Department of Pesticide Regulation
Environmental Monitoring
1001 I Street
Sacramento, California 95812
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STUDY #205: PROTOCOL FOR MONITORING THE OCCURRENCE AND TYPICAL CONCENTRATION OF ESFENVALERATE AND PERMETHRIN PYRETHROIDS.

I. INTRODUCTION

In the Sacramento and San Joaquin valleys there are more than 750,000 acres of almonds, nectarines, peaches, plums and prunes grown (Epstein et al., 2000). As part of integrated pest management, organophosporus (OP) insecticides are applied on these tree crops, generally with oil, to control the San Jose scale, the peach twig borer, aphids and other pests. This is done primarily between December and February when trees are dormant, allowing for better pesticide coverage to achieve effective control of pests. The dormant-spray application season coincides with seasonal rainfall, thus increasing the likelihood of OP insecticides to move offsite, dissolved in water or attached to sediment, to surface waters. Various monitoring studies conducted by the California Department of Pesticide Regulation (CDPR) and U.S. Geological Survey (USGS) have shown that detections of OPs such as diazinon were observed during dormant-spray seasons (Ross et al., 1996; Domagalski et al., 1997; Kratzer, 1998).

CDPR is required to protect the environment, including surface water, from environmentally harmful pesticides (Food and Agricultural Code, section 11501). CDPR has asked growers to voluntarily take measures to reduce water contamination from OPs during the rainy season (Bennett et al., 1998). Since 1992, use of OPs during the dormant-spray season has been steadily decreasing, but there are indications that they are being replaced by pyrethroids, specifically esfenvalerate and permethrin, in California (Epstein et al., 2000).

The risk of negative environmental impact to surface waters from esfenvalerate and permethrin use is uncertain. Physico-chemical characteristics indicate a potential for esfenvalerate and permethrin to move offsite with sediment and the potential for an acute toxicity threat to aquatic organisms (Table 1). The lack of monitoring data for these pesticides necessitates a need for current monitoring.

Additionally, due to their known presence in surface waters, specific organophosphate insecticides that are in use during the dormant season will be monitored. Selected herbicides that are applied during the fall will also be monitored in order to gain more information about their residues in surface waters.

II. OBJECTIVE

The purpose of this monitoring project is to determine if esfenvalerate and permethrin are moving offsite into surface waters in measurable amounts, and if so, what is the typical range of concentrations that may be observed. This data will be used to determine if there is a need for further study. This project will also help further characterize winter runoff of organophosphate insecticides and selected herbicides.

III. PERSONNEL

This study will be conducted by staff from the Environmental Monitoring Branch, Agriculture Program under the general direction of Marshall Lee, Senior Environmental Research Scientist, Supervisor. Key personnel are listed below:

Project Leader:	Juanita Bacey
Field Coordinator:	Sheri Gill (Butte County) / Keith Starner (Stanislaus County)
Senior Scientist:	Frank Spurlock
Laboratory Liaison:	Carissa Ganapathy
Chemists:	To be determined

Questions concerning this monitoring project should be directed to Juanita Bacey at (916) 445-3759.

IV. STUDY PLAN

Four monitoring sites were chosen that reflect areas with the heaviest historical applications of esfenvalerate and permethrin through the dormant-spray season (Figures 1-4). The following factors were also considered in evaluating the desirability of these sites for monitoring:

- previous detections of diazinon during dormant-spray seasons
- proximity of monitoring locations to application sites

In addition, site selection followed the general guideline in Standard Operating Procedure (SOP) FSWA002.00 (Bennett, 1997).

Monitoring will occur during two storm events in the dormant-spray season of 2001-2002. The number and frequency of samples collected will depend on the intensity and duration of the runoff event. Ideally, each site will be sampled on an hourly basis, for a total of ten hours. A sufficient number of rain event samples will be collected to maximize the likelihood that peak concentrations of pesticides were captured.

Whole water collected from each site will be analyzed for esfenvalerate and permethrin. Due to the known aquatic toxicity of currently used OPs, and their presence in surface waters during this period, these will also be monitored, along with selected triazines. Carbamates will not be monitored due to the lack of detections in past dormant-spray monitoring. Samples will also be analyzed for total suspended sediment and acute toxicity to selected sensitive aquatic species.

V. SAMPLING METHOD

Each chemical screen, toxicity sample and sediment sample will be individually collected in 1-liter amber bottles. This will equate to seven 1-liter samples, each hour for ten hours, for a total of 70 samples per site. This is a total of 280 samples. All samples collected will be grab samples, collected as close to center channel as possible. The grab pole will consist of a 1-liter amber glass bottle at the end of an extended pole. Amber bottles will be sealed with Teflon-lined lids.

Samples will be transported and stored on wet ice or refrigerated at 4^{o}C until extraction for chemical analysis or toxicity testing. Dissolved oxygen, pH, specific conductivity, and water temperature will be measured *in situ* at each site during each sampling period.

VI. CHEMICAL AND AQUATIC TOXICITY ANALYSIS

Chemical analyses will be performed by the California Department of Food and Agriculture's Center for Analytical Chemistry. Quality control will be conducted in accordance with Standard Operating Procedure QAQC001.00 (Segawa, 1995). Ten percent of the total number of analyses will be submitted with field samples as field blanks and blind spikes.

Gas Chromatography (GC) will be used to determine concentrations of OPs. A method for determining esfenvalerate and permethrin concentrations is currently being developed by CDFA. Comprehensive chemical analytical methods will be provided in the final report. The reporting limit will be used to record the lowest concentration of analyte that the method can detect reliably in a matrix blank. Method titles and reporting limits for this study are reported in Table 2. The Department of Fish and Game's Aquatic Toxicology Laboratory will perform aquatic toxicity tests. Acute toxicity will be determined using a 96-hour, static-renewal bioassay in undiluted sample water.

VII. DATA ANALYSIS

Concentrations of insecticides in water will be reported as micrograms per liter (µg/L). Toxicity data will be presented as percent survival. Water concentrations will be compared with toxicity data to aid in the interpretation of toxicity test results.

VIII. TIMETABLE

Chemical Analytical Method Development:	October through December 2001
Field Sampling:	January through February 2002
Chemical Analysis and Toxicity Testing:	January through April 2002
Preliminary Memorandum:	September 2002
Final Report:	December 2002

IX. REFERENCES

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Table 1. ESFENVALERATE AND PERMETHRIN PHYSICAL CHARACTERISTICS

Pesticide	Koc	Solubility (mg/l)	Env. Fate on Soil (days)	Env. Fate in Water (days)	Toxicity *Daphnia Magna* (ppb)
Esfenvalerate	1000-12,000[a]	0.0002 [a]	14 - 75 [a]	stable [a]	0.15 [c]
Permethrin	10,471-86,000[a]	0.006 [a]	6 - 106 [a]	3-42 [b]	0.1-0.3 [c]

a–ARSUSDA b–DPR c–U.S.EPA

TABLE 2. CALIFORNIA DEPARTMENT OF FOOD AND AGRICULTURE, CENTER FOR ANALYTICAL CHEMISTRY ORGANOPHOSPHATE AND TRIZINE/HERBICIDE PESTICIDES.

Organophosphate Pesticides in Surface Water by GC
Method: GC/FPD

Compound	Reporting Limit (µg/L)
Azinphos methyl	0.05[1]
Chlorpyrifos	0.04[1]
Diazinon	0.04[1]
DDVP (dichlorvos)	0.05[1]
Dimethoate	0.05[1]
disulfoton	0.05[1]
ethoprop	0.05[1]
Fenamiphos	0.05[1]
Fonofos	0.05[1]
Malathion	0.05[1]
methidathion	0.05[1]
Methyl Parathion	0.05[1]

Organophosphate Pesticides in Surface Water by GC
Method: GC/FPD

Compound	Reporting Limit (µg/L)
Phosmet	0.05[1]
Thimet (Phorate)	0.05[1]
Profenofos	0.05[1]
Tribufos	0.05[1]

Pyrethroid Pesticides in Surface Water
Method: To be determined

Compound	
Esfenvalerate	0.05[1]
Permethrin	0.05[1]

Triazines/Herbicides in Surface Water by HPLC
Method: HPLC/Post Column-fluorescense

Compound	Reporting Limit (µg/L)
Atrazine	0.05
Bromacil	0.05
Diuron	0.05
Hexazinone	0.05
Metribuzin	0.05
Norflurazon	0.05
Prometon	0.05
Prometryn	0.05
Simazine	0.05
AEA	0.05
ACET	0.05
DACT	0.05

1. Reporting limit subject to change pending method validation.

Document Review and Approval
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Document Title: Study #205: Protocol for monitoring the occurrence and typical concentration of esfenvalerate and permethrin pyrethroids.

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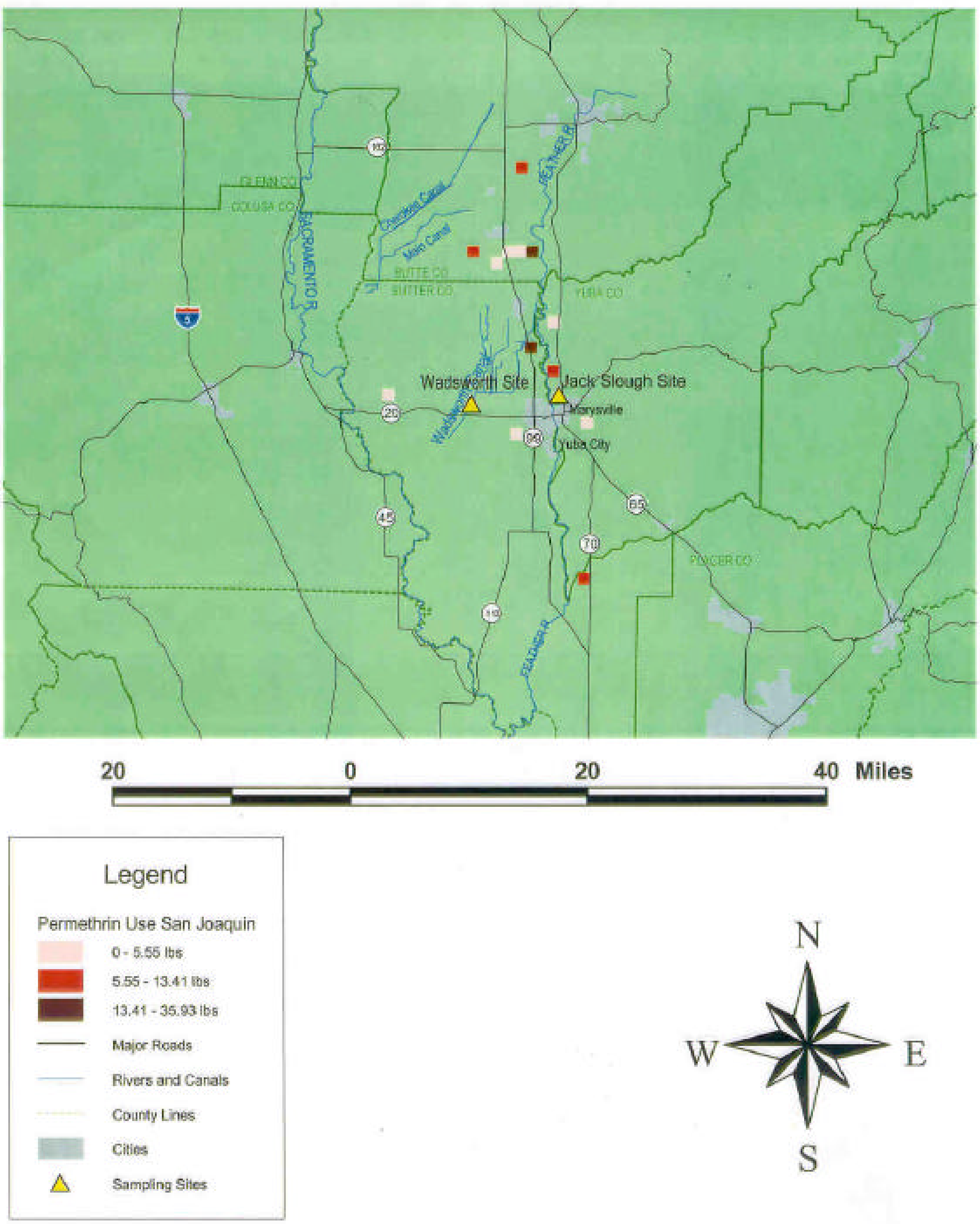
Permethrin Use Dec, Jan, Feb 2000



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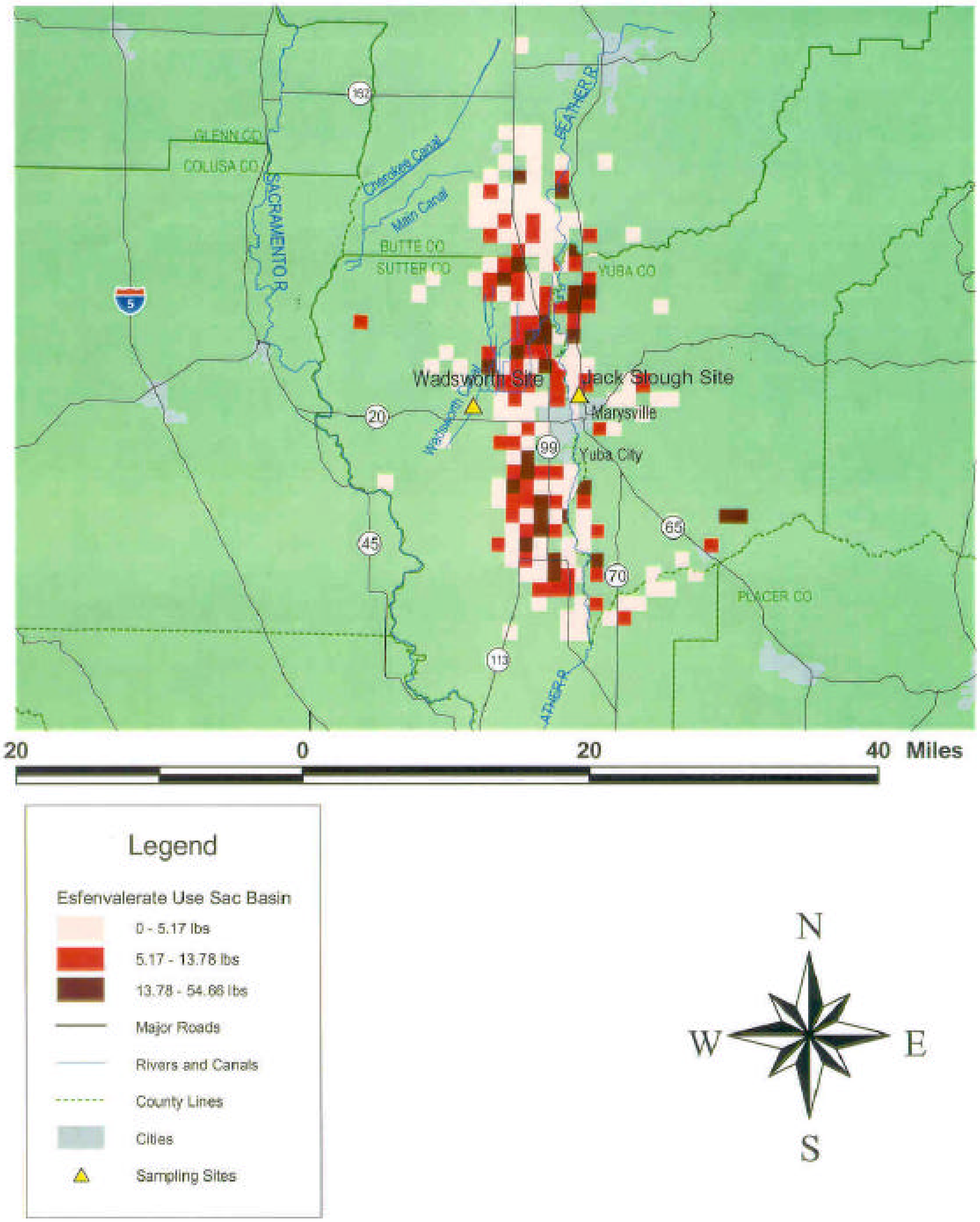

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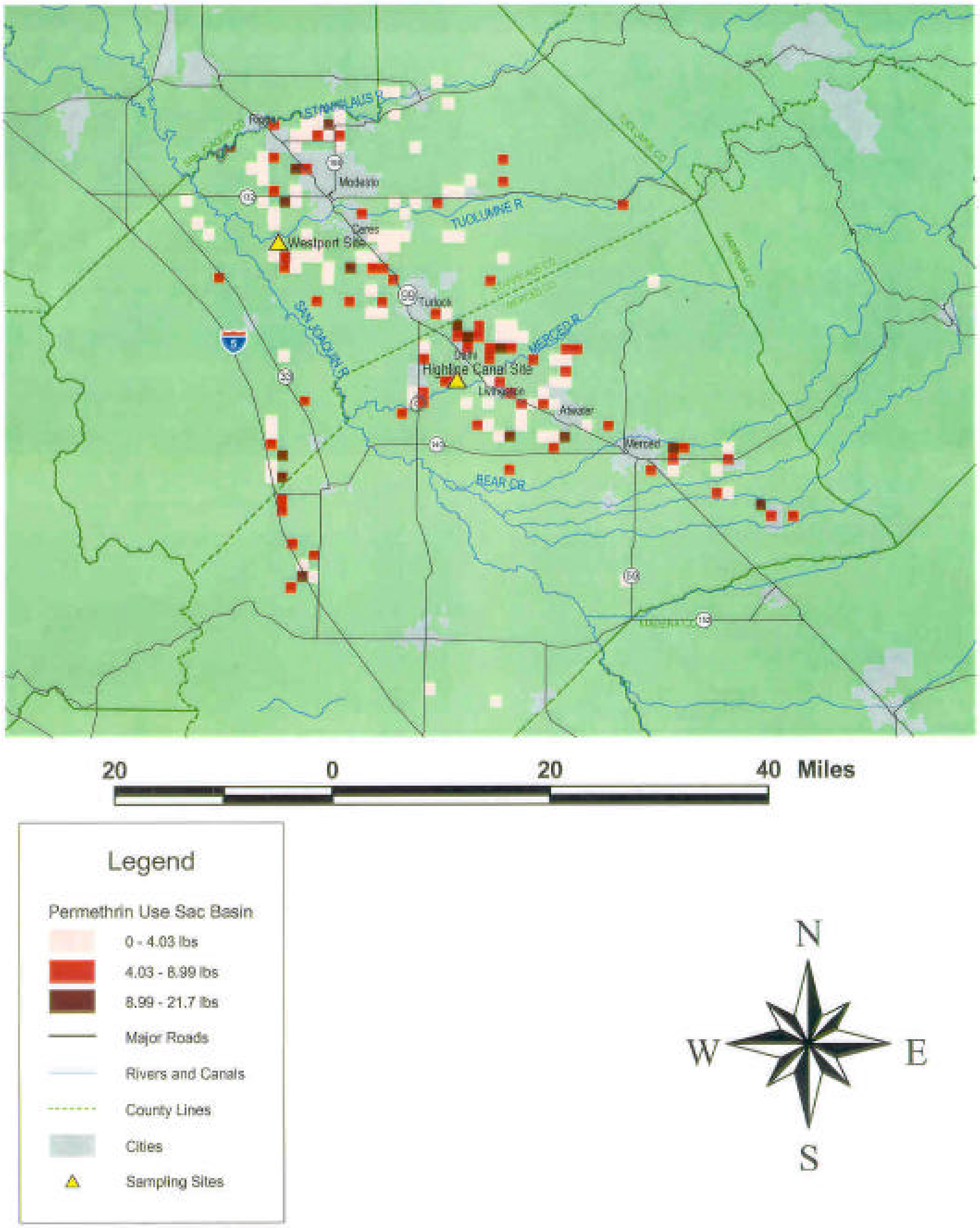

Esfenvalerate Use Dec, Jan, Feb 2000