nine samples ranging from 0.058 to 1.94 ppb. Malathion was detected in three samples ranging from 0.323 to 2.57 ppb. Methyl parathion was present in two samples with concentrations of 0.087 and 0.117 ppb. Dimethoate was detected in one sample at 3.88 ppb. Bifenthrin was detected in two samples with concentrations of 0.249 and 1.67 ppb. Fenoxycarb was detected in two samples with concentrations of 0.509 and 0.71 ppb. Hydramethylnon and pyriproxyfen were each detected in one sample with results of 0.289 and 1.34 ppb, respectively. There were no detections of fonofos, methidathion or phosmet. Of the twelve insecticides tested, only bifenthrin, chlorpyrifos, diazinon, fenoxycarb, hydramethylnon, and pyriproxyfen were allowed use in nurseries for treatment of fire ants to comply with USDA quarantine requirements. Chlorpyrifos, diazinon, malathion, dimethoate and bifenthrin detections, recorded at site D, were collected from commercial nursery runoff. Samples collected at site C in a creek showed no detections of chlorpyrifos, malathion, dimethoate, or bifenthrin. The two detections of

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

		Chemistry Concentrations (ppb)											% Acute Mortality ³		
Date	Site	bifenthrin	fenoxycarb	hydramethylnon	pyriproxyfen	chlorpyrifos	diazinon	dimethoate	fonofos	malathion	methidathion	m. parathion	phosmet	<i>C. dubia</i>	<i>N. mercedis</i>
5/21/99	A	ND ¹	ND	ND	ND	ND	0.073	ND	ND	ND	ND	ND	ND	0/0	0/20
5/21/99	B	NS ⁵	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS
5/21/99	C	ND	ND	ND	ND	ND	0.159	ND	ND	ND	ND	ND	ND	0/0	25/20
5/21/99	D	1.67	ND	ND	ND	0.246	1.94	3.88	ND	0.323	ND	ND	ND	100/0 ⁴	100/20 ⁴
5/21/99	F	ND	ND	ND	ND	ND	0.058	ND	ND	ND	ND	ND	ND	0/0	15/20
5/21/99	G	ND	0.509	0.289	1.34	ND	ND	ND	ND	ND	ND	ND	ND	10/0	15/20
5/21/99	H	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS
5/21/99	RB ²	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	NT ⁶	NT
6/25/99	A	ND	ND	ND	ND	ND	0.11	ND	ND	ND	ND	ND	ND	0/0	55/15 ⁴
6/25/99	B	ND	ND	ND	ND	ND	0.11	ND	ND	ND	ND	ND	ND	0/0	NT
6/25/99	C	ND	ND	ND	ND	ND	0.13	ND	ND	ND	ND	ND	ND	0/0	30/15
6/25/99	D	0.249	ND	ND	ND	0.103	0.79	ND	ND	2.57	ND	0.087	ND	100/0 ⁴	NT
6/25/99	E	ND	0.71	ND	ND	ND	1.31	ND	ND	0.593	ND	0.117	ND	100/0 ⁴	NT
6/25/99	G	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	0/0	NT
6/25/99	H	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS

¹ ND = none detected at the reporting limit for that chemical.

² RB = rinse blank.

³ Two numbers are reported for each toxicity test. The first number is the result from the sample; the second from the corresponding control.

⁴ The differences in mortality between the sample and the corresponding control are significant using Fisher's Test (P<0.05).

⁵ NS = no sample collected; No runoff water at site H.

⁶ NT = not tested.

methyl parathion were both associated with commercial nursery runoff, concentrations fell below the detectable level at downstream site C. The source and detection of methyl parathion will need further verification. Fenoxycarb, hydramethylnon, and pyriproxyfen detections on May 21 at site G were collected from runoff that drains both commercial nurseries and residential areas, samples collected downstream at site F fell below the detection limit for these insecticides. All of the organophosphorus insecticides listed are registered for uses in commercial agriculture, nurseries, golf courses or parks for the control of insect pests. Malathion, diazinon, and chlorpyrifos are widely available for homeowner use.

Toxicity Data

On May 21, the sample from site D containing bifenthrin, chlorpyrifos, diazinon, dimethoate and malathion was acutely toxic to *C. dubia* and *N. mercedis* causing complete mortality (Table 2). Sample from site G containing fenoxycarb, hydramethylnon, and pyriproxyfen was not significantly toxic to either organisms. On June 25, complete mortality of *C. dubia* was observed at sites D and E. Site D contained residues of bifenthrin, chlorpyrifos, diazinon, dimethoate, malathion and methyl parathion; site E contained residues of fenoxycarb, diazinon, malathion, and methyl parathion. Significant toxicity of *N. mercedis* was observed at site A with diazinon detected. Table 3 lists LC₅₀ values for rainbow trout, *D. magna*, and *C. dubia* as comparisons to the concentrations detected.

Table 3. LC₅₀'s of insecticides (ppb) for three aquatic species

Pesticide	Rainbow trout ¹	<i>D. magna</i> ¹	<i>C. dubia</i>
Bifenthrin	0.15	0.16	NA ²
Chlorpyrifos	3	1.7	0.13 ³
Diazinon	2600	0.96	0.51 ⁴
Dimethoate	6200	4700	NA
Fenoxycarb	1600	400	NA
Fonofos	50	1	NA
Hydramethylnon	160	1140	NA
Malathion	170	1.8	NA
Methidathion	10	3	NA
Methyl parathion	2700	7.3	NA
Phosmet	230	8.5	NA
Pyriproxyfen	>325 ⁵	400 ⁶	NA

¹ Data from C.D.S. Tomlin (1997)

² Data not available

³ Data from Menconi and Paul (1994)

⁴ Data from Menconi and Cox (1994)

⁵ Data from J. H. Bowman (1989)

⁶ Data from D. Burgess (1989)

Environmental Measurements

Table 4 presents the data for pH, DO, temperature, EC, alkalinity, and hardness. pH values ranged from 7.2 to 8.0. Water temperature ranged from 17 to 31°C, DO ranged from 3.1 to 17.2 mg/L, and EC ranged from 408 to 2960 µS/cm. Water hardness ranged from 324 to 684 mg/L CaCO₃ and alkalinity ranged from 94 to 378 mg/L CaCO₃. The California Regional Water Quality Control Board (1994, 1995), 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, alkalinity, or hardness. On June 25, site B fell below the water quality guidelines for DO, and sites D and G were above the maximum guideline temperature of 25.5°C.

Table 5. Water quality measurements at sampling sites, Orange County, Calif.

Date	Site	Temperature (°C)	pH	Dissolved Oxygen (mg/L)	Electroconductivity (µS/cm)	Alkalinity mg/L CaCO ₃	Hardness mg/L CaCO ₃
5/21/99	A	17	7.4	6.6	2500	442	555
5/21/99	C	20	7.9	10.4	2960	258	763
5/21/99	D	17	7.4	9.6	2280	110	740
5/21/99	F	21	7.8	17.2	2580	191	880
5/21/99	G	19	7.9	10.2	900	174	326
6/25/99	A	19	7.3	8.2	2270	378	510
6/25/99	B	20	7.2	3.1	1668	240	438
6/25/99	C	25	7.6	8.4	2740	216	684
6/25/99	D	31	7.9	7.7	408	240	438
6/25/99	E	NT	7.8	NT	1790	94	664
6/25/99	G	26	8.0	8.4	879	156	324

NT= Readings not taken

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