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MEMORANDUM

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DATE: January 5, 2004. Corrected on April 17, 2006.

SUBJECT: Preliminary Results for Study 215: Monitoring Esfenvalerate Runoff from a Dormant Spray Application in a Glenn County Prune Orchard

I. Introduction

The Glenn County Surface Water Stewardship Program (GCSWSP) is comprised of local growers, pest control advisors, academic institutions and government agencies. The program was formed in 1997 to reduce the offsite movement of agricultural pesticides, fertilizers, and soil. Activities include providing outreach to industry, developing management practice demonstration sites, and cooperating with other agencies in management practice tests (GCSWSP, 2001; DPR, 2002). This study was a cooperative project between the GCSWSP and the California Department of Pesticide Regulation (DPR), and was conducted at an orchard floor cover crop demonstration site established by GCSWSP five years ago.

Diazinon has been detected in surface waters during the winter dormant spray season at levels that may adversely affect aquatic life. Esfenvalerate is used as a replacement for diazinon in stone fruit and nut orchards. Statewide there were 8,952 lbs of esfenvalerate used in fruit and nut orchards during the 2000-2001 dormant season. Nearly 1,800 lbs were used in the six counties (including Glenn) in the upper Sacramento and Feather River Watersheds (DPR, 2001). The physicochemical properties of esfenvalerate and diazinon are different, with esfenvalerate displaying a much greater tendency to sorb to soil. However, esfenvalerate dormant season application practices are similar to diazinon, and reliable monitoring data for evaluating potential off-site movement of dormant season pyrethroids from orchards, including esfenvalerate, are sparse. Consequently the potential for esfenvalerate surface water impacts is poorly understood. This study was designed to examine the rainfall runoff potential of dormant spray esfenvalerate in a prune orchard with managed floors during two rain events.

II. Study Objectives

The objectives of this study were to (a) evaluate the potential for runoff of esfenvalerate from dormant-season applications in orchards and (b) compare the effects of two orchard floor management practices on runoff. These evaluations were based on three types of samples:

1. Whole-water rainfall runoff samples taken from orchard floor row middles,
2. Edge-of-field whole-water samples taken from a drainage ditch receiving runoff from the treated orchard, and
3. Post-runoff soil and sediment samples from the orchard floor and drainage ditch.

III. Study Site The study site was a 300-acre French prune orchard located near the town of Artois, Glenn County, California (Figure 1). Forty-eight rows in a solid block within the orchard were planted with various cover crops in 1998 as part of a research and demonstration project. This study was conducted within the demonstration block. Each orchard row measures approximately 0.25 miles in length and drains down a 3% slope to a ditch at the low end of the field. All water that collects in the drainage ditch flows into a large holding pond at the bottom of the orchard. Trees in the orchard are planted on berms that prevent water from flowing between rows. Orchard soil consists mainly of Tehama Silt Loam transitioning at the extreme upper edge from Cortina Very Gravelly Sandy Loam (USDA, 1968).

Samples were collected from twelve plots (rows) within the demonstration block (Figure 2). Six rows consist of a well-established perennial sod cover crop that had been maintained and periodically re-seeded with dwarf perennial rye (60%), creeping red fescue (20%), and Chewing's fescue (20%) over 5 years. The other six rows have bare ground floors that are treated several times a year with both contact and pre-emergent herbicides to control vegetative growth.

For this study each of the twelve rows was bermed with an earthen dam near the low end of the field to collect runoff. Small sump pumps with flow meters were installed in each row at the earthen dams. These pumps served to move water over the dam to prevent water from overflowing berms and moving between rows, and to measure runoff volume moving off-site from the experimental plots.

During January and February of 2003, there was a twenty-day gap in significant precipitation at the study site (Figure 3). Strong North winds during that time prevented esfenvalerate applications at the site and also created very dry soil conditions. The wind eventually decreased, and esfenvalerate was applied to the orchard on February 8. On February 12, four days after application, it began to rain. A rain gauge at the site recorded 8/10 inch of rain fell over night. The rainfall was sufficient to cause runoff and one set of samples was collected during the early morning of the 13th. A second, more substantial event occurred on the 15th, seven days after application. One inch of rain fell over night. Three additional runoff samples were taken at intervals throughout the second precipitation event.

IV. Study Design

A. Esfenvalerate in-field runoff and cover crop effects.

This portion of the study was a designed experiment with the objectives of quantifying within-orchard whole water esfenvalerate runoff concentrations and runoff water volumes, and to compare the effect of two different floor management treatments on off-site movement of esfenvalerate. These treatments were a perennial sod cover crop planted in row middles, and bare ground in the middles. Each treatment was replicated six times for a total of twelve study plots. Composite background soil samples were taken prior to treatment in the study rows to determine residual levels of esfenvalerate.

One whole-water sample was taken from each plot during the first significant precipitation event, 5 days following application. Three additional water samples were taken from each row at regular intervals during a second rain event, 7 days following application, for a total of 48 samples. Post-event soil samples were taken at each plot 25 days after application to determine the amount of esfenvalerate remaining on site.

B. Esfenvalerate movement off-site to edge-of-field drainage ditch and holding pond.

The second portion of this study consisted of collecting observational esfenvalerate concentration data in whole-water and bed sediment in the adjacent drainage ditch and holding pond that received runoff from the orchard. Post-runoff dissipation of esfenvalerate in the holding pond was not part of this study due to resource constraints.

Background soil samples were taken from the dry drainage ditch and whole-water grab samples were collected from the holding pond prior to application to determine residual levels of esfenvalerate. Following application, whole-water grab samples were taken from both the drainage ditch and the holding pond during the first significant precipitation event. Another set of samples was taken from the ditch and pond during the second rain event. Companion samples were collected during each sampling to determine suspended sediment concentrations in the runoff. Post-runoff event soil samples were taken from the drainage ditch 25 days after application to determine esfenvalerate remaining.

V. Materials and Methods

A. Esfenvalerate Application

Esfenvalerate was aerially applied to the entire orchard on February 8, 2003. A spray tank sample was taken from the helicopter to determine esfenvalerate concentration in the application mix, and the volume applied was recorded. These data yielded an application rate of 9.6 ounces/acre (0.05 lbs active ingredient/acre). Label rates for dormant applications of Asana ® XL range from 8 to 14.5 fluid ounces per acre (0.04 - 0.075 lbs active ingredient/acre) (Dupont, 2003). Data taken from 2000 to 2001 PUR database for prunes in the six northern counties that make up the Sacramento and Feather River Watersheds show that the majority of growers use less than full label rates for dormant applications (PUR, 2000 and 2001). Of the total of 463 dormant applications to prunes, 76% of growers used the lowest recommended label rates (Figure 4).

B. <u>Samples</u>

Background Samples

Background soil samples were taken prior to treatment in the study rows to determine residual levels of esfenvalerate. Samples were collected by driving two inch diameter steel tubes into the soil to a depth of 1 inch. Samples were composited into glass mason jars.

Whole-Water Runoff Samples

Within row whole-water samples were taken from holes augered into the orchard floor just above the earthen dam. Water was collected directly into 1 liter amber glass bottles and capped with Teflon® lined lids. Samples were stored on wet ice for transport to the lab for analysis.

Post Event Samples

Post event soil samples were collected in the same manner as the background samples described above. Two samples were taken in each treatment row, for a total of twenty-four samples. Four samples were taken from the drainage ditch.

C. <u>Chemical Analysis</u>

Esfenvalerate

All esfenvalerate analyses were conducted by the California Department of Food and Agriculture Center for Analytical Chemistry (CDFA). The esfenvalerate water samples were extracted *in tot*o, without filtration, and extracting solvent was used to rinse the sample bottles to insure complete removal of any esfenvalerate adsorbed to the glass container.

Analyses of esfenvalerate in water, soil and sediment were accomplished using gas chromatography with electron capture detection (GC/ECD). Gas chromatography with a mass selective detection (GC/MSD) was used to confirm the soil and sediment samples. Method reporting limits are given in Table 1. Ongoing quality control samples were submitted with field samples as blind spikes (Tables 2-4).

Suspended Sediment

Suspended sediment measurements were performed on companion samples collected at the same sampling location and time as the whole-water samples. Measurement was conducted by vacuum filtration of the samples and subsequent oven drying of the filtrate collected on tared oven-dried filters. The estimated suspended sediment MDL was 0.01g/L.

VI. Results

A. <u>Pre-application background samples</u>

All background soil and sediment samples taken from the orchard floor and drainage ditch were below reporting limits (Table 1). Background whole-water samples taken from the holding pond were also below reporting limits.

B. Runoff water volumes

The unexpectedly large volumes of runoff overwhelmed the pumping units, so no quantitative reliable estimates of runoff water volume were obtained from the experimental plots. However, it was evident from visual observation that runoff volumes were greatest in the bare ground rows as compared to the cover cropped rows.

C. Esfenvalerate whole-water samples

Esfenvalerate concentrations in whole-water rain runoff were highly variable, ranging from below the reporting limit of 0.05 ug/L up to a maximum of 5.39 ug/L (Table 5). Within each orchard floor treatment, esfenvalerate concentrations generally decreased as sampling progressed (Table 6). A multiple analysis of variance (MANOVA) indicated a significant difference between mean esfenvalerate concentrations in the cover crop and bare ground treatments for at least one sampling period (p=0.016). Subsequent univariate t-tests demonstrated that although mean concentrations at sampling times 1, 2 and 4 were lower in the cover crop treatment than in the bare ground treatment, only sampling times 2 and 4 were significantly different at the $\alpha = 0.05$ level (Figure 5).

The number of drainage ditch water samples was limited, but those concentrations were comparable to the esfenvalerate concentrations measured in the field runoff samples, ranging from 0.424 to 3.06 µg/L (Table 5). Concentrations of esfenvalerate measured in the drainage pond ranged from 0.0725 to 0.473 µg/L. Post-storm event dissipation of esfenvalerate in the drainage pond was not part of this study due to resource constraints.

Suspended sediment concentrations in runoff samples ranged from 0.01 to 0.60 g/L.

D. Post-runoff event samples

Esfenvalerate concentrations in post-runoff row middle soil samples were highly variable, ranging from less than reporting limits to 0.479 µg/g dry soil (Table 6). Figure 7 illustrates the wide range of soil concentrations in the post-runoff row middles samples. Although the median post-runoff row middles soil concentrations were higher in the cover crop treatment (0.043 ug/g dry soil) than the bare ground treatment (0.018 ug/g dry soil), the differences were not significant at the $\alpha = 0.05$ level based on a nonparametric Kruskal-Wallis test for equality of medians. By way of comparison, the application rate of 0.05 lbs esfenvalerate/acre corresponds to a soil concentration of ~ 0.33 ug/gram soil assuming a bulk density of 1.5g soil/cm^3. Based on a similar calculation the overall median soil concentration of 0.028 ug/ g dry soil corresponds to a recovery of approximately 10% of the initial esfenvalerate application in the row middles.

VII. Acknowledgements

We would like to extend our gratitude to Craig Vereschagin of Three V Ranch for the use of his property, without his cooperation this project would not have been possible. We would like to acknowledge Ed Romano, Bill Duckworth and Rey Lopez of the Glenn County Department of Agriculture for their outstanding work on the Glenn County Surface Water Protection Project. We thank the following collaborators: Fred Thomas of CERUS Consulting supplied cover crop expertise, Craig Compton with Avag Inc. provided the aerial application, and Fred Degiorgio and Fred Marmor of DuPont donated the Asana.

We would also like to thank Dr. Frank Zalom and Mike Oliver of UC Extension for the design and loan of the pumping units. We appreciate the hard work from DPR's Environmental Monitoring program, especially Roger Sava and Jesse Ybarra.

VIII. References

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VIII. Method detection limits, Quality Control and Analytical Data

Table 1. Method reporting limits

Pyrethroid Pesticides in Surface Water Method: GC/ECD		Pyrethroid Pesticides in Soil and Sediment Method: GC/ECD, confirmed with GC/MSD	
Compound	**Reporting Limit (µg/L)**	**Compound**	**Reporting Limit (µg/g - wet weight basis)**
Esfenvalerate	0.05	Esfenvalerate	0.011

Table 2. Continuing Quality Control- Esfenvalerate in whole water

Extraction Date	Sample Numbers	Percent Recovery Esfenvalerate
11/25/2002	100, 101, (24)	123
2/14/2003	108,109,110, 112-117	121
2/14/2003	103-107	85.0
2/19/2003	118-125	111
2/19/2003	126-134	130
2/20/2003	135-142,(158)	122
2/20/2003	152-157,(159-160)	135*
3/10/2003	143-151	110
	Average Recovery	117
	Standard Deviation	15.5
	CV	13.2
	Upper Control Limit	131
	Upper Warning Limit	121
	Lower Warning Limit	80.2
	Lower Control Limit	70.0

*Highlighted cells are percent recoveries exceeding control limits. Blind spikes in parenthesis.

Table 3. Continuing Quality Control- Sediment Analysis

Extraction Date	Sample Numbers	Percent Recovery Fenvalerate/Esfenvalerate
11/22/2002	500-507	111
3/7/2003	516-525	135
3/6/2003	508-515	84.0
3/11/2003	526-535	148
	Average Recovery	120
	Standard Deviation	28.2
	CV	23.6
	Upper Control Limit	149
	Upper Warning Limit	137
	Lower Warning Limit	87.4
	Lower Control Limit	74.7

Table 4. Blind Spike Data for Study 215 whole water samples

Extraction Date	Sample Number	Analyte	Spike Level (ug/L)	Recovery	Percent Recovery	Exceed CL [a]
11/25/2002	24	Esfenvalerate	0.25	0.290	116	No
		Permethrin	0.3	0.372	124	UWL
2/20/2003	158	Esfenvalerate	0.2	0.227	114	No
2/20/2003	159	Esfenvalerate	0.2	0.215	108	No
2/20/2003	160	Esfenvalerate	0.5	0.455	91.0	No
2/20/2003	161	Esfenvalerate	0.4	0.408	102	No

[a] CL=Control Limit; Upper CL (UCL), Lower CL (LCL).

Table 5. Whole Water Esfenvalerate Concentrations in Runoff

		Esfenvalerate Concentration (µg/L)			
		Precipitation Event 1	Precipitation Event 2		
Row	Treatment		Time 1	Time 2	Time 3
1	Cover Crop	0.705	0.589	0.849	0.293
3	Cover Crop	0.562	0.367	0.215	0.154
6	Cover Crop	1.23	0.528	0.561	0.615
7	Cover Crop	1.78	0.769	1.52	0.518
9	Cover Crop	NS*	0.332	0.456	0.168
12	Cover Crop	1.12	0.618	1.16	0.103
2	Bare Ground	1.39	1.99	0.711	0.784
4	Bare Ground	2.37	1.78	0.963	0.481
5	Bare Ground	3.44	1.9	1.26	0.635
8	Bare Ground	3.68	0.928	0.584	0.597
10	Bare Ground	5.39	1.53	0.578	0.639
11	Bare Ground	N/D**	0.948	0.643	0.555
drainage ditch 1		NS*			0.476
drainage ditch 2		3.06			0.424
pond 1		0.167			0.473
pond 2		0.0725			0.452

* NS- No sample taken- insufficient runoff.
** N/D Non-detect, concentration below reporting limit.

Table 6. Treatment mean esfenvalerate runoff concentrations in whole-water samples.

	COVER CROP		BARE GROUND	
Sample period	mean conc. ± standard error $\mu g\ L^{-1}$	N	mean conc. ± standard error $\mu g\ L^{-1}$	N
1	1.08 ± 0.22	5	2.72 ± 0.77	6[A]
2[B]	0.53 ± 0.07	6	1.51 ± 0.19	6
3	0.79 ± 0.20	6	0.79 ± 0.11	6
4[B]	0.31 ± 0.09	6	0.62 ± 0.04	6

[A] One nondetection assigned value of 1/2 reporting limit, = 0.025 $\mu g\ L^{-1}$
[B] Significant treatment effect, p=0.001 and 0.03 for sampling periods 2 and 4, respectively.

Table 7. Post-Runoff Soil Esfenvalerate Concentrations (ppm, ug/ gm dry soil)

		Esfenvalerate Concentration (ppm)	
Row	Treatment	Sample	Replicate
1	Cover Crop	0.038	0.156
3	Cover Crop	0.479	0.151
6	Cover Crop	N/D*	N/D
7	Cover Crop	0.031	0.246
9	Cover Crop	0.048	N/D
12	Cover Crop	0.026	0.099
2	Bare Ground	0.033	0.153
4	Bare Ground	0.097	0.018
5	Bare Ground	0.017	0.015
8	Bare Ground	N/D	N/D
10	Bare Ground	N/D	N/D
11	Bare Ground	0.018	0.041
drain ditch 1		N/D	
drain ditch 2		N/D	
drain ditch 3		N/D	
drain ditch 4		N/D	

* N/D Non-detect, concentration below reporting limit.

Figure 1. Study location and 2000 - 2001 dormant spray esfenvalerate use.

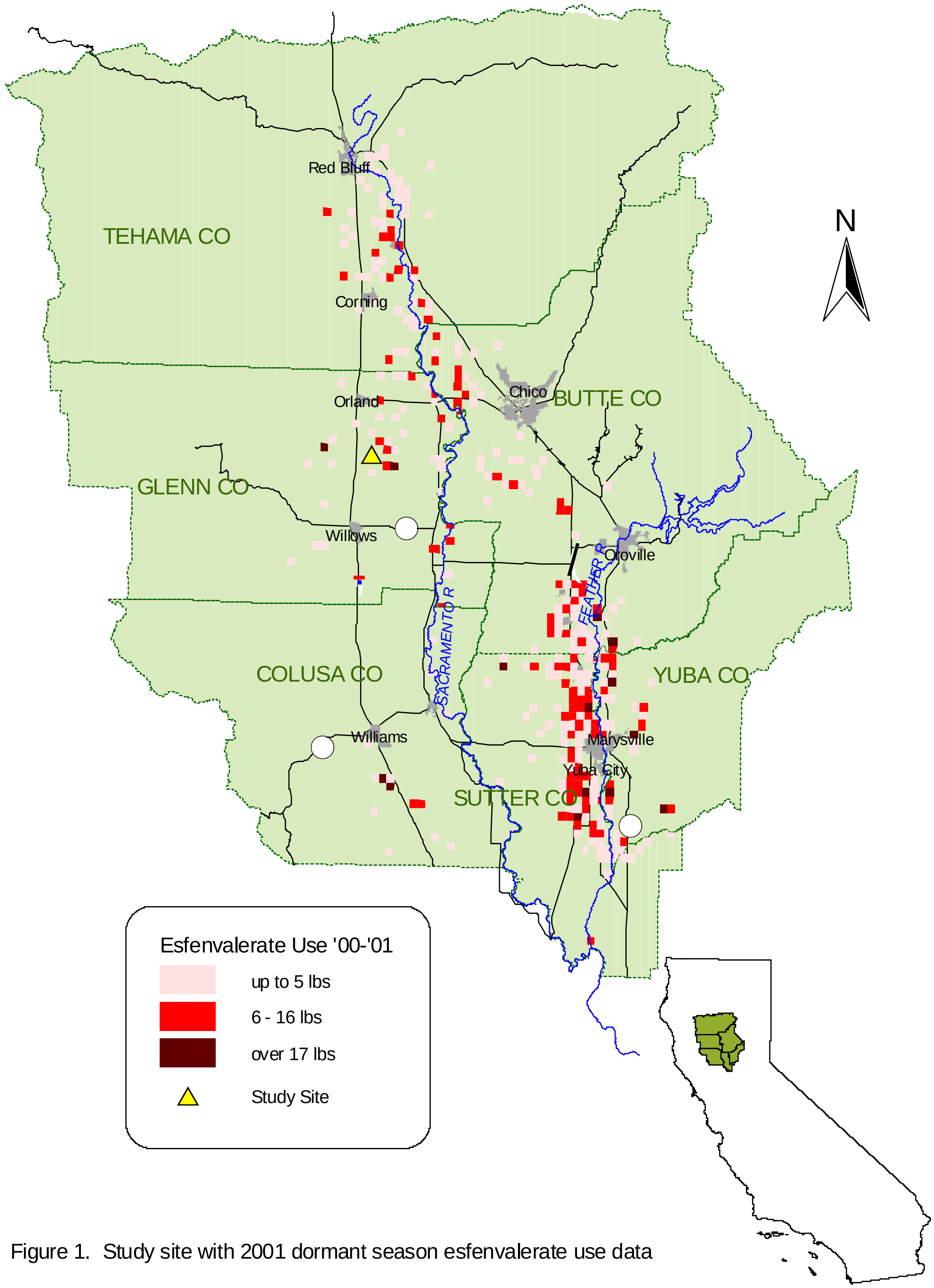
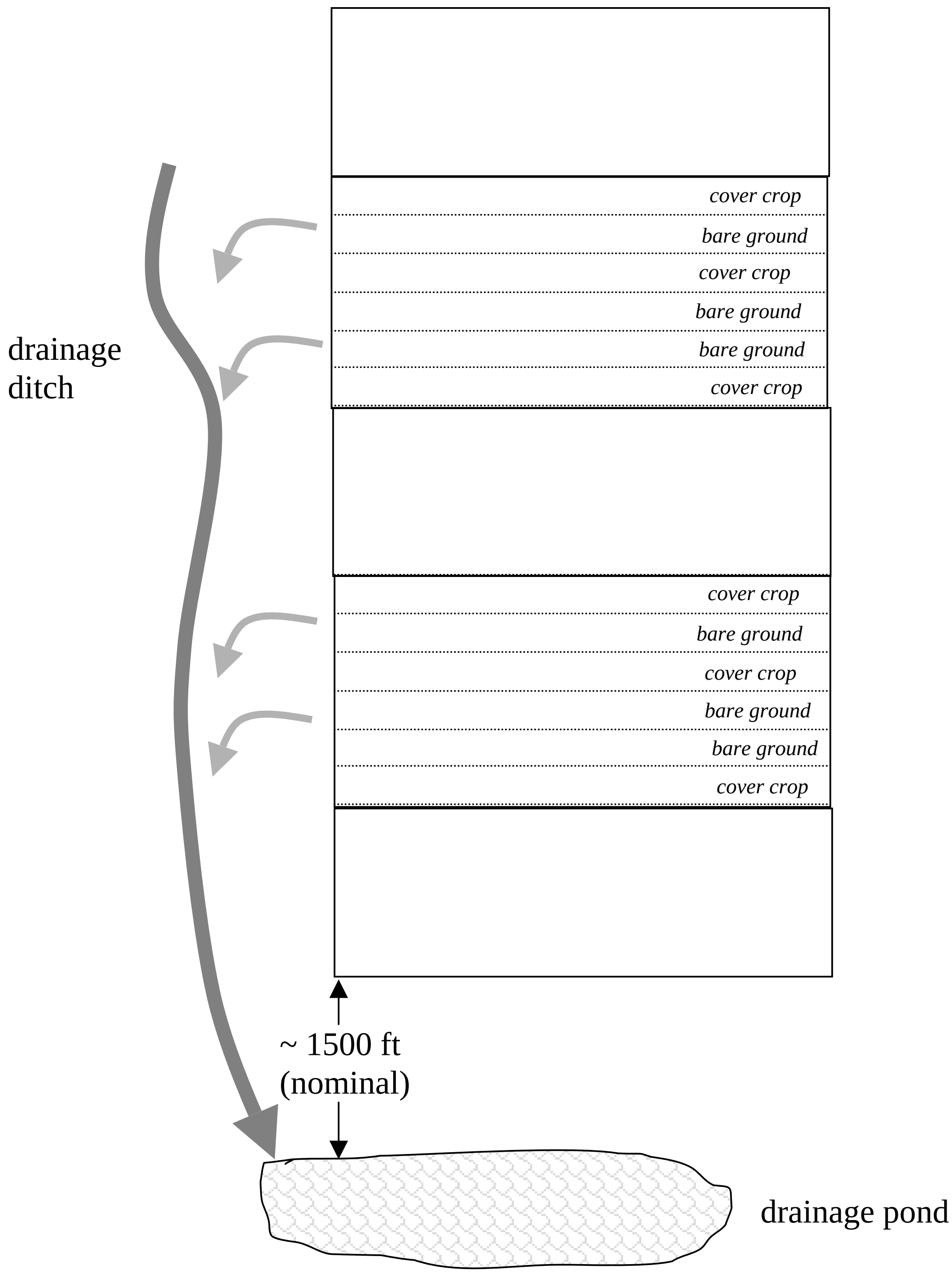


Figure 1. Study site with 2001 dormant season esfenvalerate use data

Figure 2. Schematic diagram of study area (not to scale).



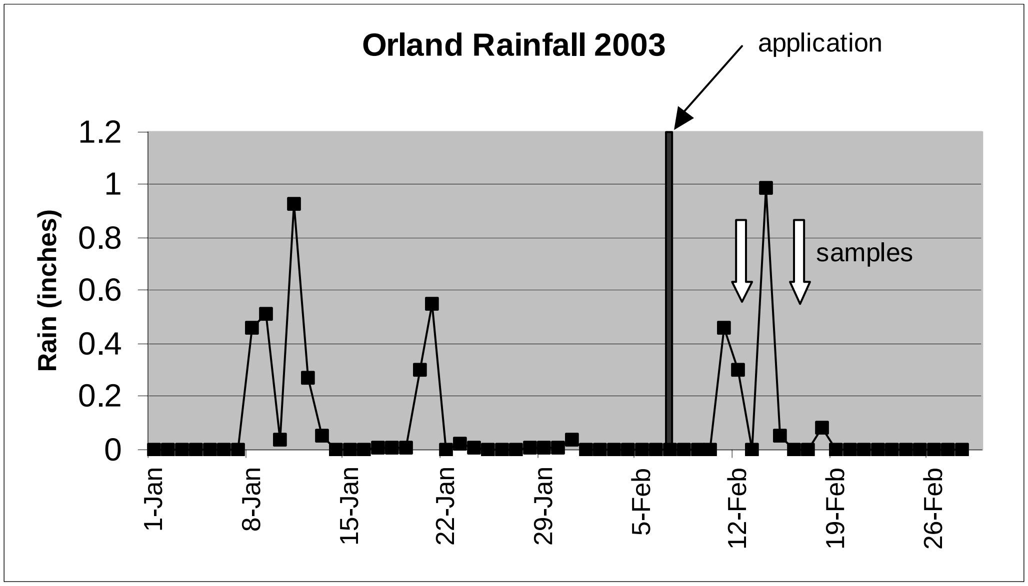


Figure 3. Precipitation data from UCIPM weather station Orland, CA (UCIPM, 2003).

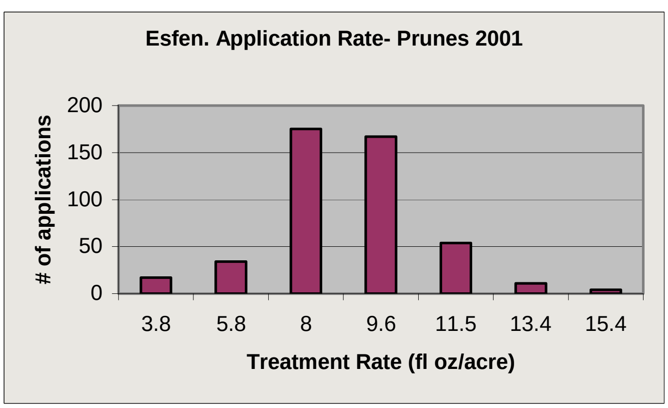


Figure 4. Dormant esfenvalerate application rates for prunes 2001.

Figure 5. Esfenvalerate concentrations (treatment mean ± standard error) for each sampling period. Treatment means for periods 2 and 4 were significantly different (p=0.001 and 0.03, respectively).

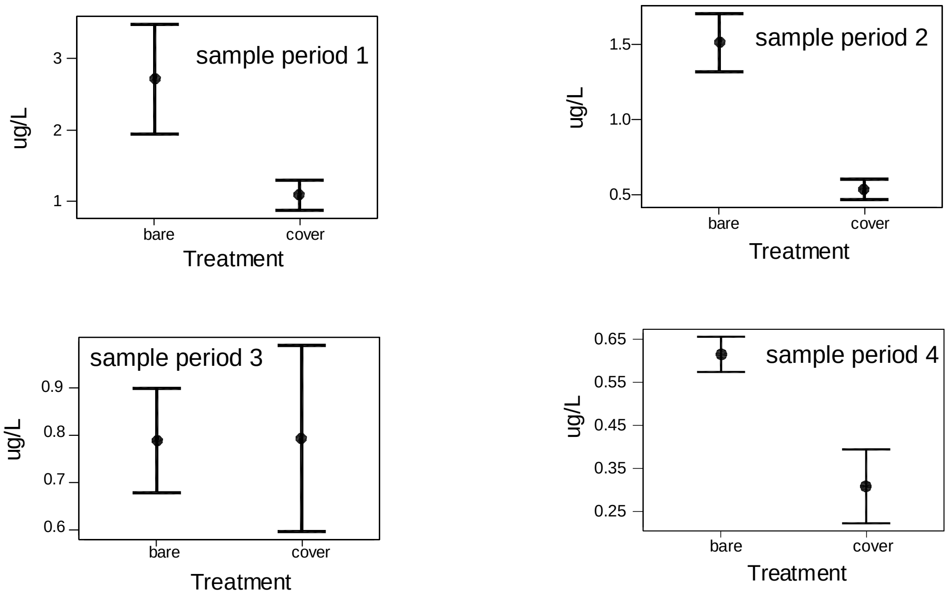


Figure 6. distribution of post-runoff esfenvalerate soil concentrations