Department of Pesticide Regulation
Environmental Monitoring Branch
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Study 248. Long-term Pesticide Monitoring in High-Use Agricultural Areas: Central Coast and Imperial Valley.

Keith Starner

I. INTRODUCTION

In California, a wide variety of pesticides are applied throughout the year; in 2005, for example, over 300 pesticide active ingredients (AIs) were applied in agricultural areas of the state (CDPR 2007a). For many of these, recent surface water monitoring data from areas of high use are lacking or outdated.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.

Pesticide active ingredients which are highly toxic to aquatic organisms and have significant use in California were identified through assessments of toxicity and pesticide use data (Starner 2007a, Starner 2007b, US EPA 2007). Two areas of the state, the Central Coast and Imperial Valley (Figure 1), have high agricultural use of several active ingredients identified in this manner (Tables 1 through 3). Recent monitoring results from these areas indicate that, for several of these AIs, concentrations exceeding water quality benchmarks can occur in aquatic environments; for several other AIs with significant aquatic toxicity, recent surface water monitoring data are lacking (Anderson *et al.* 2005, Starner *et al.* 2006, Hunt *et al.* 2006, Starner 2007c).

The purpose of this project is to establish long-term (multi-year) monitoring stations in these two areas, monitoring for pesticide AIs identified as having significant toxicity to aquatic organisms. Agriculture pesticide use in these areas is among the highest in the state for a wide variety of active ingredients, including several organophosphate, carbamate and pyrethroid insecticides and a variety of herbicide and fungicide active ingredients. The two areas represent different climates, soil types, treated crops, and agricultural practices, factors which impact the potential for offsite movement of pesticides. Pest pressures, use patterns, and management practices in the areas can vary from year to year. As such, consistent monitoring over time will provide useful data on the environmental fate of current-use pesticides under a variety of conditions, for use in the development of management responses. Targeted active ingredients will be adjusted as use and management practices dictate.

II. OBJECTIVE

The objective of this study is to provide a long-term assessment of surface water pesticide contamination in portions of the Central Coast and the Imperial Valley of California.

Results will provide useful data on the environmental fate of current-use pesticides under a variety of conditions, for use in the development of management responses.

Note: All pesticide use data cited are agricultural use data from DPR 2007 unless specified otherwise.

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, Environmental Program Manager I. Key personnel are listed below:

Project Leader:	Keith Starner
Field Coordinator:	Li-Ming He
Senior Scientist:	Frank Spurlock
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

Monitoring in the two geographic areas will be conducted during the season or seasons of historically high pesticide use (Table 4, Figures 2-13). Central Coast monitoring efforts will be focused on the irrigation season (approximately March through September) in Monterey and Santa Cruz counties. Sampling will take place approximately once per month during this period. Winter monitoring in the Central Coast will be conducted in January or February, will include monitoring for pre-emergent herbicides, and may include sampling sites in San Luis Obispo and Santa Barbara counties. When possible, winter herbicide sampling will be timed to follow or coincide with rainfall events and subsequent runoff. Imperial Valley monitoring will include spring and fall monitoring for OP and carbamate insecticides. Spring Imperial Valley monitoring will include sampling for pre-emergent herbicides. Additional AIs may be added to the monitoring plan for either area in subsequent years. Pyrethroid insecticides are not included in the current monitoring plan, but may be added in subsequent years.

Six to ten “primary” sites in each area will be sampled at least once at every sampling interval throughout the multi-year project. Primary sites will be sampled for organophosphate and carbamate insecticides at every sampling event. Samples will also be collected for additional AIs at the primary sites as appropriate based on historical pesticide use. In addition to the primary sites, additional “secondary” sites will be sampled as appropriate based on current pesticide use in the areas. Some sites (primary or secondary) may be sampled multiple times during a single sample event to collect time-series pesticide concentration data. Locations of individual sampling sites will be determined based on recent surface monitoring results and the historical pesticide use patterns in the areas. Site selection will follow the general guidelines in Standard Operating Procedure (SOP) FSWA002.00 (Bennett 1997) where applicable.

Monitoring in the two areas is planned to continue through Fall 2009. Including data previously collected, this will provide data through three complete irrigation seasons in the Central Coast and three spring/fall cycles in the Imperial Valley. The project may be extended if additional data are needed. The details presented here, including project budget, apply to year one. Sampling for year one of the assessment will commence in August 2007 and continue through June 2008.

V. SAMPLING METHODS

At each sampling site, surface water grab samples for chemical analysis will 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 glass bottles in the field. Glass bottles will be sealed with Teflon-lined lids and samples will be transported and stored on wet ice or refrigerated at 4^{o}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.

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 5. Details of the chemical analysis methods and method detection/reporting limits for newly developed methods will be provided in the final report. Quality control will be conducted in accordance with Standard Operating Procedure QAQC001.00 (Segawa 1995).

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 pesticide concentrations to aquatic toxicity benchmarks, water quality limits and other toxicity data (US EPA 2007, Marshack 2007, CDFG 1994a, 1994b, 1995, 1996a, 1996b, 1998a, 1998b, 2000); 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 2007 through June 2008
Chemical Analysis:	September 2007 through September 2008
Final Report:	April 2009

IX. BUDGET

Sample analysis	Samples	Cost per sample	Total	
Organophosphate	130	650	84500	
Carbamates	120	800	96000	
Triazines/herbicides	20	900	18000	
Dinitroanilines	25	650	16250	(estimated cost)
Oxyfluorfen	10	400	4000	(estimated cost)
Thiram	15	400	6000	
		Subtotal	**224750**	

Continuing QC	Samples	Cost per sample	Total	
Organophosphate	13	650	8450	
Carbamates	12	800	9600	
Triazines/herbicides	2	900	1800	
Dinitroanilines	3	650	1950	(estimated cost)
Oxyfluorfen	1	400	400	(estimated cost)
Thiram	2	400	800	
		Subtotal	**23000**	

Total cost **247750**

X. REFERENCES

Anderson, B.S., Phillips, B.M., Hunt, J.W., Connor, V., Richard, N., Tjeerdema, R.S. 2006. Identifying primary stressors impacting macroinvertebrates in the Salinas River (California, USA): Relative effects on pesticides and suspended particles. Environmental Pollution 141 402-408.

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

CDFG (California Department of Fish and Game)1994a. Hazard Assessment of the Insecticide Diazinon to Aquatic Organisms in the Sacramento-San Joaquin River. http://www.cdpr.ca.gov/docs/sw/hazasm/hazasm94_2.pdf

CDFG 1994b. Hazard Assessment of the Insecticide Chlorpyrifos to Aquatic Organisms in the Sacramento-San Joaquin River System. http://www.cdpr.ca.gov/docs/sw/hazasm/hazasm94_1.pdf

CDFG 1995. Hazard Assessment of the Insecticide Methidathion to Aquatic Organism in the Sacramento-San Joaquin River System.

CDFG 1996a. Hazard Assessment of the Insecticide Dimethoate to Aquatic Organisms in the Sacramento-San Joaquin River System. http://www.cdpr.ca.gov/docs/sw/hazasm/hazasm96_4.pdf

CDFG 1996b. Hazard Assessment of the Insecticide Methomyl to Aquatic Organisms in the San Joaquin River System.
http://www.cdpr.ca.gov/docs/sw/hazasm/hazasm96_6.pdf

CDFG 1998a. Hazard Assessment of the Insecticide Malathion to Aquatic Life in the Sacramento-San Joaquin River System.
http://www.cdpr.ca.gov/docs/sw/hazasm/hazasm98_2.pdf

CDFG 1998b. Hazard Assessment of the Insecticide Carbaryl to Aquatic Life in the Sacramento-San Joaquin River System.
http://www.cdpr.ca.gov/docs/sw/hazasm/hazasm98_1.pdf

CDFG 2000. Water Quality Criteria for Diazinon and Chlorpyrifos.
http://www.cdpr.ca.gov/docs/sw/hazasm/hazasm00_3.pdf

CDPR 2007a. California Department of Pesticide Regulation's Pesticide Information Portal, Pesticide Use Report (PUR) data.
http://calpip.cdpr.ca.gov/cfdocs/calpip/prod/main.cfm

Hunt, J.W., Anderson, B.S., Phillips, B.M., Tjeerdema, R.S., Richard, N., Connor, V., Worcester, K., Angelo, M., Bern, A., Fulfrost, B., Mulvaney, D. 2006. Spatial relationships between water quality and pesticide application rates in agricultural watersheds. Environmental Monitoring and Assessment 121: 245-262.

Marshack, J. 2007. A compilation of water quality goals. California Regional Water Quality Control Board, Central Valley Region.
http://www.swrcb.ca.gov/centralvalley/water_issues/water_quality_standards_limits/water_quality_goals/index.html

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

Starner, K., White, J., Spurlock, F., and Kelley, K. 2006. Pyrethroid Insecticide in California Surface Waters and Bed Sediments: Concentrations and Estimated Toxicities. California Department of Pesticide Regulation, Environmental Monitoring.
http://www.cdpr.ca.gov/docs/sw/swposters/starner_pyreth06.pdf

Starner, K. 2007a. Assessment of acute aquatic toxicity of current-use pesticides in California, with monitoring recommendations. California Department of Pesticide Regulation, Environmental Monitoring.

Starner, K. 2007b. Review of US EPA Aquatic Life Benchmarks, with Monitoring Recommendations. California Department of Pesticide Regulation, Environmental Monitoring. *In preparation.*

Starner, K. 2007c. Research Results: Preliminary Assessment of Pesticide Contamination of Surface Waters in High Use Regions of California. California Department of Pesticide Regulation, Environmental Monitoring. *In preparation.* Study protocol is available at:
http://www.cdpr.ca.gov/docs/empm/pubs/protocol/study238protocol.pdf

US EPA 2002 Reregistration Eligibility Decision for Fenamiphos.
http://www.epa.gov/pesticides/reregistration/status.htm

US EPA 2005. Dichlorvos (DDVP) Revised Ecological Risk Assessment.
http://www.epa.gov/pesticides/reregistration/status.htm

US EPA 2006a. US EPA Office of Pesticide Programs ECOTOX database.
http://mountain.epa.gov/ecotox/

US EPA 2006b. Methamidophos IRED.
http://www.epa.gov/pesticides/reregistration/status.htm

US EPA 2007. Aquatic Life Benchmark Table.
http://www.epa.gov/oppefed1/ecorisk_ders/aquatic_life_benchmark.htm

Table 1. Agricultural Use of Monitoring Candidates, Monterey County and Imperial Valley.

Chemical	**Class**	**Status this project**	**Monterey Co. Use (1)**	**Imperial Valley Use**
Chlorpyrifos	Organophosphate insecticide	included	61886	77138
DDVP (degradate of naled)	Organophosphate insecticide	included	0	0
Diazinon	Organophosphate insecticide	included	163648	39121
Dimethoate	Organophosphate insecticide	included	41678	29902
Disulfoton	Organophosphate insecticide	included	10293	1753
Ethoprop	Organophosphate insecticide	included	1351	317
Fenamiphos	Organophosphate insecticide	included	4600	0
Malathion	Organophosphate insecticide	included	69950	58358
Methidathion	Organophosphate insecticide	included	9602	69
Methyl Parathion	Organophosphate insecticide	included	100	0
Phorate	Organophosphate insecticide	included	373	3562
Profenofos	Organophosphate insecticide	included	0	443
Tribufos	Organophosphate insecticide	included	0	3698
Acephate (degrades to methamidaphos)	Organophosphate insecticide	candidate for FY 2008-09	57699	14240
Methamidophos (degradate of acephate)	Organophosphate insecticide	candidate for FY 2008-09	10	982
Naled (degrades to DDVP)	Organophosphate insecticide	not included	22069	4072
Phosmet	Organophosphate insecticide	not included	1	16
Carbaryl	Carbamate insecticide	included	4135	3568
Methiocarb (Mesurol)	Carbamate insecticide	included	50	0
Carbofuran	Carbamate insecticide	included	7024	3047
Methomyl	Carbamate insecticide	included	56957	43550
Aldicarb	Carbamate insecticide	included	35	3500
Thiram	Dithiocarbamate fungicide	included	13402	1805
Oxyfluorfen	Diphenyl ether herbicide	under dev. for FY 2007-08	31286	5623
Trifluralin	Dinitroaniline herbicide	under dev. for FY 2007-08	2922	238722
Oryzalin	Dinitroaniline herbicide	under dev. for FY 2007-08	13639	0
Pendimethalin	Dinitroaniline herbicide	under dev. for FY 2007-08	614	24511
Ethalfluralin	Dinitroaniline herbicide	under dev. for FY 2007-08	266	109
Endosulfan	Chlorinated hydrocarbon	candidate for future monitoring	525	8189
Chlorothalonil	substituted benzene fungicide	candidate for future monitoring	15340	36658
Simazine	triazine herbicide	included	16649	0
Atrazine	triazine herbicide	included	0	14750
Diuron	urea herbicide	included	1860	1339

(1) Use is average of agricultural use, 2003-2005, in pounds of active ingredient applied.

Sources: Starner 2007, US EPA 2007, Starner forthcoming (a).

Table 2. US EPA Aquatic Life Benchmarks for Monitoring Candidates

Chemical	Acute fish (all in ug/L)	Chronic fish	Acute inverts	Chronic inverts	Acute nonvascular plants	Acute vascular plants	Chronic aquatic community	Chemical Class
Azinphos-methyl	0.18	0.36	0.08	0.16	—	—	—	Organophosphate
Chlorpyrifos	0.9	0.57	0.05	0.04	140	—	—	Organophosphate
Diazinon	45	0.55	0.1	0.17	3700	—	—	Organophosphate
Dimethoate	3000	430	21.5	40	—	—	—	Organophosphate
Disulfoton	19.5	39	1.95	0.037	—	—	—	Organophosphate
Ethoprop	150	24	22	0.8	8400	—	—	Organophosphate
Malathion	2	4	0.25	0.06	—	—	—	Organophosphate
Methyl parathion	500	80	0.07	0.02	5300	—	—	Organophosphate
Phorate	0.5	1	0.3	0.21	1300	—	—	Organophosphate
Profenofos	12.5	2	0.45	0.2	—	—	—	Organophosphate
Tribufos	122.5	—	13.5	2	148	—	—	Organophosphate
Aldicarb	26	0.46	10	1	50000	—	—	Carbamate
Carbaryl	125	210	2.55	1.5	1100	—	—	Carbamate
Methiocarb (Mesurol)	218	50	3.5	0.1	—	—	—	Carbamate
Carbofuran	44	5.7	1.115	0.75	—	—	—	Carbamate
Methomyl	265	57	4.4	0.4	—	—	—	Carbamate
Oxyfluorfen	100	38	40	13	0.29	—	—	Nitrophenyl ether
Ethalfluralin	16	0.4	30	24	25	—	—	dinitroanilines
Oryzalin	1440	220	700	—	42	15.4	—	dinitroanilines
Pendimethalin	69	6.3	140	14.5	5.4	12.5	—	dinitroanilines
Trifluralin	20.5	1.14	280	2.4	7.52	43.5	—	dinitroanilines
Simazine	3200	960	500	1000	36	140	—	Triazine
Atrazine	2650	62	360	62	32	18	17.5	Triazine
Norflurazon	4050	770	7500	1000	13	86	—	Pyridazinone
Diuron	355	26	80	160	2.4	—	—	Urea
Chlorothalonil	11.5	3	34	39	190	—	—	Nitrile

Source: US EPA 2007.

Table 3. Additional Toxicity Data for Candidate AIs.

Chemical	Test Organism	Test/Endpoint	Concentration (ppb)	Source
Dichlorvos (DDVP)	Waterflea	48 hr EC50	0.07	US EPA 2005
	Stonefly	96 hr LC50	0.1	US EPA 2006a
	Waterflea	48 hr EC50	0.26	US EPA 2005
	Scud	96 hr LC50	0.5	US EPA 2006a
Fenamiphos (1)	Daphnid	LC50	1.9	US EPA 2002
	Bluegill sunfish	96 hr LC50	4.5	US EPA 2006a
	Mysid shrimp (2)	LC50	6.2	US EPA 2002
	Mysid	96 hr LC50	6.8	US EPA 2006a
	Bluegill Sunfish	LC50	9.5	US EPA 2002
	Bluegill sunfish	96 hr LC50	9.6	US EPA 2006a
Methamidophos	Blue shrimp (2)	96 hr EC50	0.00016	US EPA 2006b
	Waterflea	48 hr EC50	0.026	US EPA 2006b
	Freshwater Prawn	48 hr LC50	0.042	US EPA 2006a
	White shrimp	48 hr LC50	0.16	US EPA 2006a
Phosmet	Scud	96 hr LC50	2	US EPA 2006a
	Brown shrimp	48 hr LC50	2.5	US EPA 2006a
Thiram	Mysid	96 hr LC50	3.36	US EPA 2006a
	Harlequin fish	96 hr LC50	7	US EPA 2006a

(1) Fenamiphos degradates, sulfoxide and sulfone, are equally toxic to aquatic invertebrates. EPA 2002.
(2) Estuarine/Marine organism

Table 4. Monitoring Plan, Central Coast and Imperial Valley, 2007-2008.

Area	Analytical Screen	Season	Sample events
Central Coast	Organophosphates	Spring though Fall	6
Central Coast	Carbamates	Spring through Fall	6
Central Coast	Organophosphates	Winter	1
Central Coast	Dinitroaniline herbicides	Winter	1
Central Coast	Oxyfluorfen	Winter	1
Central Coast	Triazine herbicides	Winter	1
Imperial Valley	Organophosphates	Spring and Fall	2
Imperial Valley	Carbamates	Spring and Fall	2
Imperial Valley	Dinitroaniline herbicides	Spring	1
Imperial Valley	Triazine herbicides	Spring	1

Table 5. 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

Oxyfluorfen in Surface Water

Compound	***Method Detection Limit (µg/L)***	***Reporting Limit (µg/L)***
Oxyfluorfen	0.01	0.05

Figure 1. Monitoring regions.

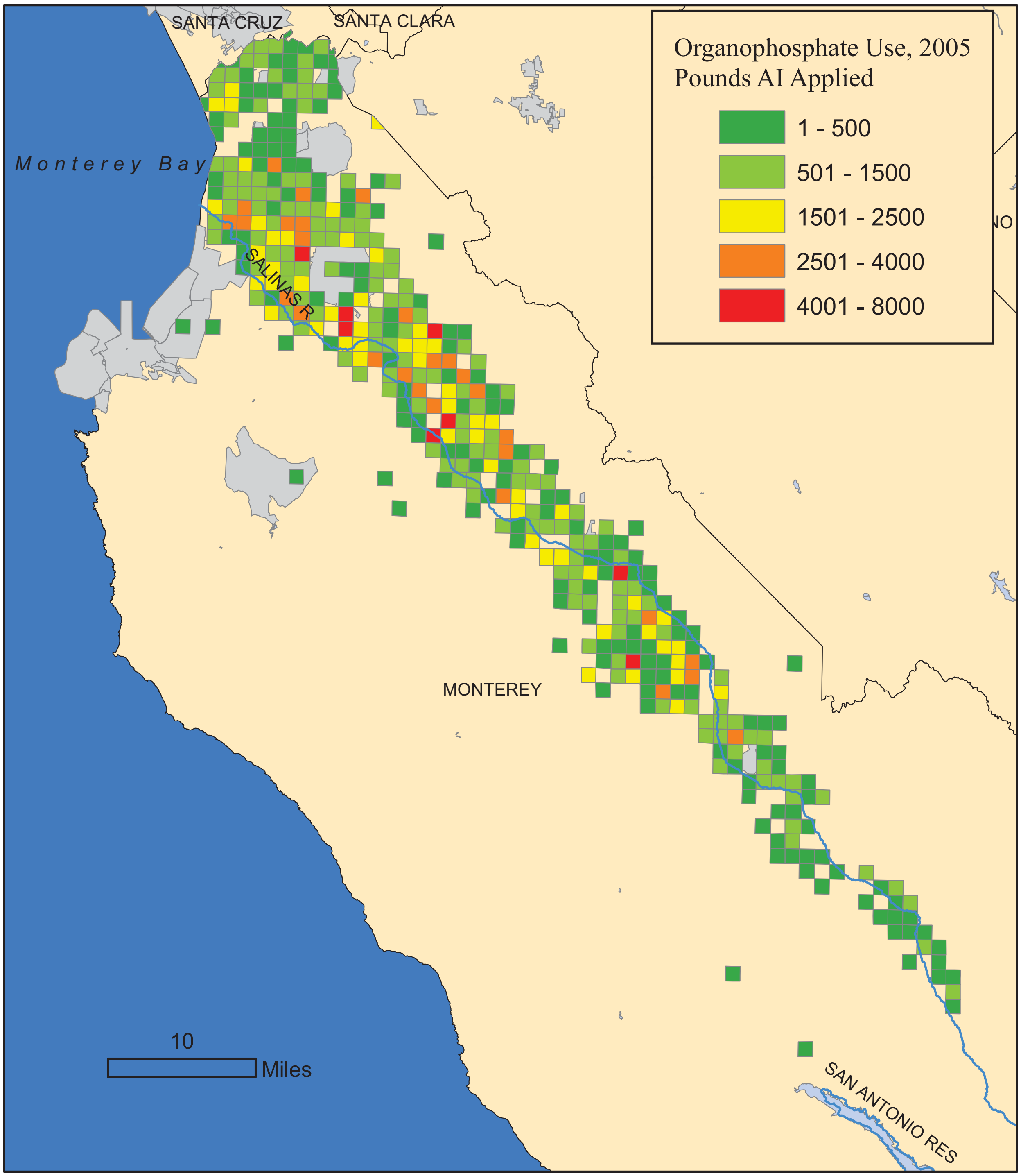


Figure 2. Monterey County Organophosphate Use, 2005.

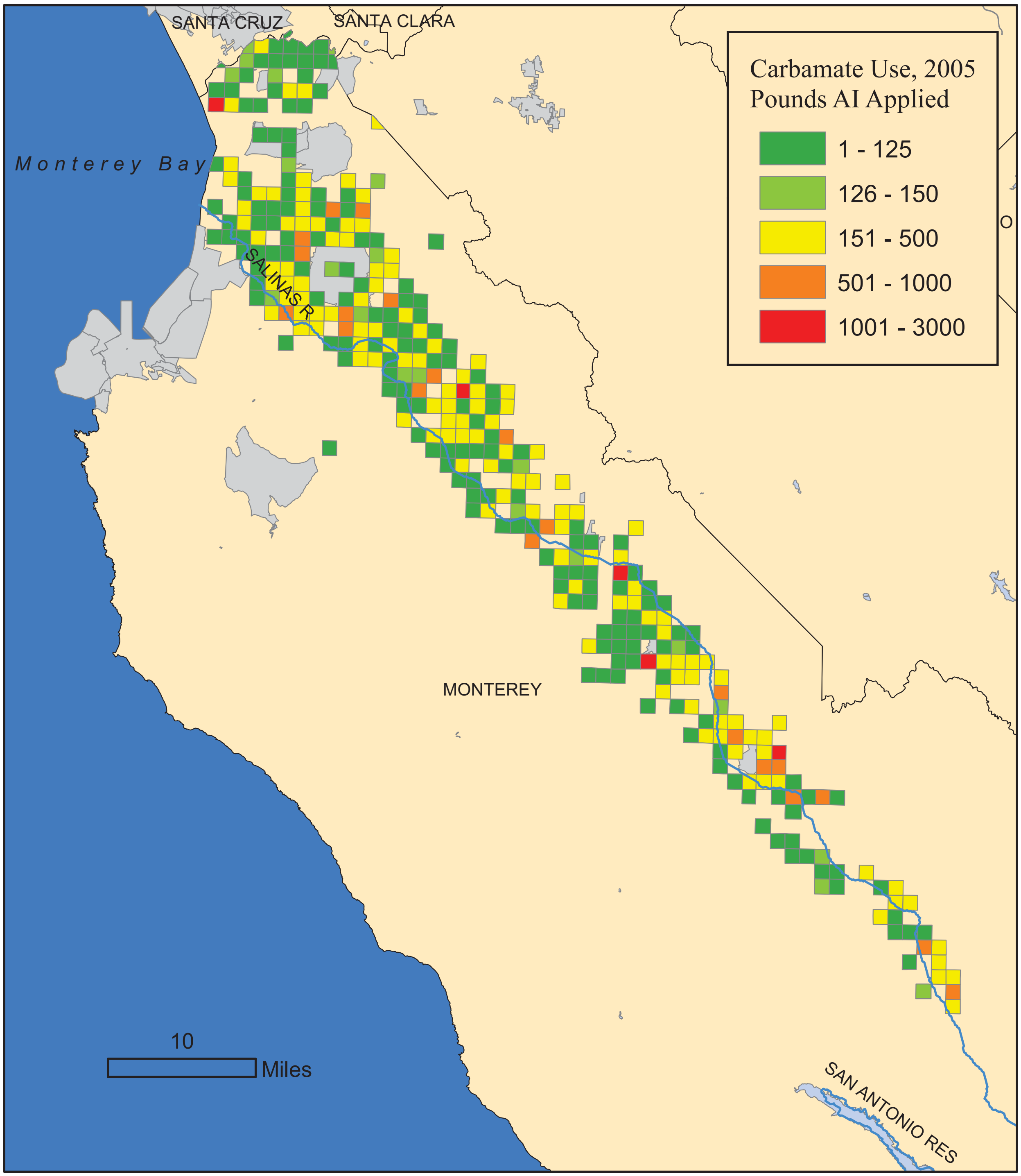


Figure 3. Monterey County Carbamate Use, 2005.

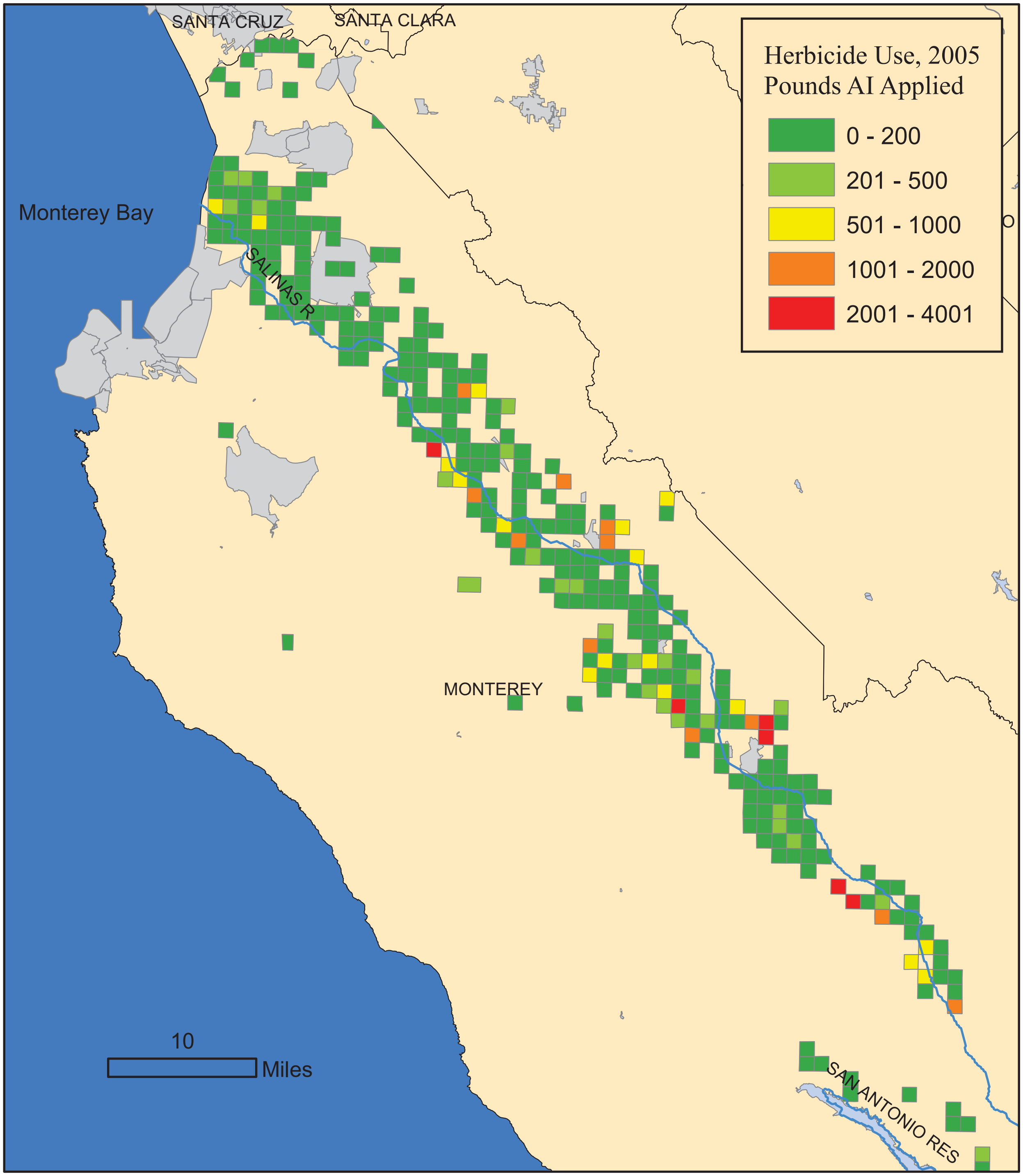


Figure 4. Monterey County Herbicide Use, 2005.

Figure 5. Average Organophosphate Use, Monterey County, 2003-2005.

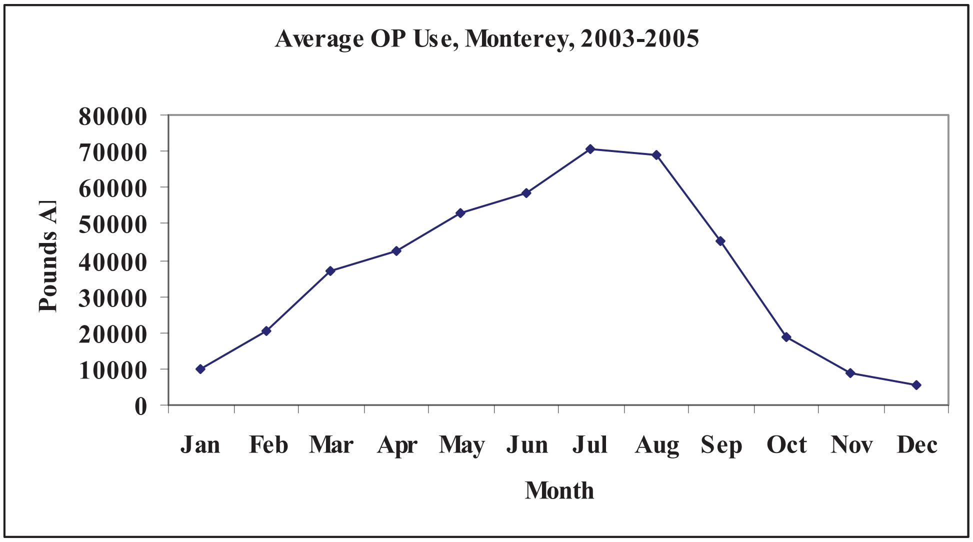


Figure 6. Average Carbamate Use, Monterey County, 2003-2005.

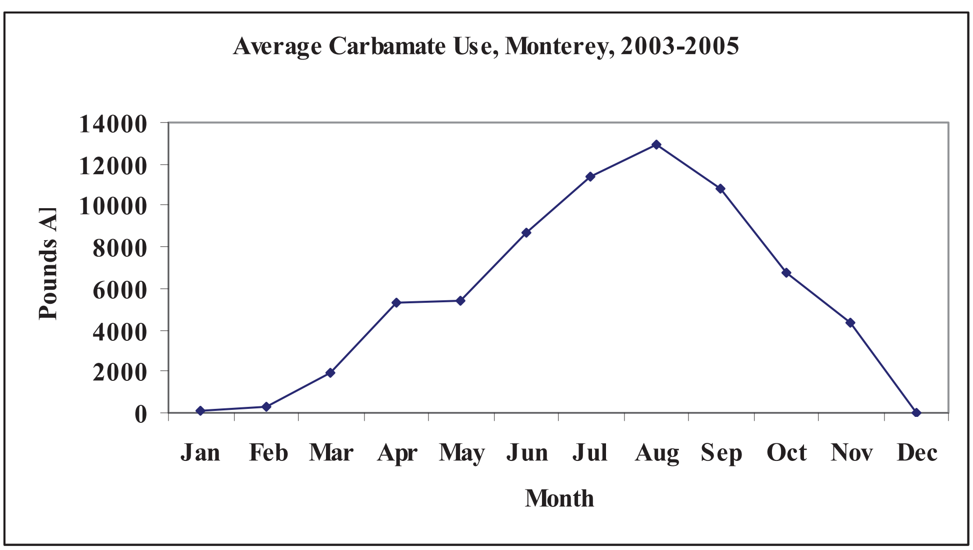
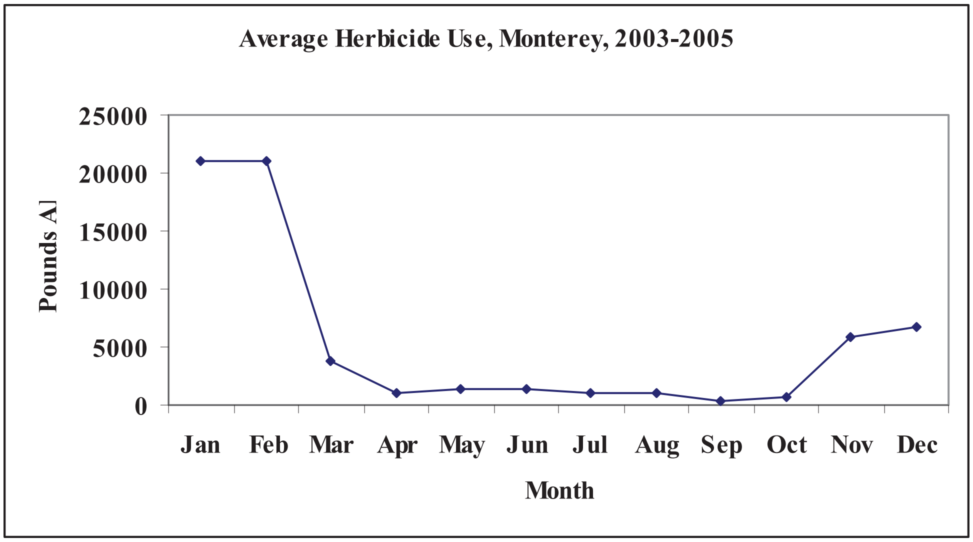


Figure 7. Average Pre-emergent Herbicide Use, Monterey County, 2003-2005.



Pre-emergent herbicides include oxyfluorfen, simazine, and the dinitroaniline herbicides.

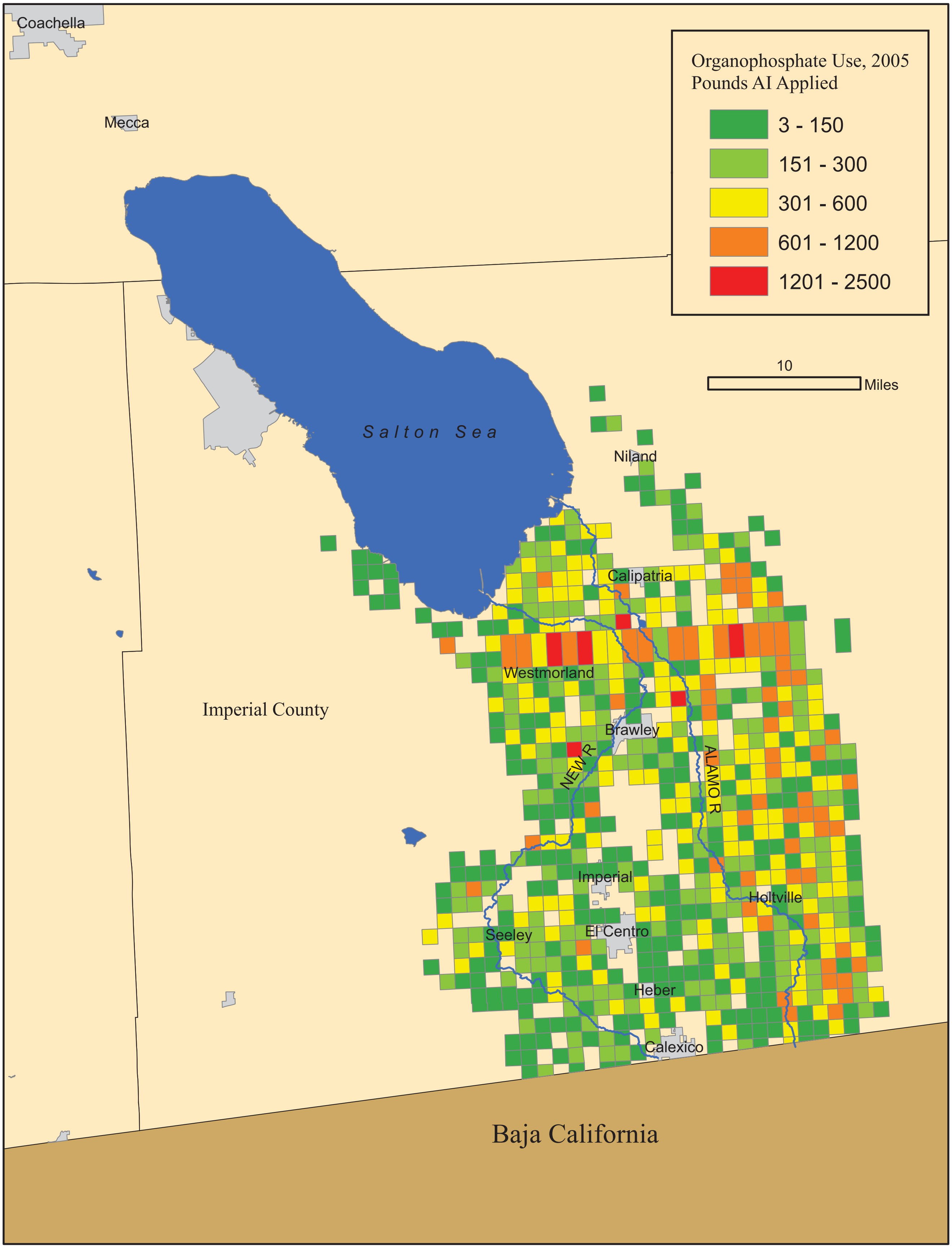


Figure 8. Imperial County Organophosphate Use, 2005.

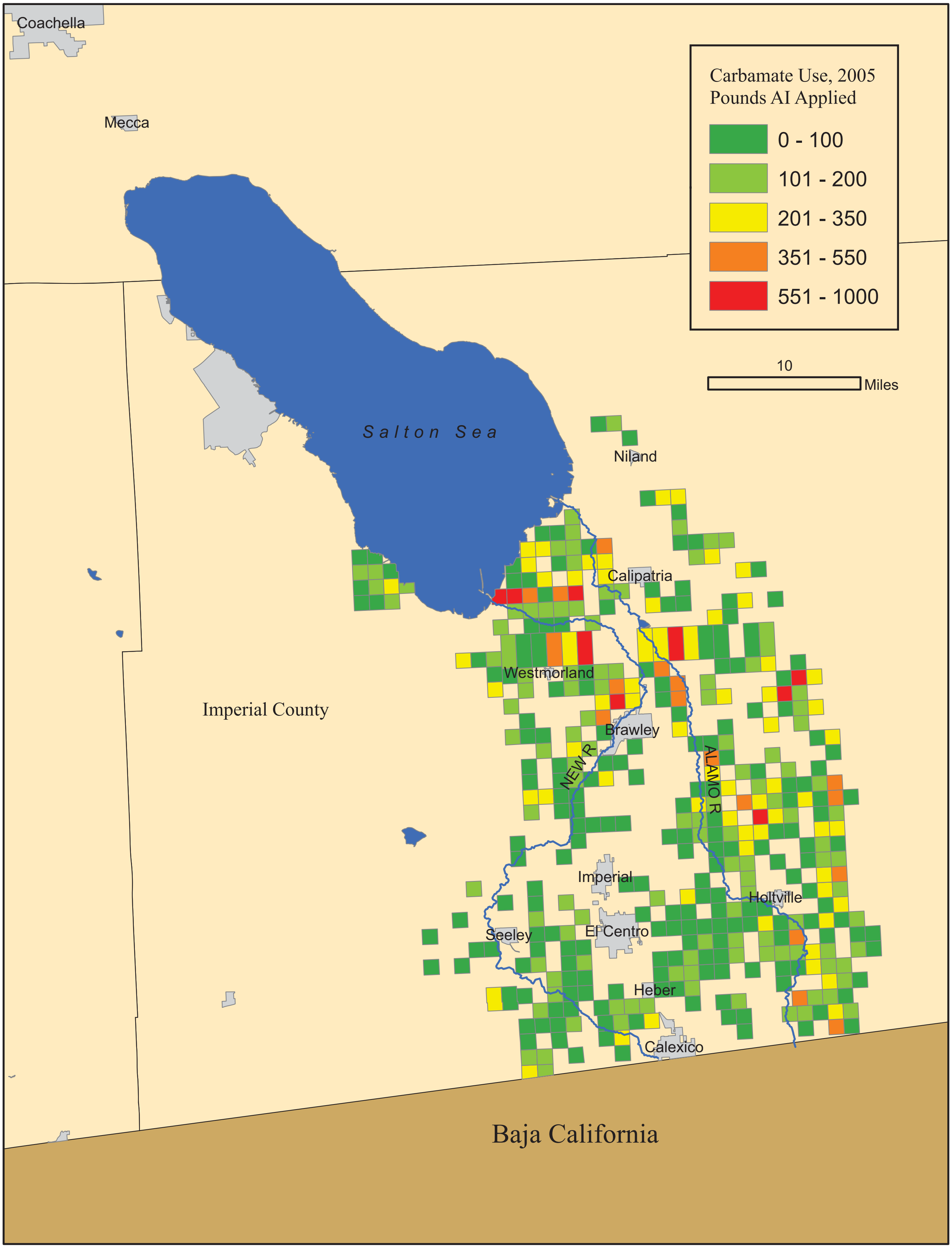


Figure 9. Imperial County Carbamate Use, 2005.

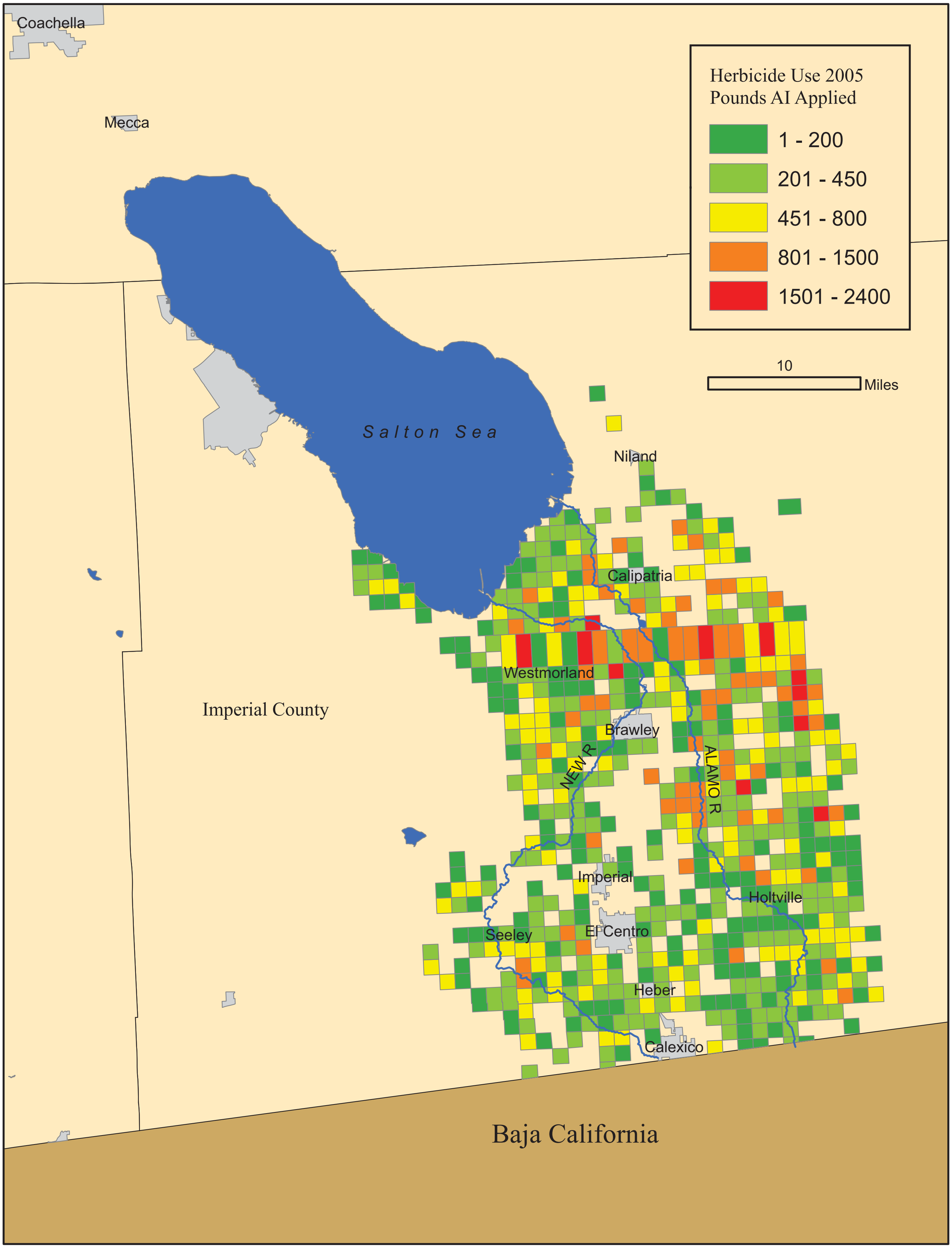


Figure 10. Imperial County Herbicide Use, 2005.

Figure 11. Average Organophosphate Use, Imperial County, 2003-2005.

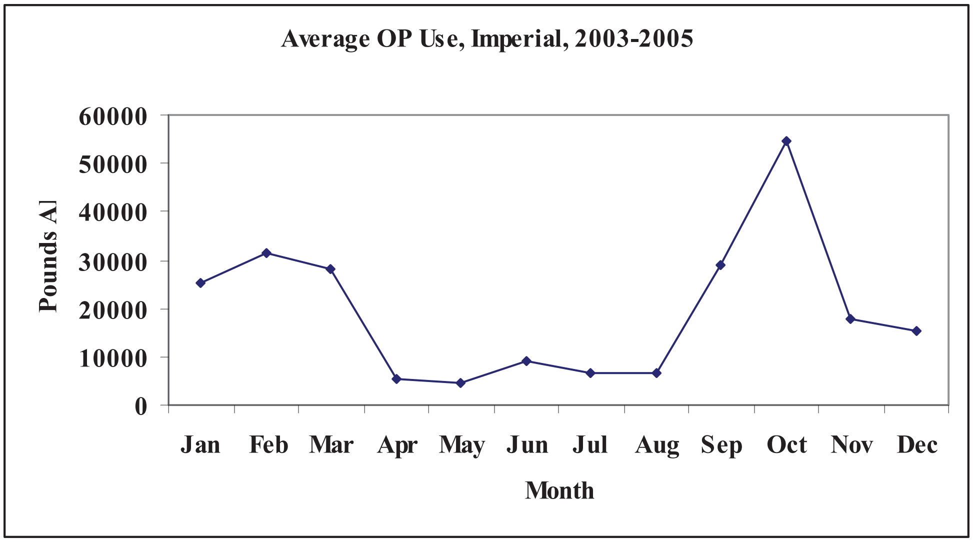


Figure 12. Average Carbamate Use, Imperial County, 2003-2005.

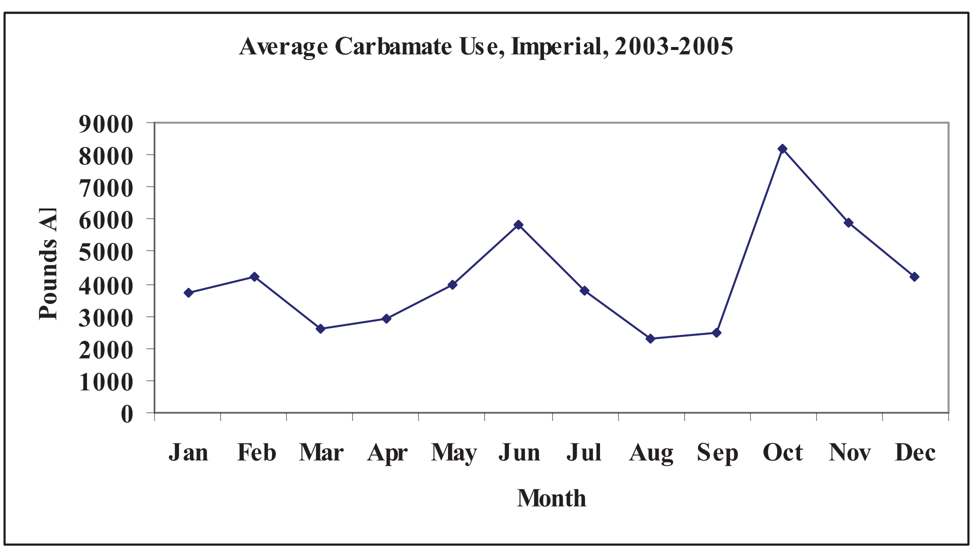


Figure 13. Average Herbicide Use, Imperial County, 2003-2005.