Department of Pesticide Regulation
Environmental Monitoring Branch
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Study 238. Preliminary Assessment of Pesticide Contamination of Surface Waters in High Use Regions of California: Malathion, Methomyl, Simazine, Atrazine and Thiram

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I. INTRODUCTION

In California, a wide variety of pesticides are applied throughout the year; in 2004, for example, over 300 pesticide active ingredients (a.i.s) were applied in agricultural areas of the state (DPR 2006a). For many of these, recent surface water monitoring data from areas of high use are lacking or outdated. Such monitoring data are needed in order to assess the potential impacts of California pesticide use on aquatic systems.

To begin addressing this issue, several pesticide active ingredients were selected for focused monitoring in a year-long statewide surface water monitoring project. Pesticide active ingredients were selected for monitoring based on their toxicity to aquatic organisms (Starner, in preparation), their relatively high agricultural use in geographic regions near surface water (DPR 2006a), and the lack of recent surface water monitoring data from the regions of high use (DPR 2006b).The selected pesticides and their physical-chemical properties, aquatic toxicity, and numerical water quality limits are shown in Tables 1-3.

Malathion/organophosphate insecticides

Malathion is an organophosphate (OP) insecticide applied to a variety of crops; over 225,000 pounds of malathion was applied in California in 2004 (DPR 2006a). High use of malathion occurs in several regions, including the Salinas Valley/Monterey area (primarily on strawberries), Santa Maria and Oxnard areas in Santa Barbara/Ventura counties (lettuce, celery and strawberries), and the Imperial Valley (alfalfa) (Figures 1-7). Malathion surface water monitoring data in these regions during historical periods of high use is lacking. Malathion toxicity data and water quality limits are shown in Tables 2 and 3.

In addition to malathion, several additional OP insecticides are applied in these regions during the peak malathion use periods. These a.i.s include diazinon, chlorpyrifos, dimethoate, methidathion, disulfoton and fenamiphos. While not the primary focus of this study, these a.i.s will be included in the OP analytical screen (Table 4), providing additional useful surface water monitoring data.

Methomyl/carbamate insecticides

Methomyl, a carbamate insecticide, is applied throughout California to control aphids, armyworms, and other agricultural pests. California use in 2004 was over 165,000 pounds of active ingredient (DPR 2006a). High use of methomyl occurs in the Salinas Valley/Monterey area (strawberries and lettuce), Santa Maria/Oxnard areas (strawberries, lettuce and peppers) and Imperial Valley (lettuce and sugarbeets) (Figures 1, 8-13). Methomyl toxicity data and numerical water quality limits are shown in Tables 2 and 3.

As with the OP analytical screen, the carbamate analytical screen utilized for analysis of methomyl (Table 4) will include several additional active ingredients that are used in these regions. These include carbaryl,

Note: All pesticide use data cited are 2004 agricultural use data from DPR 2006 unless specified otherwise.

carbofuran, oxamyl and aldicarb. While not the primary focus of the study, inclusion of the additional a.i.s in the analytical screen will provide additional useful monitoring data.

Simazine/herbicides

Simazine is a triazine herbicide used to control broadleaf weeds and annual grasses. Use of simazine is high in several agricultural regions of California, and it has been detected frequently in the San Joaquin River during the winter wet season (DPR 2006b). Simazine is applied in high amounts in the Sonoma/Napa area and in Monterey County during California's wet season (Figures 1, 14-17). No simazine monitoring data are available from these regions.

According to the U.S. EPA "there is the potential for direct adverse acute effects" to nontarget aquatic plants, including *A. flos-aquae* (Table 2) from the use of simazine. The EPA additionally stated that "the results of future studies on atrazine's potential sublethal effects to amphibians………may be applicable to simazine because the two chemicals share a similar… mechanism of toxicity, a similar mechanism of herbicidal action, and the same degradates" (U.S. EPA 2006a). See below for discussion of atrazine.

Atrazine/herbicides

Atrazine is a triazine herbicide used in California primarily on forage crops (Sudangrass, etc.) and forest lands to control broadleaf and grassy weeds. Use is high in the Imperial Valley and Tuolumne county and other areas (Figures 1, 18-21). No recent atrazine surface water monitoring data are available for the regions of high use. Atrazine toxicity and water quality limits are given in Tables 2 and 3.

Atrazine is acutely toxic to non-target aquatic plants (Table 2). Additionally, according to the U.S. EPA, there are "ecological risk concerns from the use of atrazine…the Agency has identified the potential for community-level and population-level risk to aquatic ecosystems at concentrations of atrazine from 10 to 20 ppb." Additionally, atrazine "has been associated with sub-lethal effects in aquatic organisms and amphibians in research presented in the open, peer-reviewed literature. These include potential effects on endocrine-mediated processes in frogs at ~ 0.1 ug/L and in the largemouth bass at ~ 50 ug/L" (U.S. EPA 2003a). The EPA indicates that these results have not been conclusively confirmed, but recommends additional monitoring and more definitive testing regarding this issue (U.S. EPA 2003a, 2003b).

Thiram/fungicides

Thiram is a dithiocarbamate fungicide widely used as a seed protectant, and is also applied in the field to protect crops from a variety of fungal diseases. In California, the primary use of thiram is foliar application to strawberries to prevent gray mold. Use is high in Monterey/Santa Cruz counties and the Santa Maria/Oxnard areas (Figures 1, 22-25). Thiram is toxic to fish and other aquatic organisms (Table 2).

The U.S. EPA has stated that thiram applied foliarly, as it is applied to California strawberries, "is expected to be sufficiently mobile and persistent in some cases to reach surface waters in concentrations high enough to impact aquatic life". Additionally, the U.S. EPA states that "typical agricultural practices for growing strawberries………could increase the risk of thiram entering adjacent aquatic organism habitats" (U.S. EPA 2004).

No surface water monitoring data for thiram in strawberry-growing regions of California is available.

II. OBJECTIVE

The objective of this study is to provide a preliminary assessment of California surface water pesticide contamination for several high use pesticide active ingredients. The pesticides to be monitored are malathion, methomyl, simazine, atrazine, and thiram.

Results will be used to aid in the development of priorities for future monitoring and/or mitigation efforts.

III. PERSONNEL

The study will be conducted by staff from the Environmental Monitoring Branch, Surface Water Protection Program, under the general direction of Kean S. Goh, Ph.D., Agricultural Program Supervisor IV. Key personnel are listed below:

Project Leader:	Keith Starner
Field Coordinator:	Kevin Kelley
Senior Scientist:	Frank Spurlock, Ph.D.
Laboratory Liaison:	Carissa Ganapathy
Chemists:	California Department of Food and Agriculture, Center for Analytical Chemistry Staff Chemists

Questions concerning this monitoring project should be directed to Keith Starner at (916) 324-4167 or by email at kstarner@cdpr.ca.gov.

IV. STUDY PLAN

Rivers and streams in each of five geographic regions will be sampled for the designated high-use pesticide(s) at least once during the study (Figure 1). Sampling for each active ingredient will be conducted during the season or seasons of historically high pesticide use in the respective region (Figures 2-25). Regions with multiple or extended use seasons will be sampled more frequently. In general, OP and carbamate samples will be collected more frequently than herbicide samples. Locations of individual sampling sites within a region will be determined based on the historical pesticide use patterns and proximity to the water bodies of interest. When possible, late fall and winter herbicide sampling will be timed to follow or coincide with rainfall events and subsequent runoff.

Site selection will follow the general guidelines in Standard Operating Procedure (SOP) FSWA002.00 (Bennett 1997) where applicable.

Sampling will commence in August 2006 and continue through June 2007.

V. SAMPLING METHODS

At each sampling site, surface water grab samples for chemical analysis be collected into 1-liter amber glass bottles. Grab samples will be collected as close to center channel as possible using either a grab pole consisting of a glass bottle at the end of an extendable pole, or other sampling equipment designed to collect a sample directly into a 1-liter glass bottle. Samples may be collected into a stainless steel Kemmerer sampler (Wildlife Supply) and transferred to amber bottles in the field. Amber bottles will be sealed with Teflon-lined lids and samples will be transported and stored on wet ice or refrigerated at 4°C until extraction for chemical analysis.

Dissolved oxygen, pH, specific conductivity, and water temperature will be measured *in situ* at each site during each sampling period. Flow data will be collected using a digital flow meter.

VI. CHEMICAL ANALYSIS

Chemical analysis will be performed by the California Department of Food and Agriculture's Center for Analytical Chemistry. Analytical method titles, analytes, method detection limits, and reporting limits for this study are given in Table 4. Details of the chemical analysis methods will be provided in the final report. Quality control will be conducted in accordance with Standard Operating Procedure QAQC001.00 (Segawa 1995). Ten percent of the total number of analyses will consist of field blanks and blind spikes, to be submitted to the laboratory with field samples.

VII. DATA ANALYSIS

Concentrations of pesticides in water will be reported as micrograms per liter (µg/L) / parts per billion (ppb) or nanograms per liter (ng/L) / parts per trillion (ppt).
Resulting data will be analyzed and reported as appropriate, potentially including the following: Comparison of analytical concentrations to concurrent use data, toxicity data, and water quality limits (Marshak 2003, CDFG 1996 and 1998);

Spatial analysis of data in order to identify correlations between observed pesticide concentrations and region-specific geographical features such as climate, soil type, cropping patterns and agricultural practices.

VIII. TIMETABLE

Field Sampling:	August 2006 through June 2007
Chemical Analysis:	August 2006 through September 2007
Final Report:	April 2008

IX. BUDGET

Primary Analysis				Cost
Organophosphate screen (cost = $650 per sample)	9 sites x 12 events =	108 samples	=	70,200
Carbamate screen (cost = $800 per sample)	9 sites x 12 events =	108 samples	=	86,400
Herbicide Screen (cost = $900 per sample)	9 sites x 5 events =	45 samples	=	40,500
Thiram (sample cost to be determined (TBD))	9 sites x (TBD) events =	(TBD) samples	=	43,200 (est.)
		subtotal		240,300
Quality Control				
Blind spikes (est.)		16 samples	=	12,800
Field blanks (est.)		16 samples	=	12,800
Continuing QC (est. cost $800 ea.)		37 QC samples	=	29,600
Total				**295,500**

X. REFERENCES

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

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http://www.epa.gov/oppsrrd1/reregistration/atrazine/

US EPA 2004. Reregistration eligibility decision for thiram. EPA 738-R-04-012.
http://www.epa.gov/oppsrrd1/REDs/0122red_thiram.pdf

US EPA 2006a. Reregistration eligibility decision for simazine. EPA 738-R-06-008.
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US EPA 2006b. US EPA Office of Pesticide Programs ECOTOX database.
http://mountain.epa.gov/ecotox/

Table 1. Pesticide physical-chemical properties.

Pesticide	K_{OC} (cm^3/g)	Solubility (mg/L)	Half-life Soil (days, aerobic/anaerobic)	Hydrolytic (pH 7) half-life (days)
Malthion	291	125	2.50/30.0	6.2
Methomyl	43.3	54,700	46/1	30
Thiram	1,650	16.5	15.2/No data[A]	3.48
Simazine	340	6.15	110/70	28
Atrazine	92.9	32.5	146/159	30

Source: DPR 2006c except as noted. DPR data are averages of multiple values.
A. USDA ARS Pesticide Properties Database.

Table 2. Acute aquatic toxicity data.

Pesticide	Organism	Concentration (ug/L)
Malathion	Scud (*Gammarus fasciatus*)	0.5
Malathion	Rainbow trout (Oncorhynchus mykiss)	4.1
Malathion	Opossum shrimp (*Americamysis bahia*)	2.2
Methomyl	Waterflea (*Daphnia magna*)	7.6
Methomyl	Channel Catfish (*Ictalurus punctatus*)	320
Thiram	Opossum shrimp (*Americamysis bahia*)	3.36
Thiram	Bluegill sunfish (*Lepomis macrochirus*)	42
Thiram	Harlequinfish, red rasbora (*Rasbora heteromorpha*)	7
Simazine	Blue green algae (*Anabaena flos-aquae*)	36 (a)
Atrazine	Algae (*Isochrysis galbana*)	22 (a)

Source: U.S. EPA 2006b (U.S. EPA Office of Pesticide Programs ECOTOX database)
All test types 96-hour LC50 except as indicated.
(a) 5 day EC50

Table 3. Water quality limits.

Pesticide	Continuous Concentration (Four-day Average)	Maximum Concentration (1-hour Average)	Instantaneous Maximum
Malathion	none	0.43 (a)	0.1 (b)
Methomyl	0.52 (a)	5.5 (a)	none
Simazine	none	none	10 (e)
Atrazine	12 (c)	350 (c)	1 (d)

All concentrations in ug/L. Source: Marshak 2004. See also CDFG 1996, CDFG 1998.
No criterion available for thiram.
(a). Water Quality Criterion derived by the California Department of Fish and Game.
(b). This criterion is from a 1976 U.S.EPA reference and also appears in the current list of recommended criteria published by U.S.EPA.
(c). Draft / tentative / provisional.
(d). Advisory concentration; U.S. EPA Water Quality Advisory.
(e). This criterion is from a 1973 U.S. EPA reference, but it does not appear in the current list of recommended criteria published by U.S.EPA.

Table 4. Department of Food and Agriculture, Center for Analytical Chemistry analytical method details.

Organophosphate Insecticides in Surface Water by GC/FPD

Compound	***Method Detection Limit (µg/L)***	***Reporting Limit (µg/L)***
Azinphos methyl	0.0099	0.05
Chlorpyrifos	0.0008	0.01
Diazinon	0.0012	0.01
Dichlorvos	0.0098	0.05
Dimethoate	0.0079	0.04
Disulfoton	0.0093	0.04
Ethoprop	0.0098	0.05
Fenamiphos	0.0125	0.05
Fonofos	0.008	0.04
Malathion	0.0117	0.04
Methidathion	0.0111	0.05
Methyl Parathion	0.008	0.03
Phorate	0.0083	0.05
Profenofos	0.0114	0.05
Tribufos	0.0142	0.05

Carbamate Insecticides by LCMS.

Compound	***Method Detection Limit (µg/L)***	***Reporting Limit (µg/L)***
Aldicarb SO	0.0277	0.05
Aldicarb SO2	0.0214	0.05
Oxamyl	0.0255	0.05
Methomyl	0.0265	0.05
Mesurol SO	0.0264	0.05
3 OH-Carbofuran	0.0232	0.05
Mesuol SO2	0.0299	0.05
Aldicarb	0.0196	0.05
Carbofuran	0.0244	0.05
Carbaryl	0.0136	0.05
Mesurol	0.0270	0.05

Herbicides in Surface Water by LC/MS/MS.

Compound	***Method Detection Limit (µg/L)***	***Reporting Limit (µg/L)***
Atrazine	0.02	0.05
Simazine	0.013	0.05
Diuron	0.022	0.05
Prometon	0.016	0.05
Bromacil	0.031	0.05
Prometryn	0.016	0.05
Hexazinone	0.04	0.05
Metribuzin	0.025	0.05
Norflurazon	0.019	0.05
DEA	0.010	0.05
ACET	0.030	0.05
DACT	0.016	0.05

Thiram in Surface Water

Compound	***Method Detection Limit (µg/L)***	***Reporting Limit (µg/L)***
Thiram	To be determined (TBD)	TBD, $\leq$ 5.0

Figure 1. Monitoring regions and targeted pesticides.

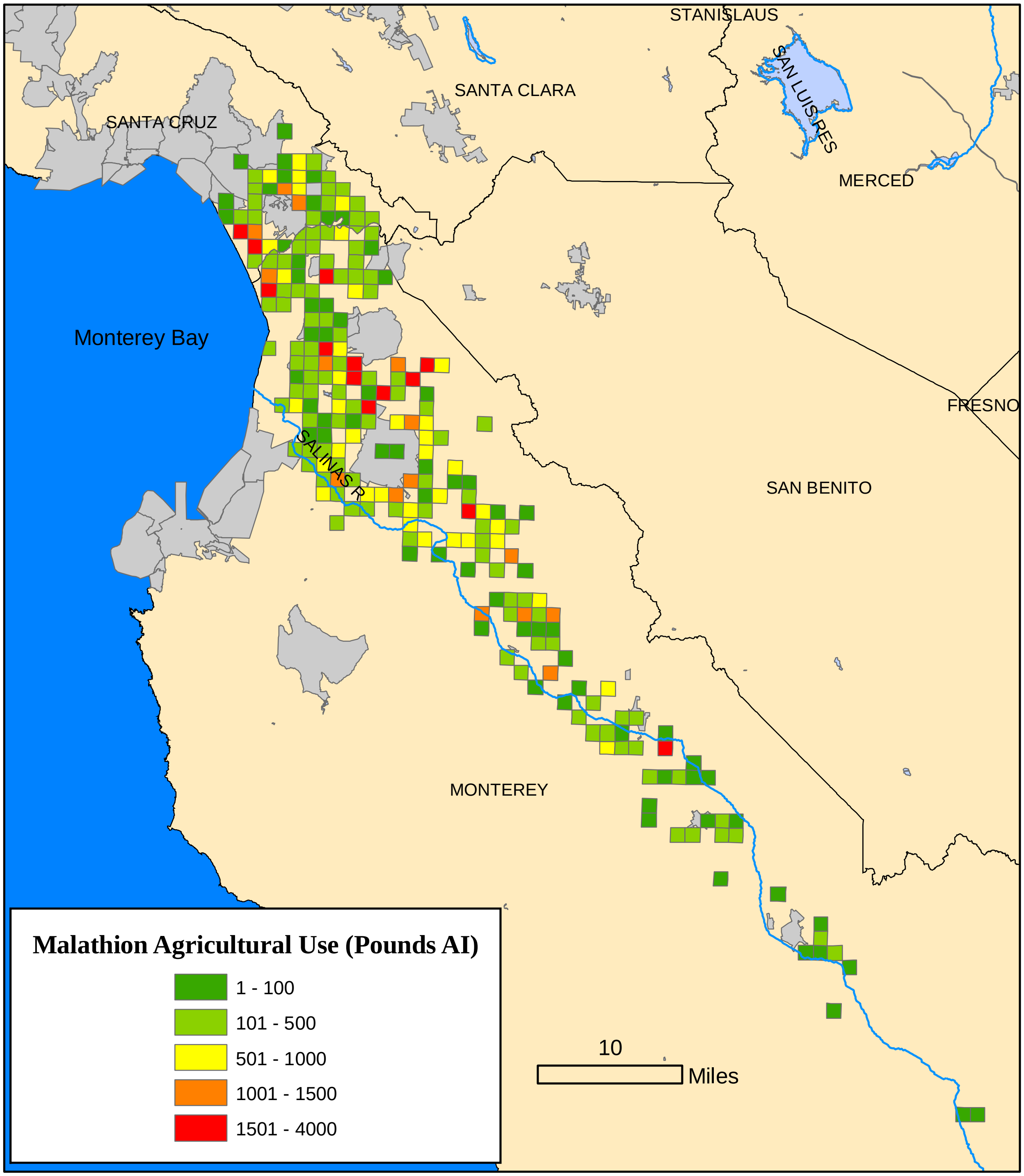


Figure 2. Malathion Use, Monterey County, 2004.

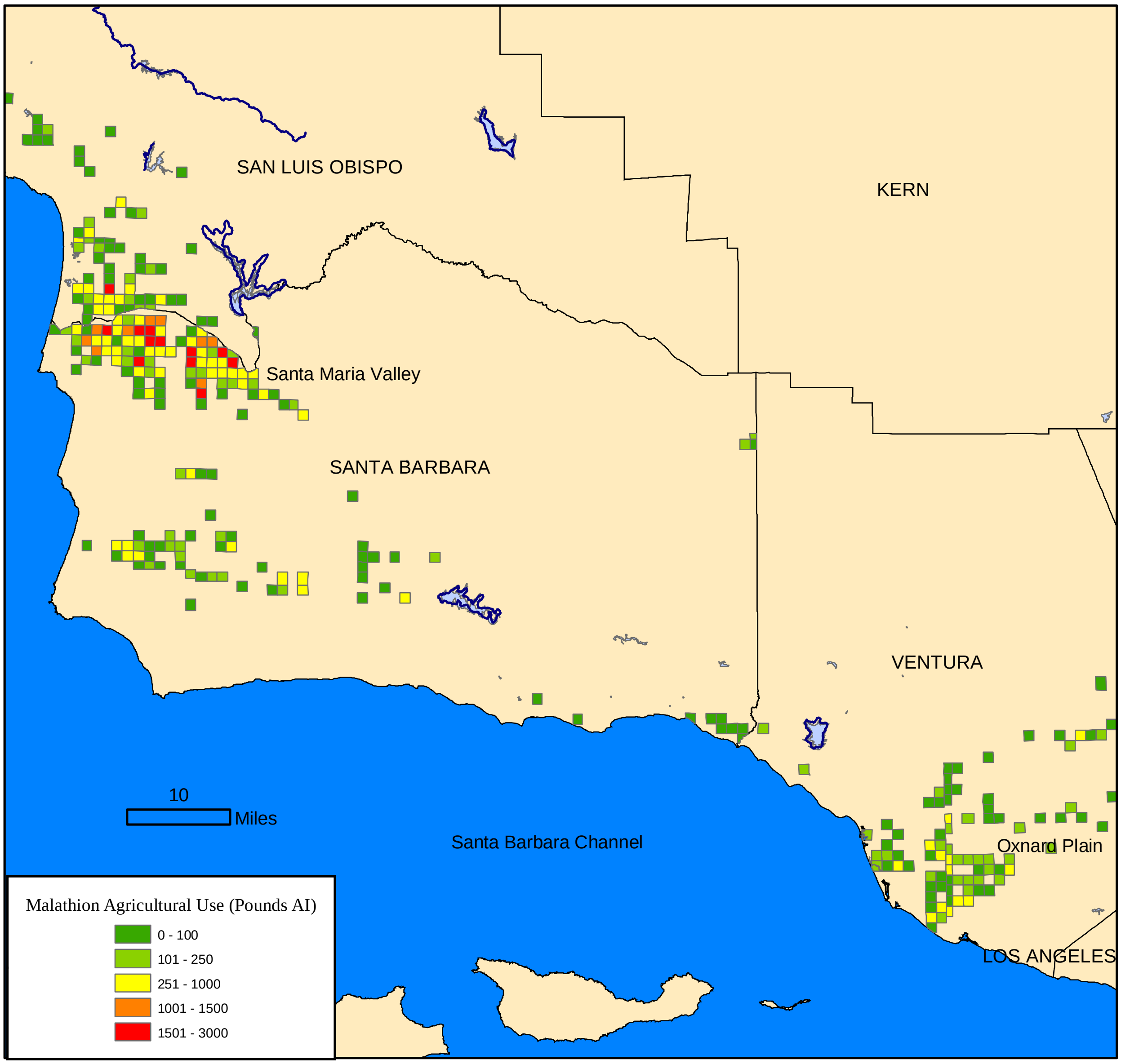


Figure 3. Malathion Use, Santa Maria/Oxnard, 2004.

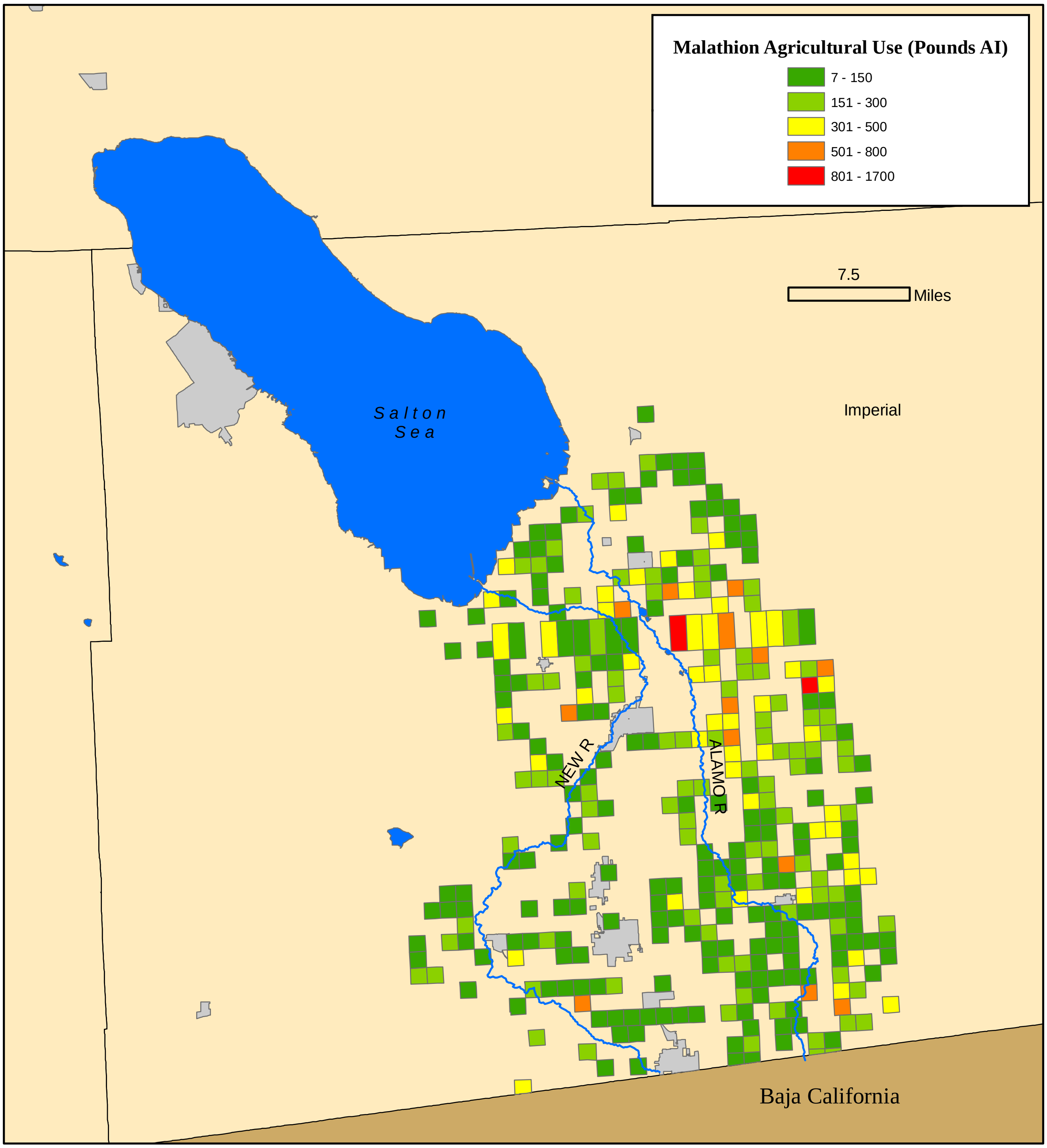


Figure 4. Malathion Use, Imperial Valley, 2004.

Figure 5. Monterey Malathion Use, 2002-2004.

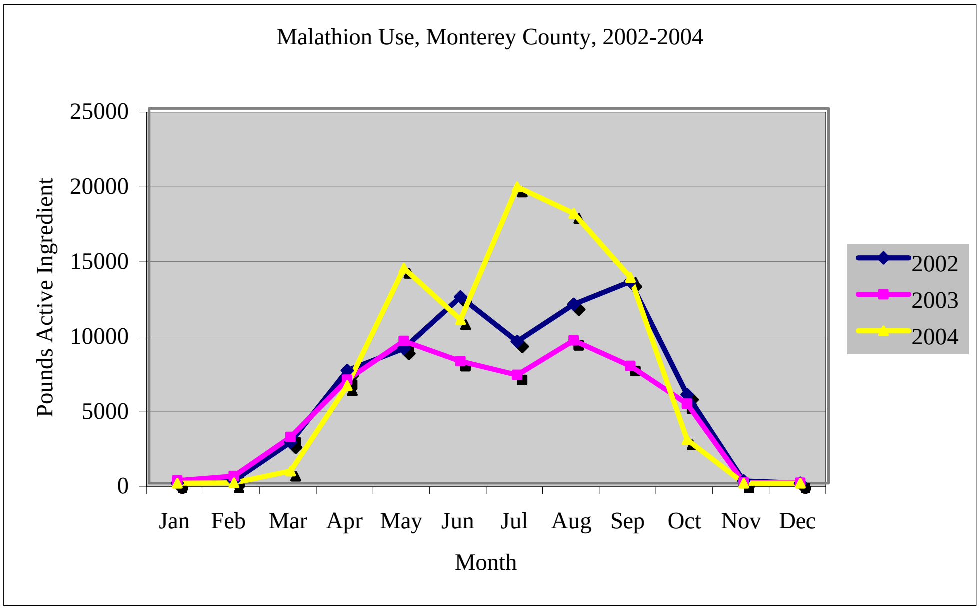


Figure 6. Santa Maria/Oxnard Malathion Use, 2002-2004.

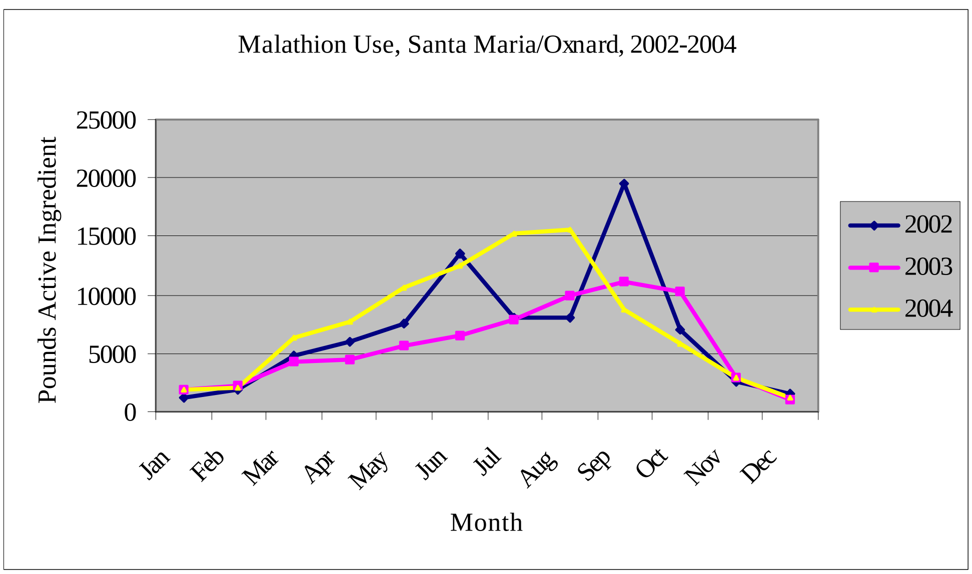
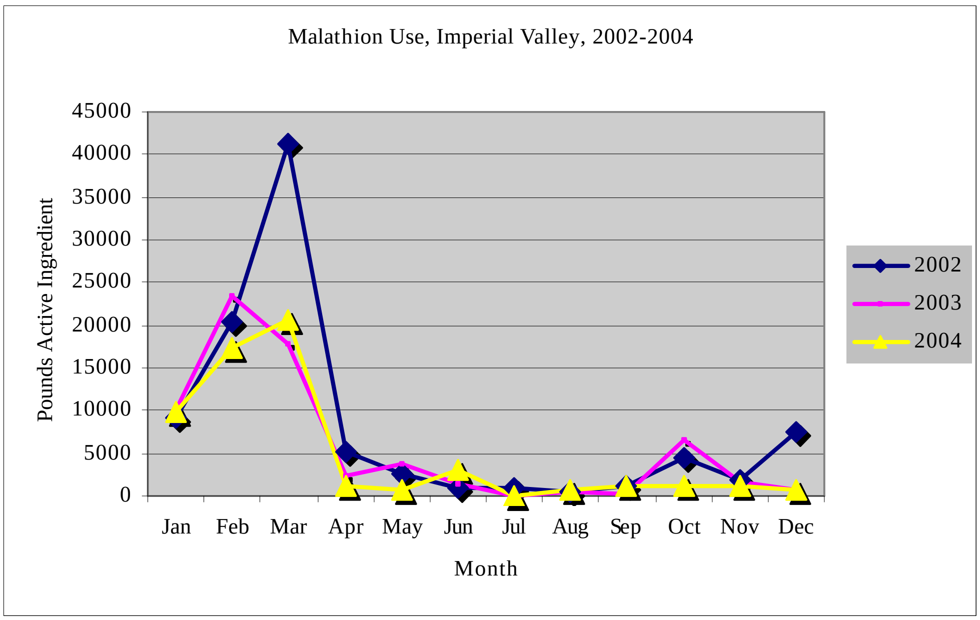


Figure 7. Imperial Valley Malathion Use, 2002-2004.



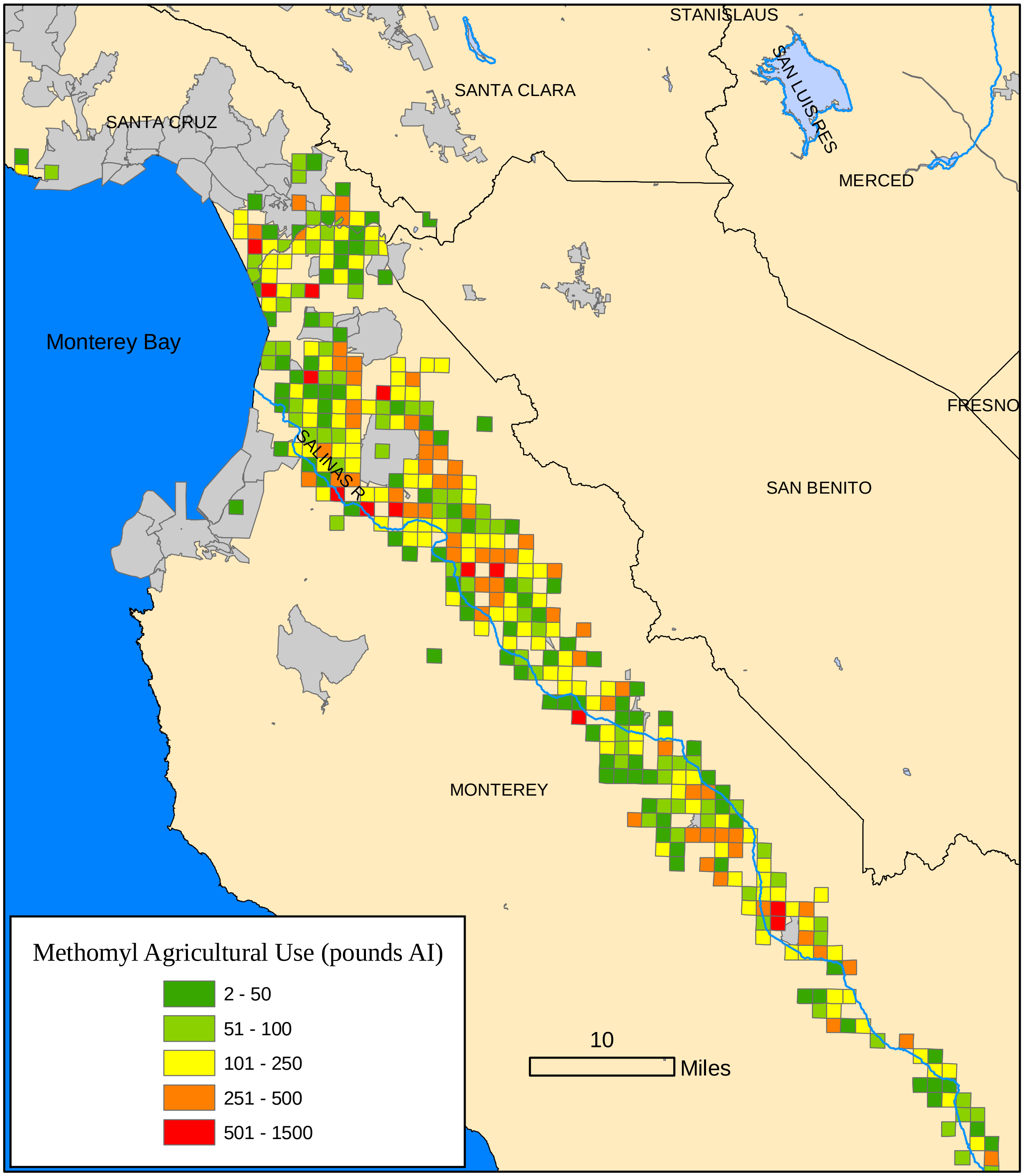


Figure 8. Methomyl Use, Monterey County, 2004.

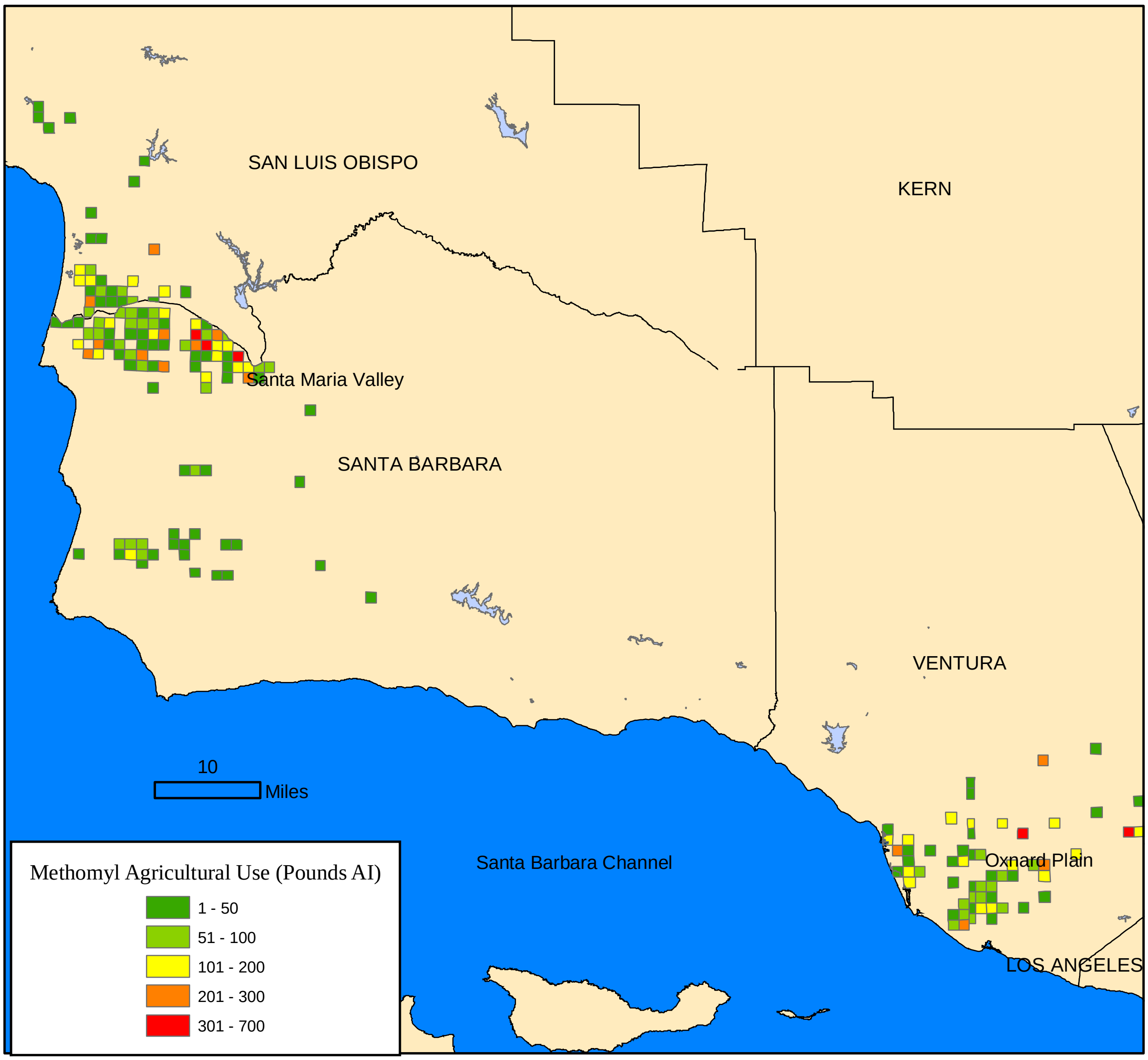


Figure 9. Methomyl Use, Santa Maria/Oxnard, 2004.

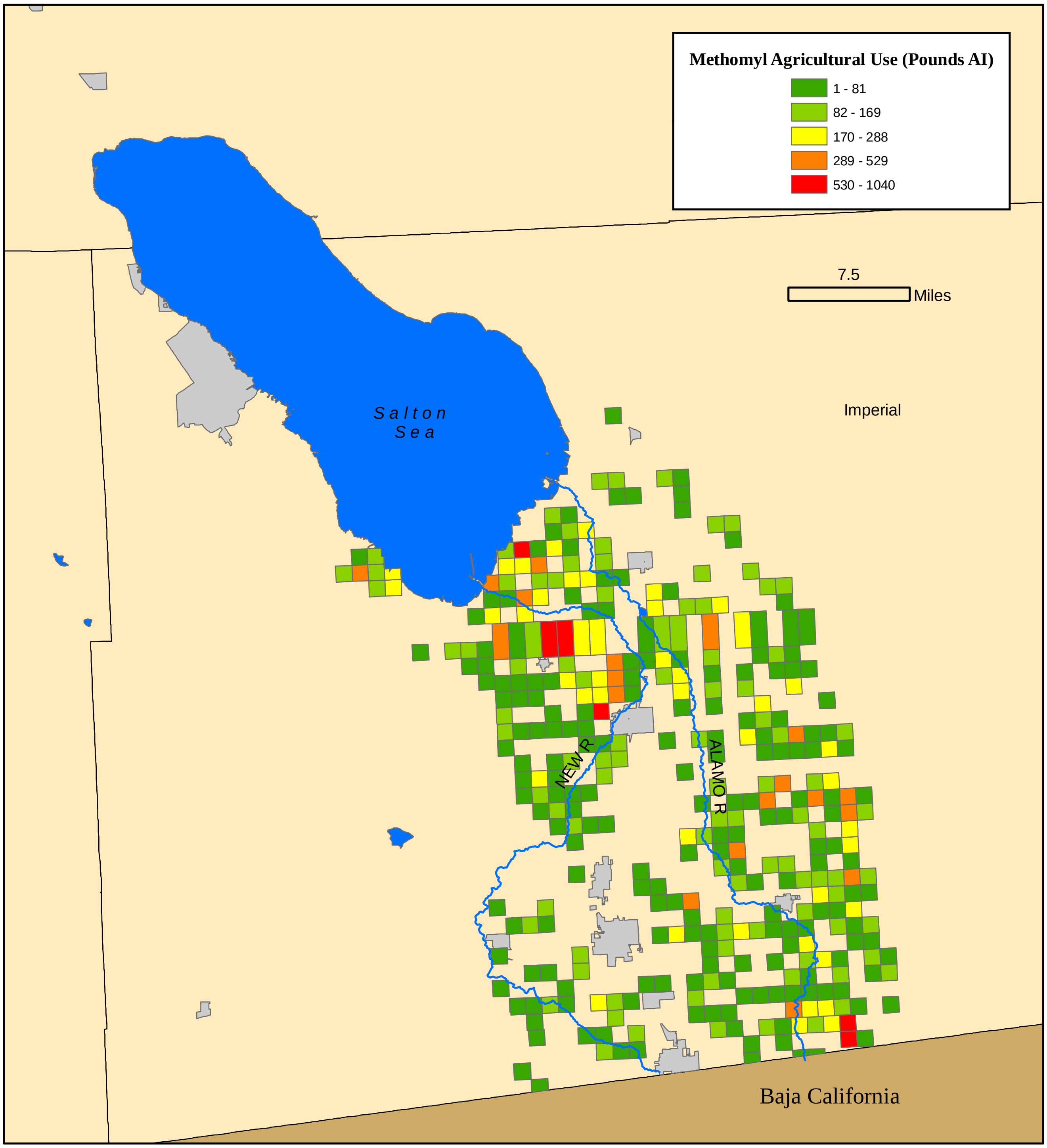


Figure 10. Methomyl Use, Imperial Valley, 2004.

Figure 11. Monterey Methomyl Use, 2002-2004.

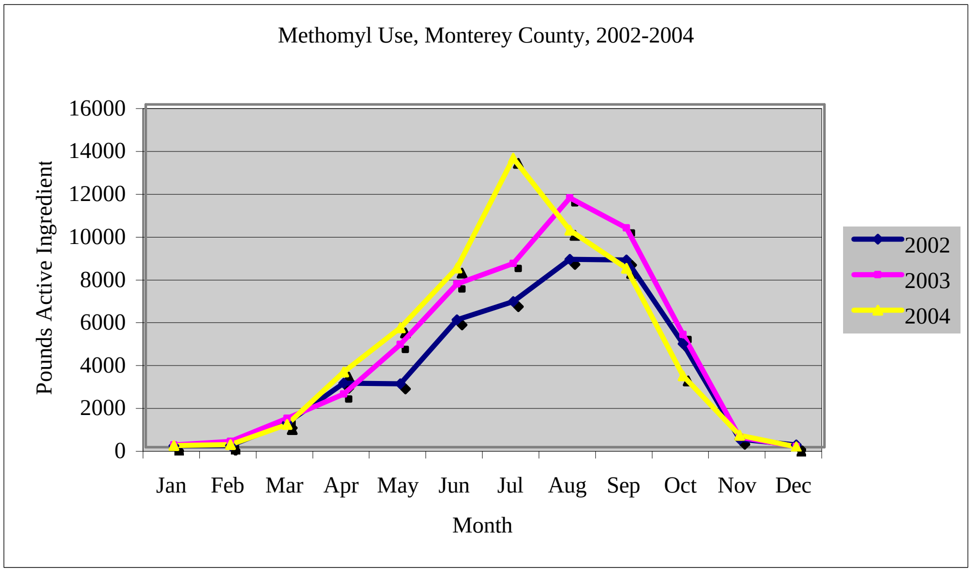


Figure 12. Santa Maria Methomyl Use, 2002-2004

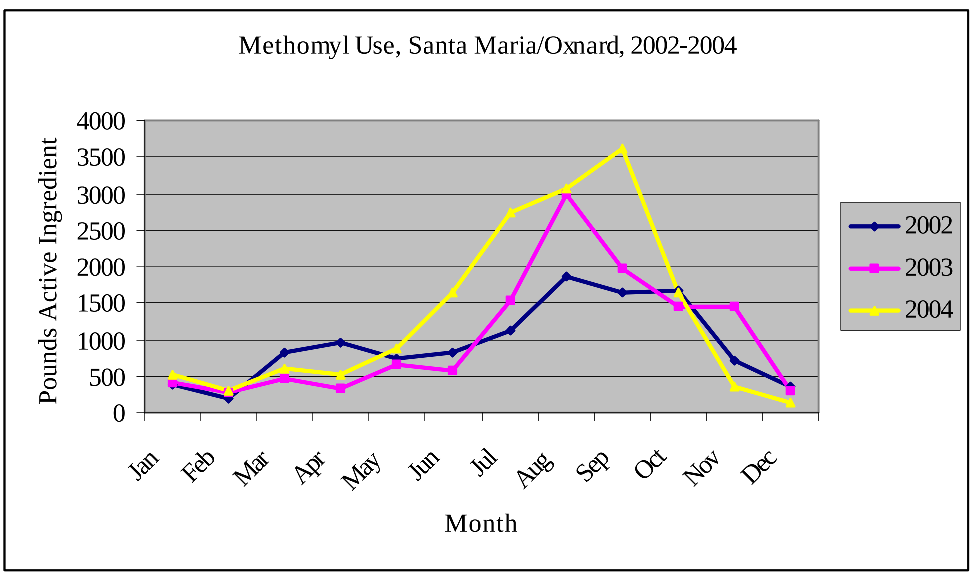
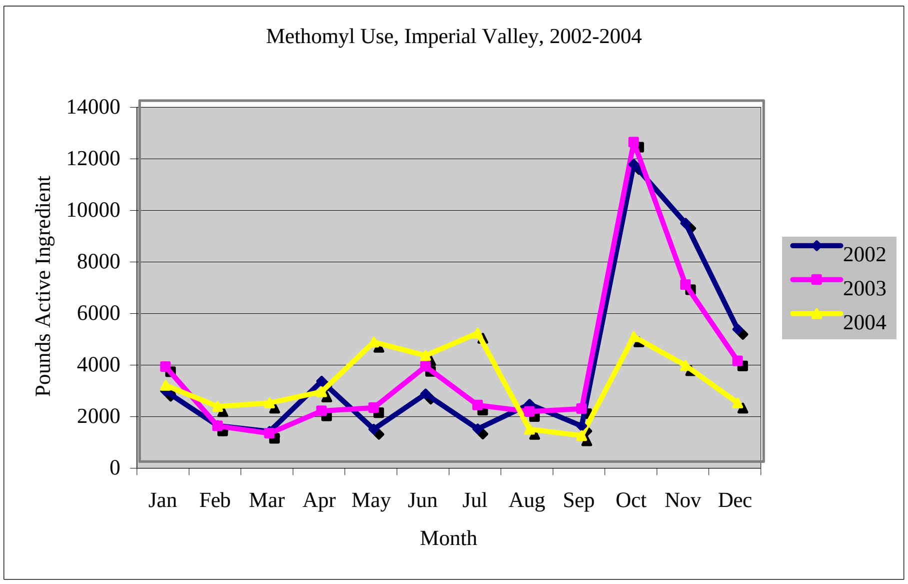


Figure 13. Imperial Valley Methomyl Use, 2002-2004.



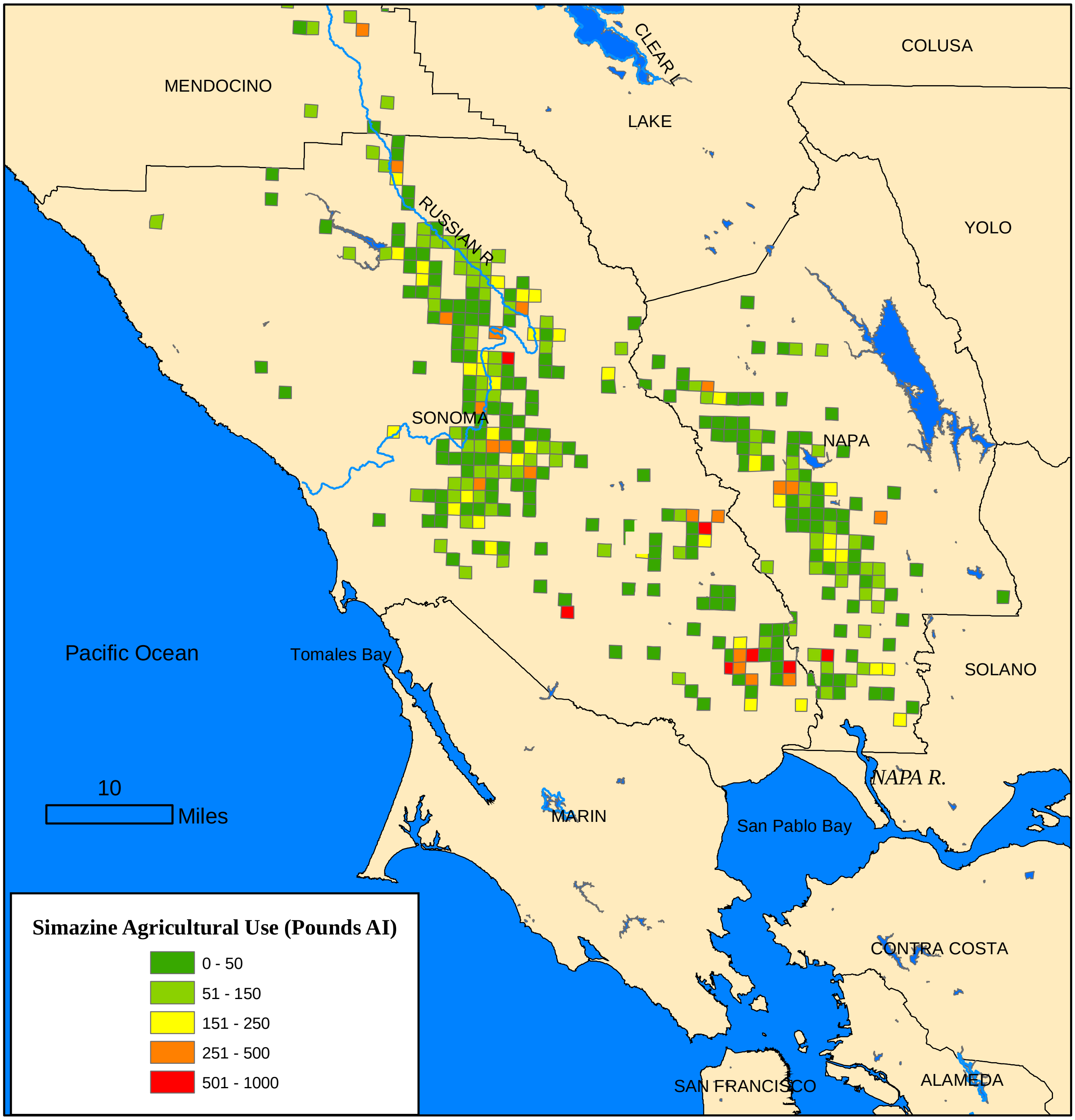


Figure 14. Simazine Use, Napa/Sonoma, 2004.

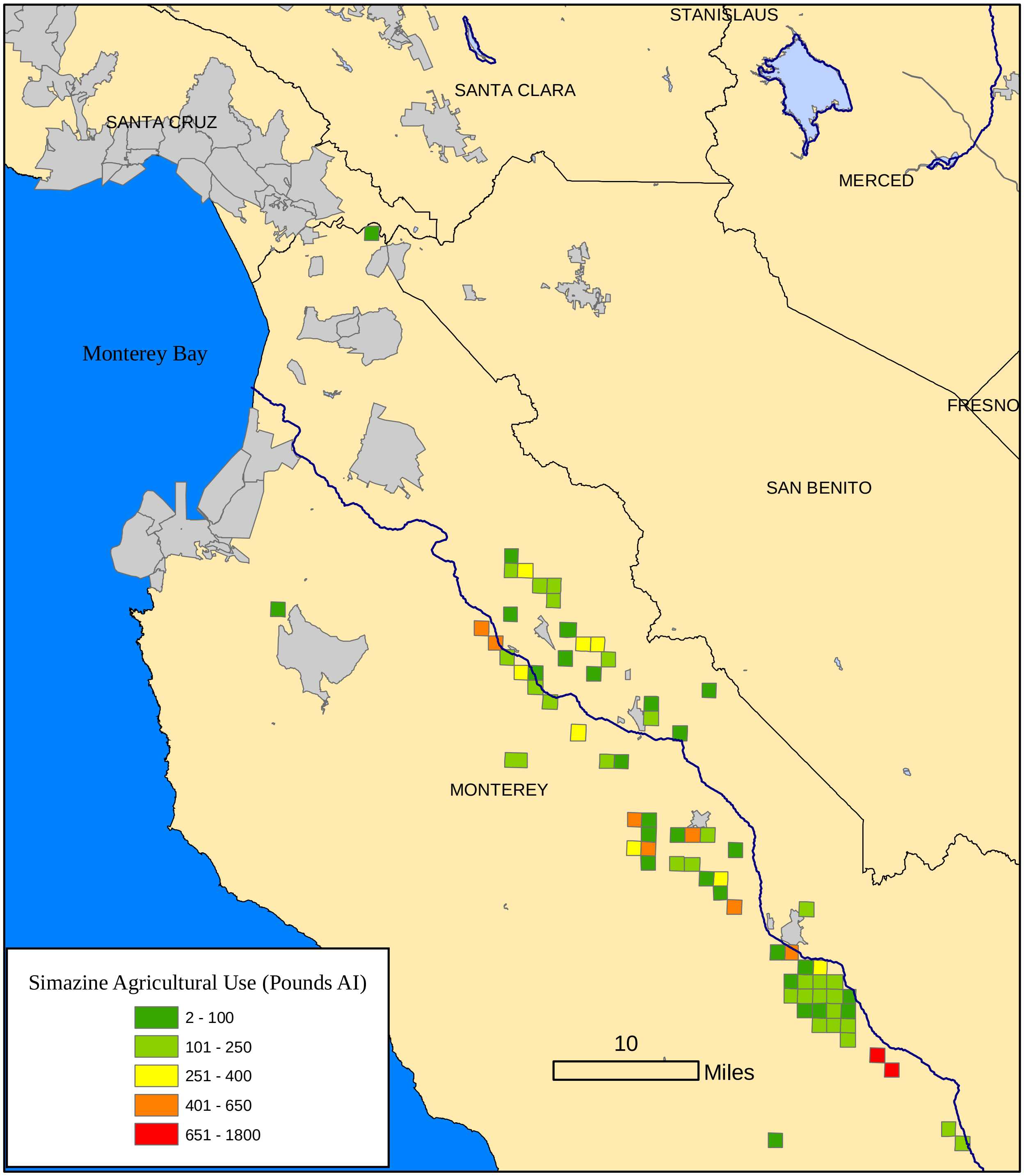


Figure 15. Simazine Use, Monterey County, 2004.

Figure 16. Napa/Sonoma Simazine Use, 2002-2004

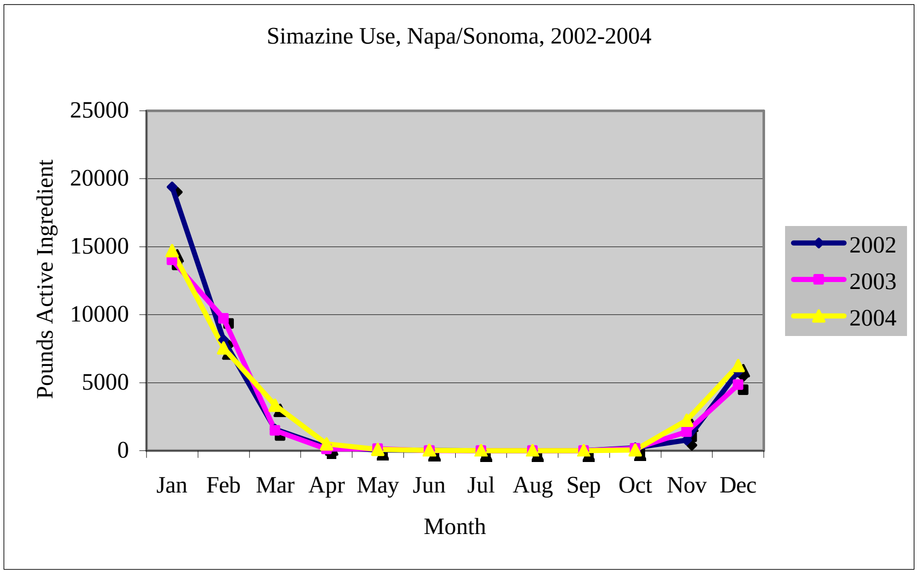
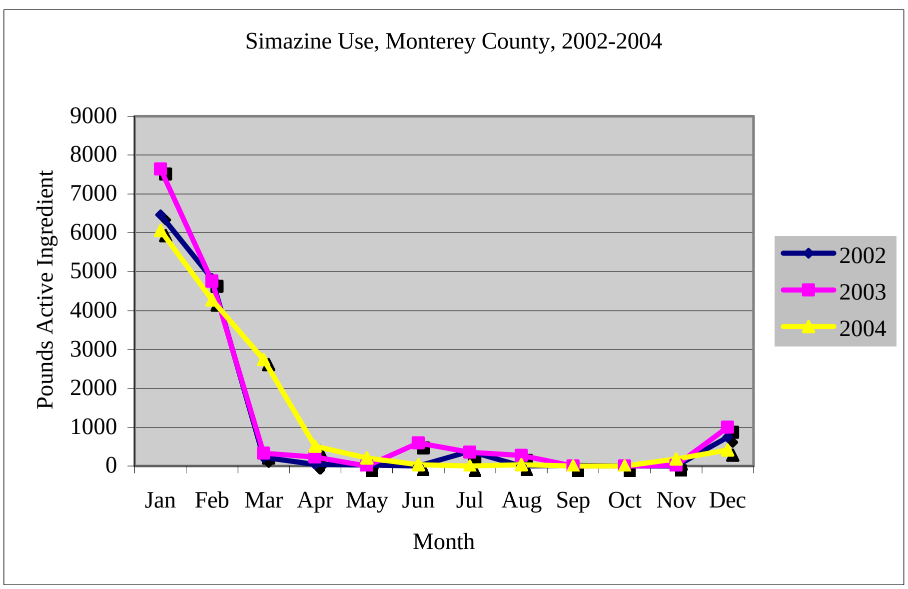


Figure 17. Monterey Simazine Use, 2002-2004



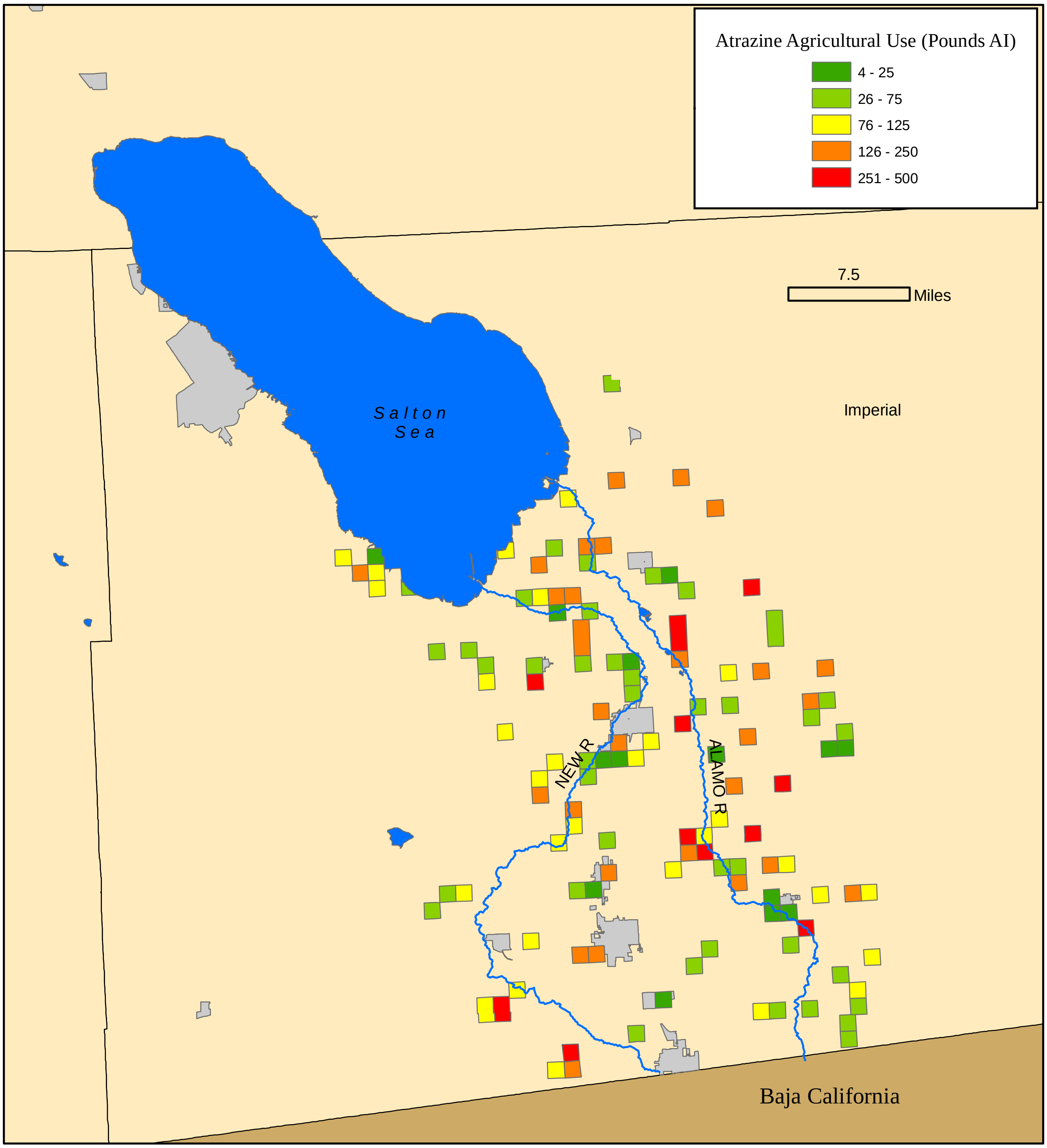


Figure 18. Atrazine Use, Imperial Valley, 2004.

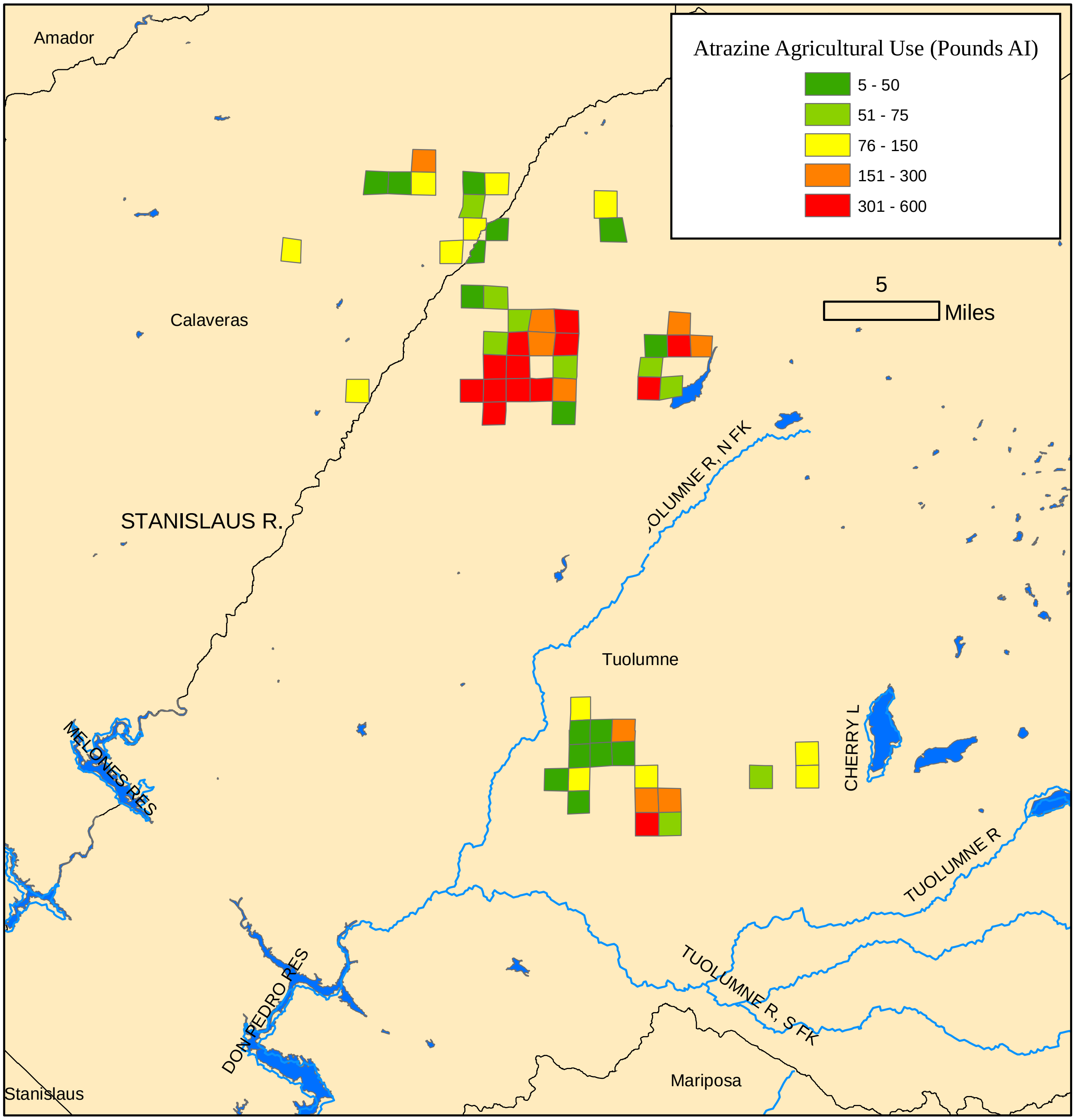


Figure 19. Atrazine Use, Tuolumne/Calaveras, 2004.

Figure 20. Imperial Valley Atrazine Use, 2002-2004.

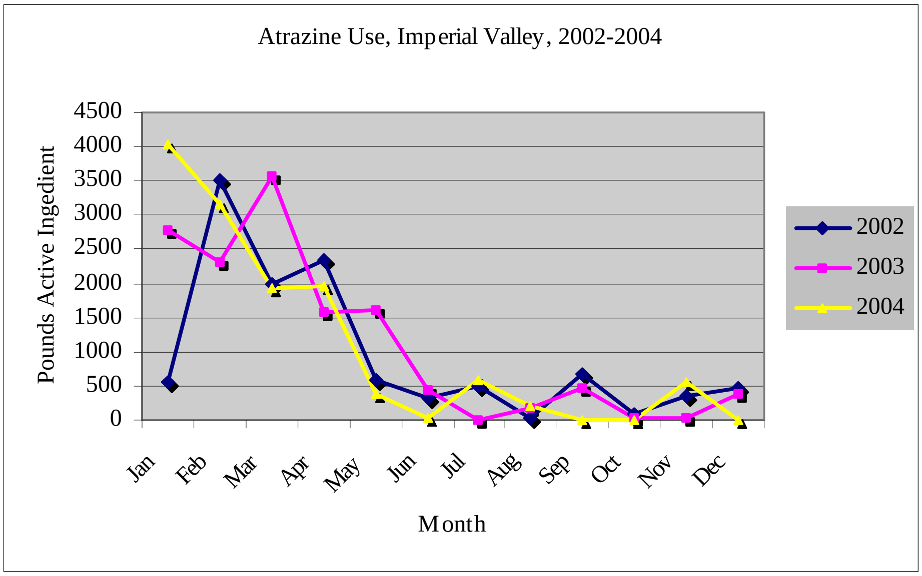
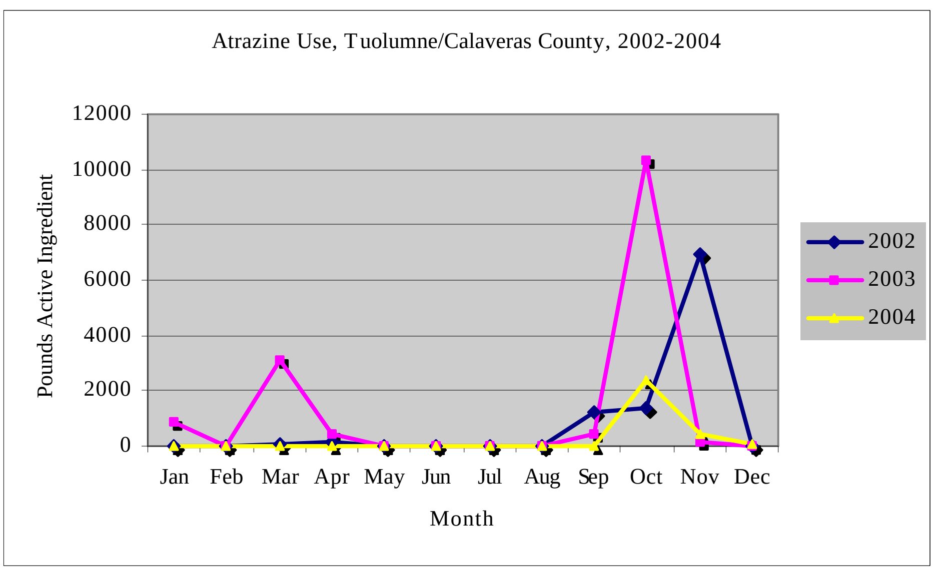


Figure 21. Tuolumne Atrazine Use, 2002-2004.



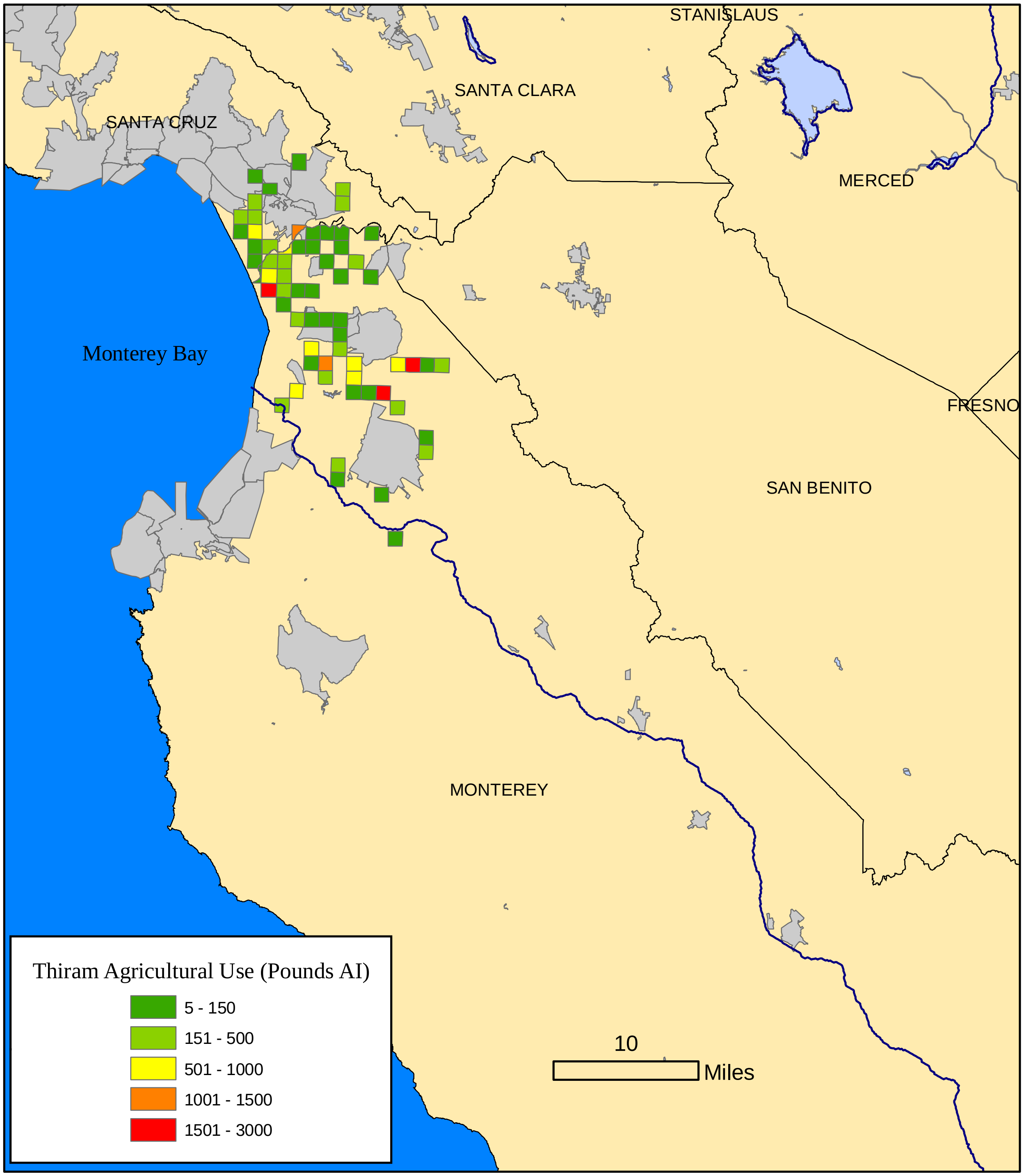


Figure 22. Thiram Use, Monterey County, 2004.

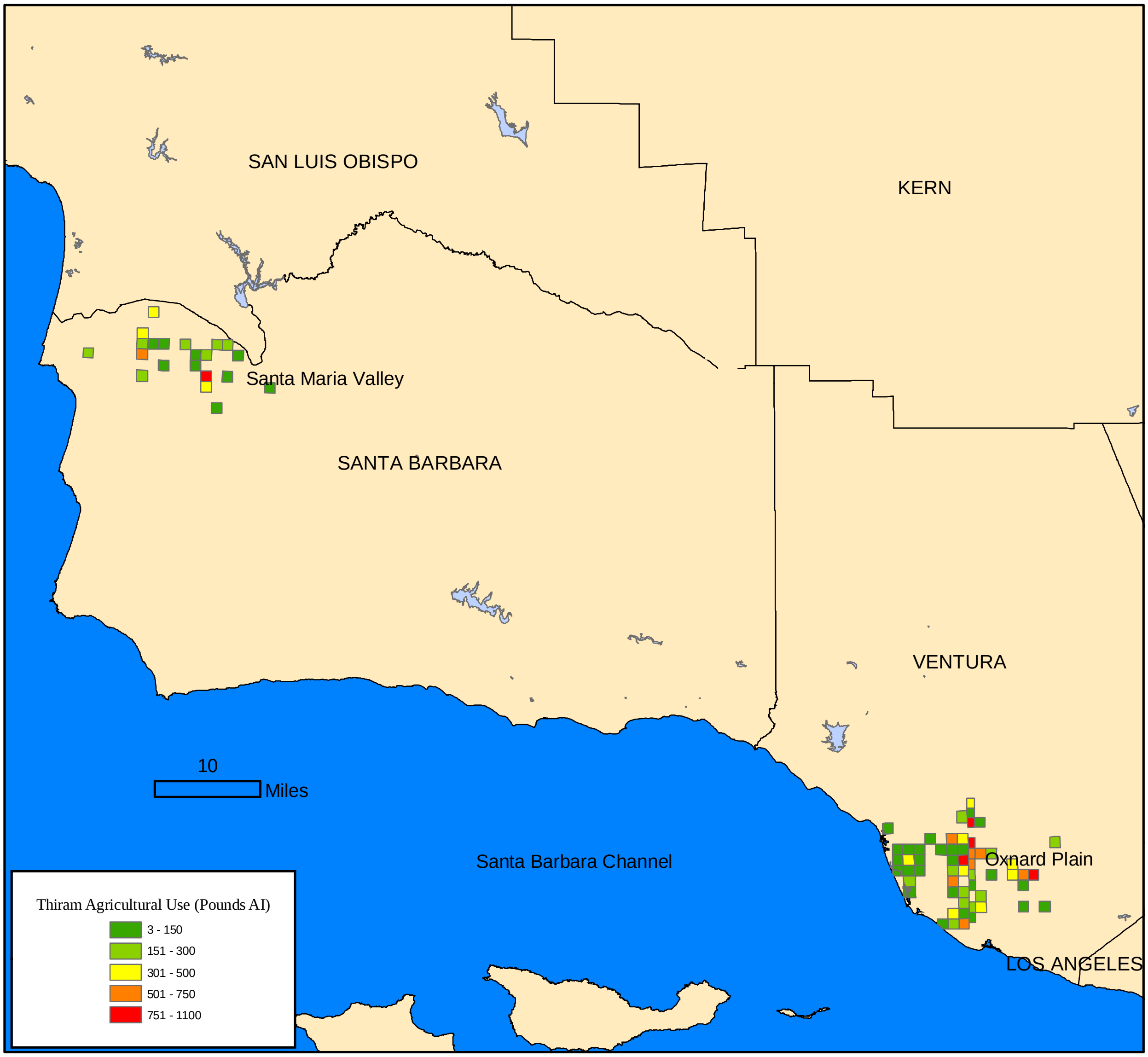


Figure 23. Thiram Use, Santa Maria/Oxnard, 2004.

Figure 24. Monterey Thiram Use, 2002-2004.

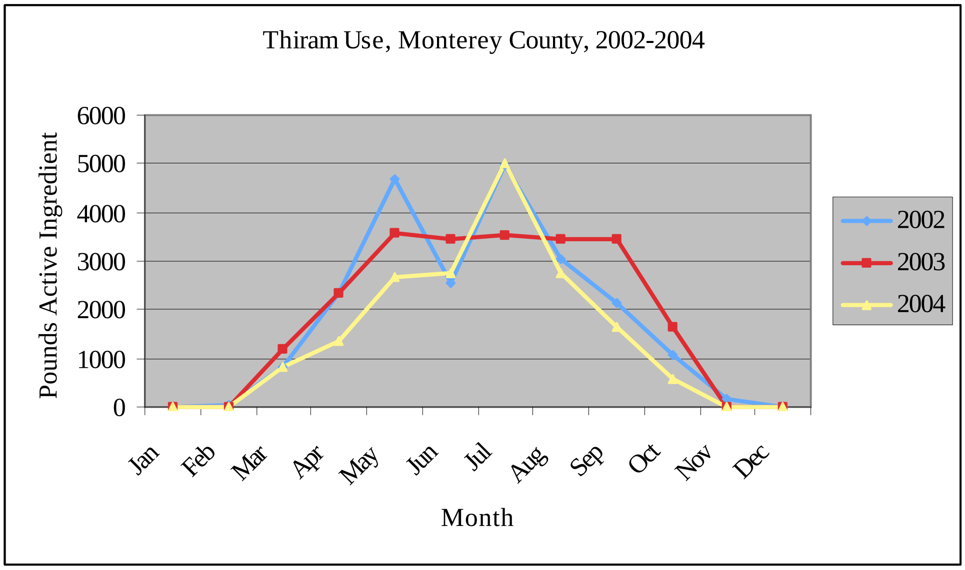


Figure 25. Santa Maria/Oxnard Thiram Use, 2002-2004.