Department of Pesticide Regulation
Environmental Monitoring
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Sacramento, California 95812

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STUDY #214: PROTOCOL FOR MONITORING THE OCCURRENCE AND 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 dormant 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 (DPR) 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).

DPR is required to protect the environment, including surface water, from environmentally harmful pesticides (Food and Agricultural Code, section 11501). DPR 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). Previous monitoring was conducted during two storm events in the dormant-spray season of 2001-2002 (study memo 205). However, sampling events were not representative of typical winter dormant spray runoff events due to very limited rainfall. Consequently the study is being repeated this year to achieve the study objectives.

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, Surface Water Protection Program under the general direction of Kean S. Goh, Agriculture Program Supervisor IV. Key personnel are listed below:

Project Leader:	Juanita Bacey
Field Coordinator:	Keith Starner
Senior Scientist:	Frank Spurlock
Laboratory Liaison:	Carissa Ganapathy
Chemists:	CDFA Center for Analytical Chemistry Staff

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): Wadsworth canal at South Butte road and Jack Slough at highway 70 both in the Yuba City area, and Del Puerto creek at Vineyard road and Highline canal at Griffith road in the Turlock area. 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 2002-2003. 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 minimum of 8 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.

Sediment samples will also be collected and analyzed for esfenvalerate and permethrin. Background samples will be collected once in November prior to the start of dormant-spray applications. Samples will then be collected at the start and at the end of each water-sampling event, and then again seven and fourteen days after the storm event.

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 total suspended sediment sample will be individually collected in 1-liter amber bottles. This will equate to seven 1-liter samples, each hour for approximately 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.

Sediment samples will be collected using a hand scoop. The top 1-inch of sediment will be collected in the waters edge and placed into a 1-pint clear, glass jar. This will be repeated approximately 3 times until the 1-pint jar is three-quarters full.

All water samples will be transported and stored on wet ice or refrigerated at $4^{o}C$ until extraction for chemical analysis or toxicity testing. Sediment samples will be transported on wet ice and then placed in a freezer until extraction. 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.

The following will be used to determine concentrations of pesticides:

- OPs - GC/FPD - gas chromatography/flame phometric detector
- Pyrethroids - GC/ECD - gas chromatography/electron capture detector, confirmed with GC/MS
- Triazines - LC/MS/MS – liquid chromatography/atmospheric pressure chemical ionization mass spectrometry

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 2002
Field Sampling:	January through February 2003
Chemical Analysis and Toxicity Testing:	January through April 2003
Preliminary Memorandum:	September 2003
Final Report:	December 2003

IX. BUDGET

Primary Analysis			Cost ($300/sample)
OPs	10 samples x 4 sites x 2 storm events	= 80 samples =	$ 24,000
DI	10 samples x 4 sites x 2 storm events	= 80 samples =	24,000
Triazines	10 samples x 4 sites x 2 storm events	= 80 samples =	24,000
Esfen./Permethrin	10 samples x 4 sites x 2 storm events	= 80 samples =	24,000
Esfen./Permethrin[1]		32 samples =	9,600
Toxicity	10 samples x 4 sites x 2 storm events	= 80 samples =	24,000
Quality Control			
Blind spikes	8 samples x 5 analysis	= 40 samples =	12,000
Field blanks	4 samples x 2 sites x 2 storm events	= 16 samples =	4,800
Total Analysis Cost			**$146,400**

1. Sediment chemistry analysis

Personnel: 14 hours estimated per storm event

Staff	Rate	Hours	Cost	Overtime Rate	
(1) Assoc. Env. Scientist	$25/hr	8	$200	$25/hr	
(5) Env. Scientist	$20/hr	8	800	$31/hr	
(1) Senior & Supervision	$32/hr	1	32	$32/hr	
Staff Benefits	31%		320	31%	
(1) Scientific Aides	$11/hr	8	88	$16.50/hr	
Staff Benefits	10.73%		10	10.73%	
(1) Student Assistants	$10/hr	8	80	$10/hr	
Admin. on personnel services	31.15%		477	31.15%	
Total (straight time)			$ 2,007	Total Overtime	$2,135 to $4,902[1]

1. Estimated at 6 to 14 hours, depending on when the storm event occurs, for staff members as listed above.

Per diem & lodging: Necessary only if an overnight stay is required. $260/site/storm event

Total Staff/Lodging Costs: **$4,142 to $5,942/storm event**

IX. REFERENCES

ARSUSDA. 2001. Agricultural Research Service, U.S. Department of Agriculture. [Online] Available: http://www.arsusda.gov/ppdb2.html

Bennett, K. 1997. Conducting Surface Water Monitoring for Pesticides. Environmental Hazards Assessment Program FSWA002.00. Department of Pesticide Regulation, Sacramento, CA.

Bennett K.P., C.E. Nordmark, J. Schuette, et al. 1998. Occurrence of aquatic toxicity and dormant-spray pesticide detections in the San Joaquin River Watershed, Winter 1996-1997. Environmental Hazards Assessment Program EH 98-02. Department of Pesticide Regulation, Sacramento, CA.

DPR. 2001. The California Department of Pesticide Regulation. Pesticide Chemistry Database.

Domagalski, J.L., N.M. Dubrovsky, and C.R. Kratzer. 1997. Pesticides in the San Joaquin River, California: Inputs from Dormant Sprayed Orchards. U.S. Geological Survey. Published in J. Environ. Qual. 26:454-465.

Epstein, L., S. Bassein, F.G. Zalom. 2000. Almond and stone fruit growers reduce OP, increase pyrethroid use in dormant sprays. California Agriculture, 54(6):14-19.

Kratzer C.R. 1998. Pesticides in storm runoff from agricultural and urban areas in the Tuolumne River Basin in the vicinity of Modesto, California. U.S. Geoogcl Survey. National Water-Quality Assessment Program. Water-Resources Investigations Report 98-4017.

Laskowski, D.A. 2002. Physical and Chemical Properties of Pyrethroids. Rev. Environ. Contam. Toxical., 174: 49-170.

Ross, L.J., R. Stein, J.Hsu, J. White, and K. Hefner. 1996. Distribution and mass loading of insecticides in the San Joaquin River, California: Winter 1991-2 and 1992-3. Department of Regulation. Environmental Hazards Assessment Program. Sacramento, California. Report # EH96-02.

Segawa, R. 1995. Chemistry Laboratory Quality Control. Environmental Hazards Assessment Program QAQC001.00. Department of Pesticide Regulation, Sacramento, CA.

U.S. EPA. 2002. ECOTOX Database System. [Online] Available: http://www.epa.gov/ecotox/

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]	72 [b]	0.15 [c]
Permethrin	10,471-86,000[a]	0.006 [a]	6 - 106 [a]	3-42 [d]	0.1-0.3 [c]

a–ARSUSDA b–Laskowski c–U.S.EPA d-DPR

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

Organophosphate Pesticides in Water
Method: GC/FPD

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

Pyrethroid Pesticides in Sediment
METHOD: GC/ECD, confirmed with GC/MSD (µg/g)

Esfenvalerate	0.01
Permethrin	0.01

Organophosphate Pesticides Water
Method: GC/FPD

Compound	**Reporting Limit (µg/L)**
Phosmet	0.05
Thimet (Phorate)	0.05
Profenofos	0.05
Tribufos	0.05

Pyrethroid Pesticides in Surface Water
Method: GC/ECD, confirmed with GC/MSD (µg/g)

Compound	
Esfenvalerate	0.05
Permethrin	0.05

Triazines/Herbicides in
Method: LC/MS/MS

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
DEA	0.05
ACET	0.05
DACT	0.05

Figure 1

Esfenvalerate use in the Sacramento watershed area of Yuba City, CA, Dec 2000, Jan - Feb 2001

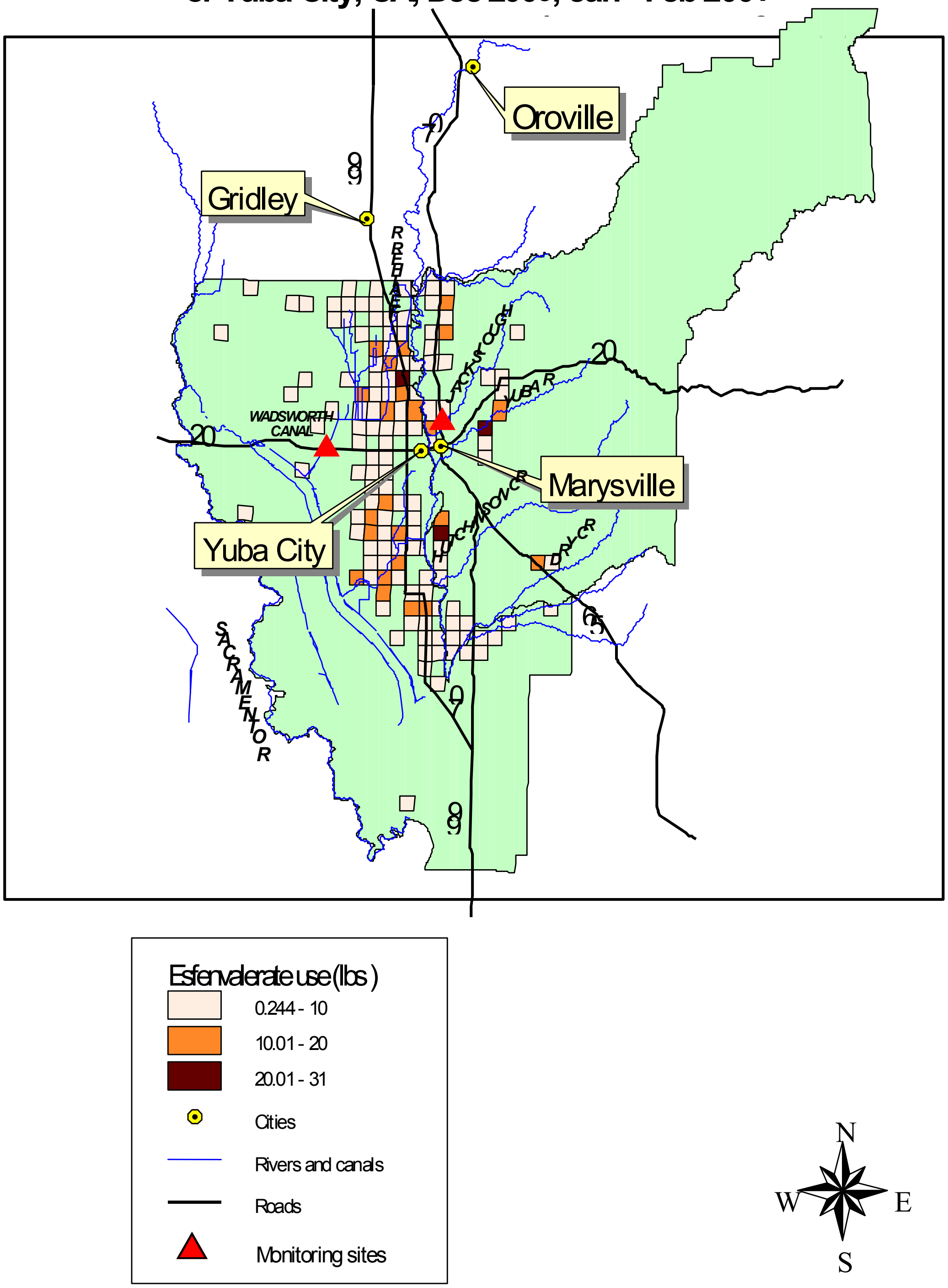


Figure 2

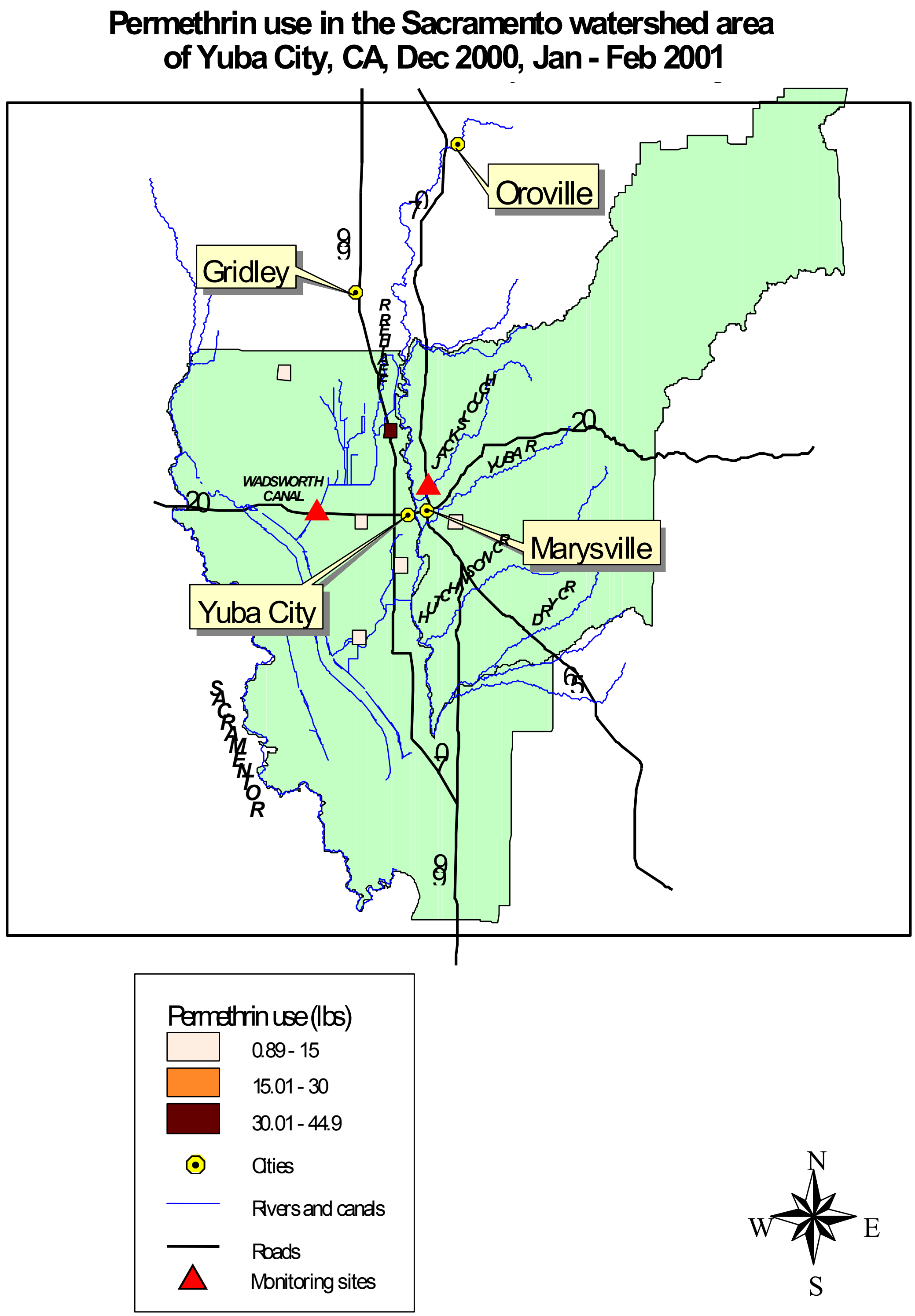

Permethrin use in the Sacramento watershed area
of Yuba City, CA, Dec 2000, Jan - Feb 2001
Oroville
Gridley
Marysville
Yuba City
WADSWORTH CANAL
YUBA R
DRY CR
SACRAMENTO R
20
70
99
65
Permethrin use (lbs)
0.89 - 15
15.01 - 30
30.01 - 44.9
Cities
Rivers and canals
Roads
Monitoring sites
N
W
E
S

Figure 3

Esfenvalerat use in the San Joaquin watershed area of Modesto, CA, Dec 2000, Jan - Feb 2001

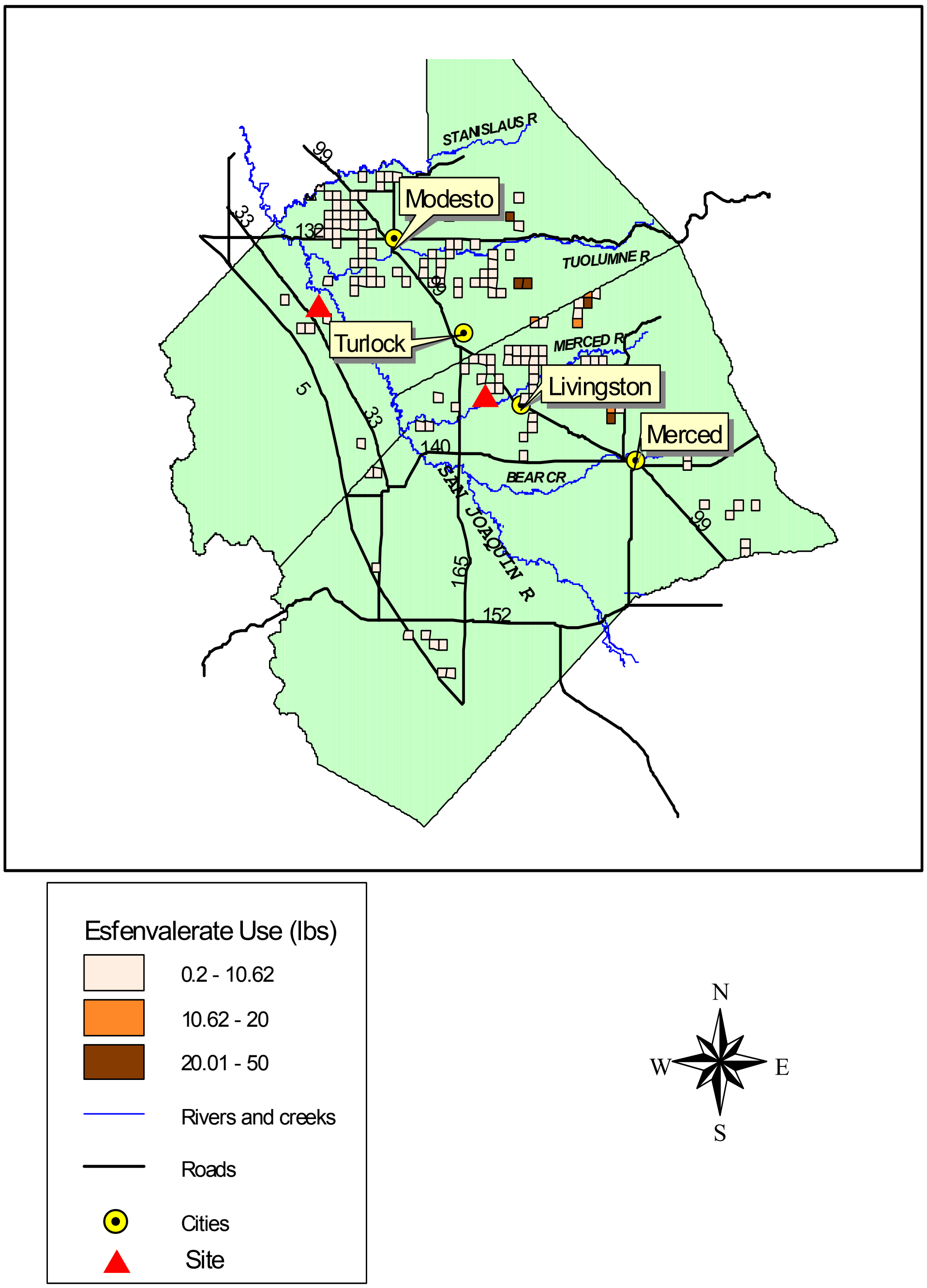
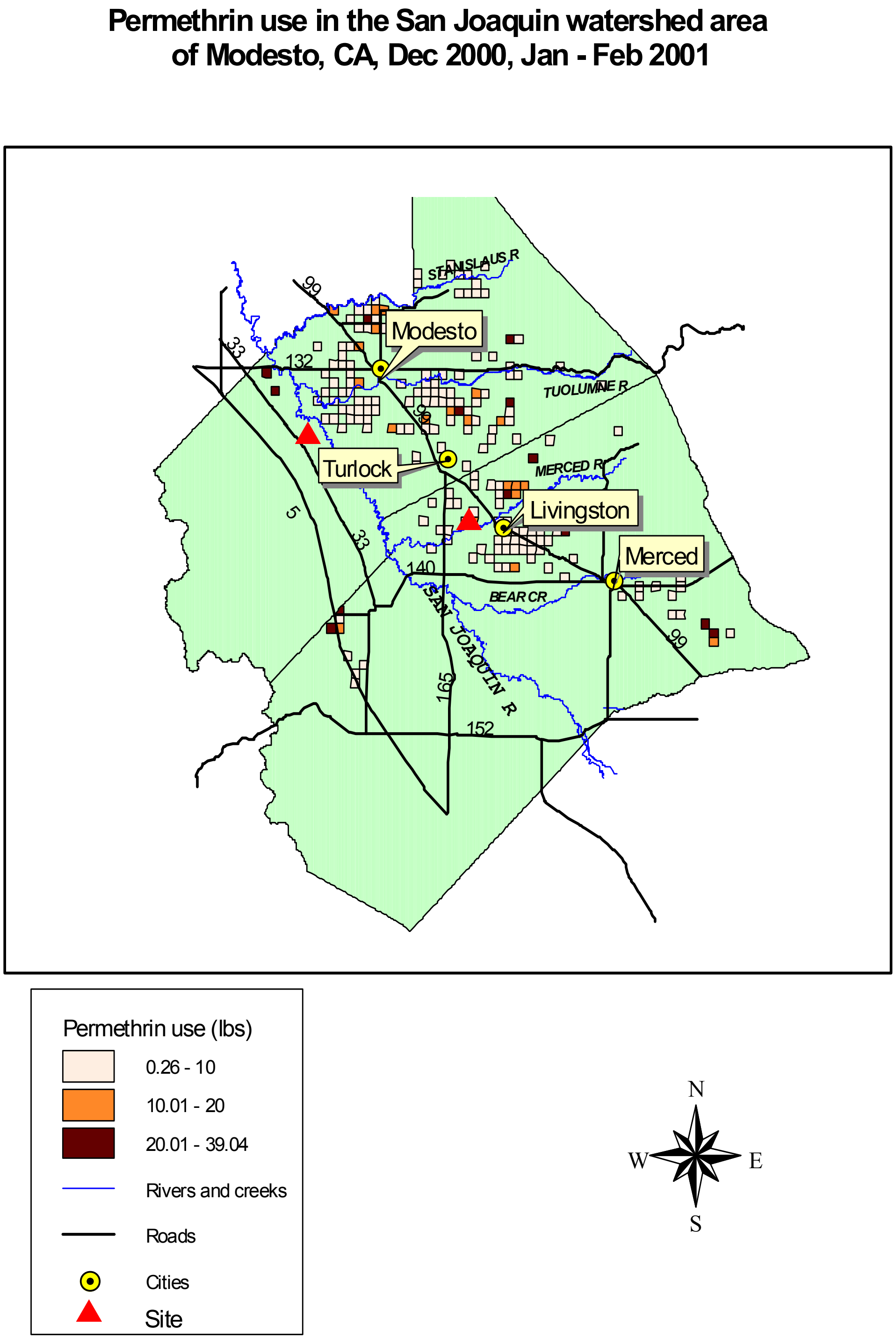


Figure 4


Permethrin use in the San Joaquin watershed area
of Modesto, CA, Dec 2000, Jan - Feb 2001
STANISLAUS R
99
Modesto
33
132
TUOLUMNE R
Turlock
MERCED R
Livingston
5
33
Merced
140
BEAR CR
SAN JOAQUIN R
99
165
152
Permethrin use (lbs)
0.26 - 10
10.01 - 20
20.01 - 39.04
Rivers and creeks
Roads
Cities
Site
N
W
E
S