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DATE: May 30, 2000

SUBJECT: RESULTS OF PESTICIDE ANALYSIS AND ACUTE TOXICITY TESTING OF RAIN RUNOFF MONITORING FOR THE RED IMPORTED FIRE ANT PROJECT IN ORANGE COUNTY, JANUARY 2000 (STUDY 183)

SUMMARY

During January 2000, 38 rain runoff samples collected from eight sites in Orange County, California, showed no detectable residues of hydramethylnon and pyriproxyfen. There were 18 detections of bifenthrin ranging from 0.319 to 3.79 parts per billion (ppb) at the three nursery sites. Fenoxycarb was detected in five samples ranging from 0.18 to 0.404 ppb at two sites that drain nurseries. There were 21 detections of chlorpyrifos ranging from 0.06 to 0.349 ppb, ten at nursery sites and the others from creeks that drain residential areas. All sites had 100% mortality to *Ceriodaphnia dubia* in the water collected. The toxicity can be attributed to diazinon, chlorpyrifos, bifenthrin and malathion.

SCOPE OF THIS MEMORANDUM

This memorandum reports results of surface 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 January 25 and 26, 2000, rain runoff 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 2000 pesticide use report becomes available. Stream discharge measurements will be available for some of our sampling sites and will also be included in the final report.

The rain runoff sampling event was conducted during the first rainfall of the rainy season following months of dry weather and RIFA insecticide applications. DPR also conducts monthly surface water monitoring. Previous sampling result memos may be requested by calling the number above or you may download or review 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 January 25 and 26, 2000, surface water samples were collected at eight creeks within the Orange County treatment area (Table 1 and Figure 1). Sites C, D, E, F, G, and H were sampled six times at roughly 1.5-hour intervals; sites I and J were sampled one time on January 25. No samples were taken at sites A and B because of staffing and equipment constraints. Sampling began in the afternoon of January 25 and ended just after midnight on January 26. This sampling event coincided with measurable rainfall. From the morning of January 24 through the morning of January 26, 0.44 inches of rain was measured in San Juan Canyon (Arroyo Trabuco and San Juan Creek); most of the rain fell on January 25. Rainfall was measured at 0.4 inches in the Santa Ana region on January 25. The Santa Ana station covers the San Diego Creek watershed (sites C, D, E, F, G, and H).

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, 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 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 a 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

A total of 38 samples were analyzed for the eight organophosphorus insecticides, bifenthrin and the three RIFA insecticide baits (Table 2, Figure 2). Chlorpyrifos was detected in 21 samples with concentrations ranging from 0.06 to 0.349 ppb. Diazinon was detected in all samples and ranged from 0.088 to 1.079 ppb. Dimethoate was detected in two samples with concentrations of 0.06 and 0.083 ppb. Malathion was detected in 37 samples with concentrations ranging from 0.069 to 1.47 ppb. Bifenthrin was detected in 18 samples with concentrations ranging from 0.319 to 5.3 ppb. Fenoxycarb was detected in five samples with concentrations ranging from 0.18 to 0.404 ppb. There were no detections of hydramethylnon, pyriproxyfen, fonofos, methidathion, methyl parathion, or phosmet. Diazinon and malathion were detected at all eight sites, diazinon during all six intervals and malathion during all six intervals except for one at site G. Site C, which drains residential areas, and site E, which drains both residential and nursery, each had chlorpyrifos detections in five out of six intervals (non detects were during the second interval for both sites). Bifenthrin was detected at three sites (F, G, and H) all associated directly with nursery runoff. Residues were found during each of the six sampling intervals. Fenoxycarb detections were also associated with nursery runoff, with detections at sites G and H. Site H also had chlorpyrifos detections during all six sampling intervals. Sites I and J were sampled one time during the rain event. Site I showed detections of chlorpyrifos, diazinon, dimethoate and malathion. Site J, which drains into site I, showed residues of diazinon and malathion. Of the 12 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 (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.

Toxicity Data

Every sampling interval at all sites was acutely toxic to *C. dubia* causing 100% mortality (Table 2). Four samples, one at site C, two at site E, and one at site F exceeded the LC_{50} of *C. dubia* for chlorpyrifos (Table 3). All sites contained residues of diazinon; 20 samples exceeded the LC_{50} of *C. dubia* for diazinon, all six sampling intervals at site C, three at site D, five at site E, four at site G, and one at sites I and J. The toxicities were attributable mostly to chlorpyrifos, diazinon, malathion, and bifenthrin. Table 3 lists LC_{50} values for rainbow trout, *D. magna,* and *C. dubia* and water quality criteria as comparisons to the concentrations detected.

Environmental Measurements

Table 4 presents the data for temperature, pH, DO, EC, ammonia, alkalinity and hardness. Water temperature ranged from 14.7 to 17.4°C; pH ranged from 7.36 to 8.4; DO was not taken; EC ranged from 286 to 3199 µS/cm; ammonia was between <1 and 10.2 ppb NH_3; alkalinity ranged from 30 to 188 mg/L $CaCO_3$; and hardness ranged from 40 to 1170 mg/L $CaCO_3$. 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. All water quality measurements were within the acceptable guidelines.

Table 2. Insecticide concentrations and acute toxicity in rainwater runoff samples, January 25 and 26, 2000, Orange County, California.

	Concentration in pbb													Acute Mortality[1, 2]
Site	Time	bifenthrin	fenoxycarb	hydramethylnon	pyriproxyfen	chlorpyrifos	diazinon	dimethoate	fonofos	malathion	methidathion	m. parathion	phosmet	*C. dubia*
C	1420	ND[3]	ND	ND	ND	0.111	0.678	ND	ND	0.242	ND	ND	ND	100/0[3]
C	1540	ND	ND	ND	ND	ND	1.079	ND	ND	0.194	ND	ND	ND	100/0[3]
C	1700	ND	ND	ND	ND	0.063	1.077	ND	ND	0.393	ND	ND	ND	100/5[3]
C	1830	ND	ND	ND	ND	0.094	0.555	ND	ND	0.196	ND	ND	ND	100/5
C	2310	ND	ND	ND	ND	0.231	0.686	ND	ND	0.383	ND	ND	ND	100/5[3]
C	0030	ND	ND	ND	ND	0.099	0.598	ND	ND	0.315	ND	ND	ND	100/10[3]
D	1510	ND	ND	ND	ND	ND	0.456	ND	ND	0.208	ND	ND	ND	100/5[3]
D	1630	ND	ND	ND	ND	ND	0.628	ND	ND	0.288	ND	ND	ND	100/0[3]
D	1750	ND	ND	ND	ND	ND	0.515	ND	ND	0.314	ND	ND	ND	100/5[3]
D	1920	ND	ND	ND	ND	ND	0.515	ND	ND	0.25	ND	ND	ND	100/5[3]
D	2240	ND	ND	ND	ND	ND	0.383	ND	ND	0.245	ND	ND	ND	100/5[3]
D	0005	ND	ND	ND	ND	ND	0.404	ND	ND	0.222	ND	ND	ND	100/10[3]
E	1450	ND	ND	ND	ND	0.121	0.591	ND	ND	0.350	ND	ND	ND	100/0
E	1615	ND	ND	ND	ND	ND	0.836	0.06	ND	0.188	ND	ND	ND	100/0
E	1732	ND	ND	ND	ND	0.108	0.566	ND	ND	0.395	ND	ND	ND	100/5
E	1900	ND	ND	ND	ND	0.081	0.542	ND	ND	0.533	ND	ND	ND	100/5
E	2215	ND	ND	ND	ND	0.163	0.498	ND	ND	1.47	ND	ND	ND	100/5
E	2350	ND	ND	ND	ND	0.206	0.537	ND	ND	0.251	ND	ND	ND	100/10
F	1431	3.79	ND	ND	ND	0.122	0.324	ND	ND	0.106	ND	ND	ND	100/0
F	1600	2.06	ND	ND	ND	ND	0.373	ND	ND	0.082	ND	ND	ND	100/0
F	1725	1.35	ND	ND	ND	ND	0.319	ND	ND	0.069	ND	ND	ND	100/5
F	1900	0.319	ND	ND	ND	ND	0.243	ND	ND	0.09	ND	ND	ND	100/5
F	2255	2.45	ND	ND	ND	0.078	0.199	ND	ND	0.088	ND	ND	ND	100/10
F	2355	1.93	ND	ND	ND	0.349	0.271	ND	ND	0.155	ND	ND	ND	100/10
G	1515	2.57	ND	ND	ND	ND	0.842	ND	ND	0.176	ND	ND	ND	100/0
G	1642	2.67	ND	ND	ND	ND	0.369	ND	ND	0.093	ND	ND	ND	100/5
G	1833	0.792	ND	ND	ND	0.06	0.126	ND	ND	ND	ND	ND	ND	100/5
G	1934	1.4	ND	ND	ND	ND	0.921	ND	ND	0.322	ND	ND	ND	100/5
G	2333	1.8	0.18	ND	ND	ND	0.599	ND	ND	0.314	ND	ND	ND	100/10
G	0033	1.24	ND	ND	ND	ND	0.526	ND	ND	0.105	ND	ND	ND	100/10
H	1454	1.77	0.224	ND	ND	0.121	0.152	ND	ND	0.096	ND	ND	ND	100/0
H	1620	2.27	ND	ND	ND	0.062	0.182	ND	ND	0.136	ND	ND	ND	100/5
H	1815	5.3	0.312	ND	ND	0.045	0.105	ND	ND	0.126	ND	ND	ND	100/5
H	1915	1.95	ND	ND	ND	0.062	0.088	ND	ND	0.22	ND	ND	ND	100/5
H	2315	2.06	0.404	ND	ND	0.076	0.144	ND	ND	0.129	ND	ND	ND	100/10
H	0013	1.57	0.336	ND	ND	0.093	0.201	ND	ND	0.175	ND	ND	ND	100/10
I	1630	ND	ND	ND	ND	0.083	0.585	0.083	ND	0.114	ND	ND	ND	100/0
J	1650	ND	ND	ND	ND	ND	0.576	ND	ND	0.429	ND	ND	ND	100/5

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

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

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

Table 3. LC_{50}'s (ppb) of insecticides for three aquatic species and U.S. EPA acute fresh water quality criteria.

Pesticide	Rainbow trout[1]	*D. magna*[1]	*C. dubia*	Water Quality Criteria
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	2.2[9]	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.
[9] Data from Menconi and Siepmann, 1996

Table 4. Water quality measurements at sampling sites, February 2000, Orange County, Calif.

Site	Time	Temperature (^{o}C)	pH	Dissolved Oxygen (mg/L)	Electroconductivity (µS/cm)	Ammonia ppb NH_3	Alkalinity mg/L $CaCO_3$	Hardness mg/L $CaCO_3$
C	1420	17.4	7.82	NT[1]	1290	2.94	32	64
C	1540	16.6	8.04	NT	286	1.9	40	72
C	1700	16.0	7.99	NT	298	<1	40	100
C	1830	16.2	7.72	NT	510	1.94	64	82
C	2310	NT	7.36	NT	176	1.16	30	50
C	0030	15.8	7.52	NT	190	<1	32	40
D	1510	15.4	7.95	NT	2379	<1	188	500
D	1630	NT	7.87	NT	2252	<1	178	580
D	1750	NT	7.91	NT	1990	<1	174	410
D	1920	15.2	7.84	NT	1944	<1	176	410
D	2240	NT	7.83	NT	1905	<1	188	430
D	0005	14.9	7.8	NT	1975	<1	186	390
E	1450	NT	7.95	NT	688	2.44	64	176
E	1615	NT	7.89	NT	804	1.82	70	250
E	1732	16.5	7.96	NT	1046	<1	90	240
E	1900	16.4	7.96	NT	988	1.29	88	210
E	2215	16.4	7.87	NT	870	1.01	84	180
E	2350	16.2	7.76	NT	870	<1	82	200
F	1431	16.6	8.4	NT	1424	1.21	74	490
F	1600	16.7	8.1	NT	1527	<1	82	500
F	1725	15.9	8.0	NT	1704	<1	84	580
F	1900	15.6	8.0	NT	1634	1.02	90	460
F	2288	15.1	7.91	NT	1672	<1	88	540
F	2355	14.9	7.9	NT	1452	1.06	68	460
G	1515	17.2	8.2	NT	1866	1.82	112	660
G	1642	16.4	8.19	NT	2075	1.24	120	750
G	1833	15.6	7.85	NT	1082	1.94	80	310
G	1934	15.5	8.13	NT	1280	<1	88	460
G	2333	14.8	7.96	NT	1478	1.43	82	540
G	0033	14.7	8.03	NT	1966	1.92	40	220
H	1454	16.5	7.4	NT	3050	10.2	76	1170
H	1620	16.7	7.64	NT	3199	2.07	56	1160
H	1815	15.8	7.72	NT	3190	6.25	60	1100
H	1915	15.5	7.75	NT	2807	2.15	64	930
H	2315	14.8	7.6	NT	2120	1.4	46	720
H	0013	14.7	7.67	NT	2434	1.32	112	560
I	1630	NT	7.78	NT	1194	1.14	108	270
J	1650	NT	7.9	NT	678	<1	100	220

[1] NT= Sample not taken.

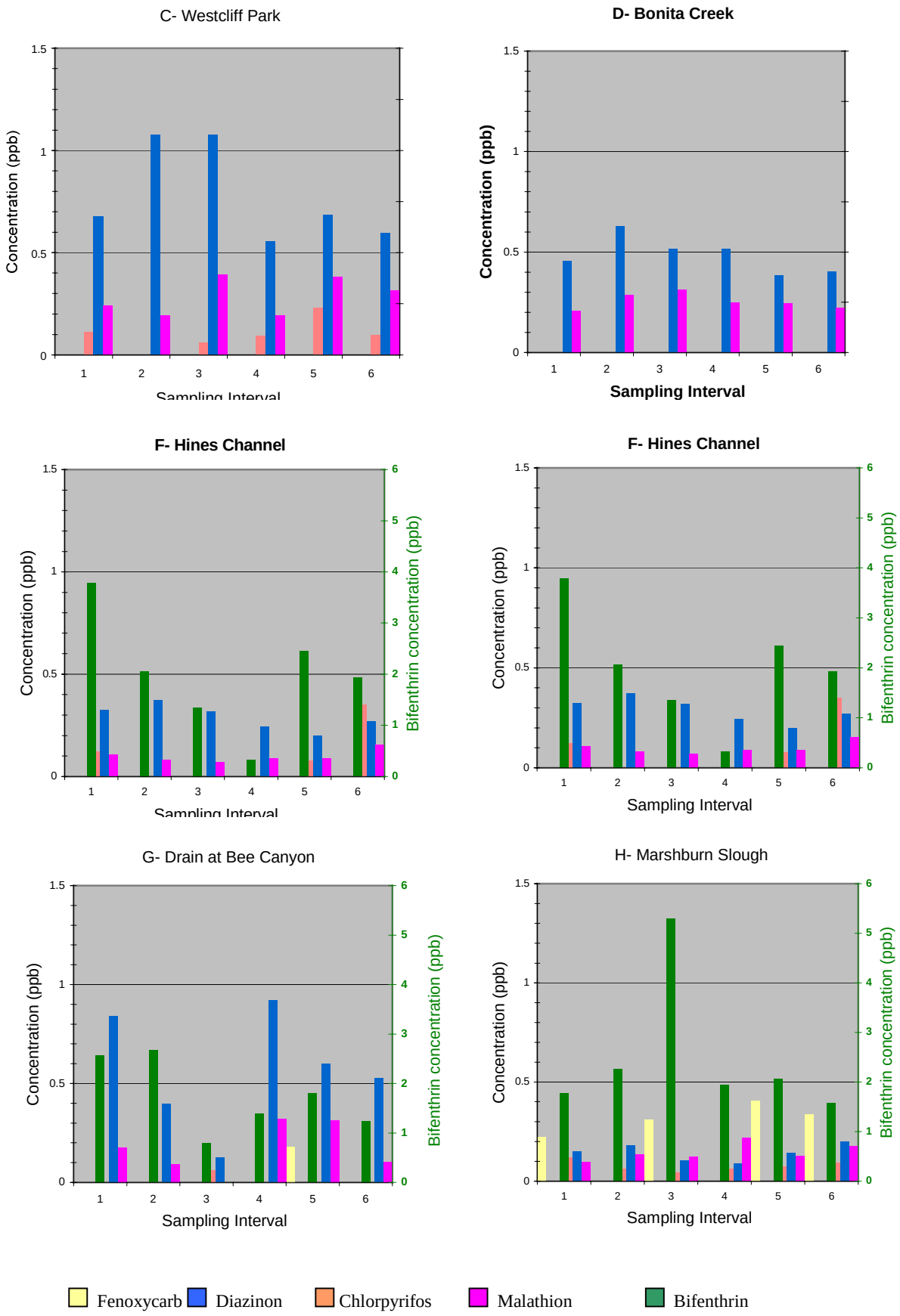

Figure 2. Concentration of insecticides in surface rain-runoff water at six sites in Orange County, January 25-26. Sample taken at one- to three-hour intervals.

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