



**Department of Pesticide Regulation
Environmental Monitoring Branch
Surface Water Protection Program
1001 I Street
Sacramento, California 95812**

Analysis of Chlorpyrifos Agricultural Use in Regions of Frequent Surface Water Detections in California, USA

Xuyang Zhang, Keith Starner, and Frank Spurlock

April 24, 2012

Abstract

For seven agricultural regions in California, USA, the frequency of chlorpyrifos detection in surface water was determined from recent monitoring data. For each region, chlorpyrifos use data was summarized by crop treated, product formulation and application method. Among the seven regions, higher frequencies of chlorpyrifos detections and exceedances occurred in the Central Coast regions and Imperial Valley region. Chlorpyrifos detection frequency and the primary crops treated varied significantly among regions; the application method did not. Regarding formulation, granular products were only used in high detection regions. However, available data for the effect of granular formulation on runoff potential relative to other formulations are limited. The results suggest that the variation in chlorpyrifos detection frequencies likely did not occur primarily due to application method. The observed variation may be due to but not limited to differences in use density, irrigation methods, and seasonal use patterns.

Introduction

Chlorpyrifos is a broad-spectrum organophosphorus insecticide currently used in California on a variety of crops. The major uses include nut orchards, citrus, alfalfa, wine grapes and vegetable crops. Between 2006 and 2010, more than 1.45 million pounds of chlorpyrifos active ingredient (AI) were used annually in California. Non-agricultural uses of chlorpyrifos were phased out during 2002-2004, after which detections of chlorpyrifos in urban areas decreased significantly (Philips et al., 2007). However, the pesticide was still frequently detected in streams in agricultural areas of California. In 2002 and 2003, DPR and the Central Valley Regional Water Quality Control Board (CVRWQCB) collected water samples from rivers and tributaries of the San Joaquin Valley, the Sacramento/San Joaquin Delta, and Monterey County tributaries. Analysis of the monitoring data revealed numerous chlorpyrifos detections at levels that exceeded water quality criteria (Spurlock, 2004). Consequently in 2004, DPR placed all agricultural use products containing chlorpyrifos into reevaluation. In 2006, DPR adopted dormant spray regulations to restrict pesticide application during the dormant season, which coincides with the rainy season in winter (DPR, 2005a). After that, dormant uses of chlorpyrifos on tree crops have dropped significantly; however, a substantial amount of chlorpyrifos is still

being used during the irrigation season on tree crops and year-round on other crops. Recent monitoring studies showed frequent detections of chlorpyrifos with concentrations exceeding water quality criteria (Ensminger *et al.*, 2011, Corbin *et al.*, 2009, Philips *et al.*, 2007). To further reduce chlorpyrifos contamination to the surface waters of California, more investigations are needed to examine the processes and associated factors that contribute to off-site movement of chlorpyrifos. The objective of this analysis was to identify chlorpyrifos use scenarios that potentially contribute to its frequent detections in surface waters of California.

Materials and Methods

This analysis targeted chlorpyrifos use scenarios in the major agricultural production areas. First, monitoring sites with the most frequent exceedances of the target concentration were identified using monitoring data from 2006 to 2010. The chronic U.S. EPA benchmark for aquatic invertebrates (0.04 ug/L), the lowest value for aquatic organisms, was used as the target concentration (U.S. EPA, 2012). Second, drainage areas contributing to these sites were identified using CalWater 2.2 watershed maps that were developed by the California Interagency Watershed Mapping Committee (USDA 2009). Finally, chlorpyrifos use data in the drainage areas were summarized to identify the top use scenarios.

Pesticide surface water monitoring data were queried from the DPR surface water monitoring database (DPR, 2012a) for seven major agricultural regions in California: Sacramento, San Joaquin, and Tulare from the Central Valley; Pajaro, Salinas and Santa Maria from the Central Coast; and Imperial Valley from Southern California (Fig 1). All surface water monitoring data available as of February 2011 were included in the analysis. In addition, the data from the Central Coast Monitoring Program, which were not in DPR's surface water monitoring database, were added for analysis. Monitoring data from 2006 to 2010, with 2,495 samples collected from 222 sample sites, were included in the final dataset (Table 1). For each monitoring site, the total number of samples, detections, and detected concentrations greater than the target concentration were determined. Based on these data, the frequency of detection and the frequency of benchmark exceedance were calculated.

Chlorpyrifos use information between 2006 and 2010 was collected from DPR's Pesticide Use Reporting (PUR) database (DPR, 2012b). PUR data were mapped with the basic spatial unit of township/range/sections, which is a one-square-mile land unit defined by the U.S. Department of Interior's Public Lands Survey Coordinate System. Applications occurring within each region were identified by overlaying the GIS maps of township/range/sections with CalWater2.2 watershed boundaries. Crops with top chlorpyrifos use (pounds of AI) were then identified in each drainage region.

Results and Discussion

Overall, a total of 2,495 samples were collected with 441 detections and 248 exceedances yielding frequencies of 17.7% and 9.9%, respectively (Table 1). The highest concentration (3.7 ug/L) was reported in July of 2007 from a sample in Black Rascal Creek in Merced County (San Joaquin Region) (Table 2). Among the seven regions, Santa Maria Valley had the most frequent detections and exceedances with chlorpyrifos detected in 79.8% of the samples, among which 57% exceeded the U.S. EPA benchmark of 0.04 ug/L (Table 1). The three regions in the Central

Coast plus the Imperial Valley had higher detection and exceedance frequencies than the three regions in the Central Valley.

From 2006 to 2010, statewide chlorpyrifos use decreased by 33 and 29% in total pounds of AI and applied acreage, respectively (Fig. 2). Chlorpyrifos use in the Tulare Region was the highest among all regions, accounting for 58% of the total pounds and 55% of the applied acreages (Fig. 2). San Joaquin Valley ranked second accounting for 14% of the statewide use followed by the Sacramento Valley with 12% (Fig. 2). Use in the Salinas, Imperial, Pajaro and Santa Maria valleys was relatively lower accounting for only 10% altogether.

Table 1. Summary of chlorpyrifos monitoring and pesticide use data (2006-2010) for the 7 California use regions.

Region	Monitoring Results in Surface Water						Pesticide Use		
	Sites	samples	No. Detect	No. Exceed ^a	Detect%	Exceed%	lbs/year ^b	acre/year ^c	lbs/acre
Santa Maria	19	84	67	48	79.8	57.1	27,705	16,878	1.64
Imperial	15	72	34	22	47.2	30.6	47,946	31,726	1.51
Salinas	20	241	106	63	44.0	26.1	56,908	44,982	1.27
Pajaro	21	68	12	9	17.6	13.2	6,723	4,878	1.38
San Joaquin	96	1575	203	103	12.9	6.5	270,871	216,430	1.25
Sacramento	35	352	18	2	5.1	0.6	154,617	107,545	1.44
Tulare	16	103	1	1	1.0	1.0	779,716	605,869	1.29
All Regions	222	2495	441	248	17.7	9.9	1,344,486	1,028,308	1.31

^a A target concentration of 0.04 ug/L, the lowest U.S.EPA benchmark, was used to determine number of exceedances and percent exceedances.

^b Total pounds of applied active ingredient per year

^c Total acreage of crop land per year that received chlorpyrifos application

Previous studies have shown that use amount of pesticides was significantly correlated with their surface water detections within a watershed (Guo *et al.*, 2004, Spurlock 2004). Pesticide use intensity as expressed by pounds of active ingredient per acre of applied crop land (lbs/acre) was shown in Table 1. The use intensities in the seven regions were correlated with their exceedance frequencies (Pearson's coefficient = 0.7).

Table 2: Summary statistics of chlorpyrifos monitoring data by region (2006-2010)

	Santa Maria	Imperial	Salinas	Pajaro	San Joaquin	Sacramento	Tulare
Median	0.0583	0	0	0	0	0	0
Minimum	0	0	0	0	0	0	0
25th Percentile	0.0197	0	0	0	0	0	0
Mean	0.1408	0.0445	0.0959	0.0092	0.0173	0.0011	0.0045
75th Percentile	0.1817	0.0587	0.0431	0	0	0	0
95th Percentile	0.519	0.152	0.526	0.066	0.051	0.002	0.000
Maximum	0.978	0.61	2.377	0.0826	3.7	0.083	0.46
Standard Deviation	0.1858	0.1001	0.291	0.0224	0.1319	0.0064	0.0453
Sample Variance	0.0345	0.01	0.0847	0.0005	0.0174	4E-05	0.0021
Kurtosis	4.9285	20.333	28.796	3.8044	441.82	92.636	103
Skewness	2.0545	4.2541	4.9798	2.2938	18.631	8.8253	10.149
Count	84	72	241	68	1575	352	103

The regions with higher detection/exceedance frequencies (e.g. Santa Maria, Imperial) applied a higher amount of chlorpyrifos per unit crop land than regions with lower detection/exceedance frequencies (Table 1). This could be associated with more repeated pesticide applications and multiple cropping of vegetables within a year in the high detection/exceeding regions. In the Central Coast, two or three vegetables crops per year were common, whereas in the Central Valley where tree crops were the top uses, only one crop is grown throughout the year. Besides use intensity, other factors may also affect chlorpyrifos runoff into surface water, such as the way the pesticide was applied (application method), the type of products applied (product formulation), irrigation type, and timing of pesticide application in relation to rainfall / irrigation events. Use information on treated crops including application method and product formulation was summarized and compared between the regions with high and low exceedance frequencies.

Regions with high use and low exceedance frequencies (Tulare, San Joaquin and Sacramento)

In the Tulare Region, 16 sites were monitored for chlorpyrifos from 2006 to 2009. Of the 103 samples taken, only one sample exceeded the target concentration of 0.04 ng/L (Table 1). That sample was taken in July 2006 in Goshen Ditch with a concentration of 0.46 ug/L. Between 2006 and 2010, over 3.89 million pounds of chlorpyrifos were used in this region accounting for 58% of the use in the entire state. Chlorpyrifos was mainly used on almond, orange, alfalfa and cotton, accounting for 73% of the total use in the region (Table 3). Since dormant use of chlorpyrifos had decreased significantly, most of the applications occurred during summer months from May to September (Fig. 3). On almond and orange, chlorpyrifos was applied mainly via ground spray, while on alfalfa and cotton, aerial spray was the dominant type. Regarding product formulation, both emulsifiable concentrate (EC) and liquid concentrate (LC) formulated products were used with EC being the more popular type. Almost no products applied were formulated as granular (GR).

In the San Joaquin Valley region, a total of 96 sites were monitored for chlorpyrifos from 2006 to 2010. Among the 1,575 samples taken, 6.5% exceeded the target concentration of 0.04 ug/L (Table 1). Exceedance occurred in 46 of the 96 sites. Between 2006 and 2010, a total of 1.35 million pounds of chlorpyrifos were used in this region. Chlorpyrifos was mainly used on almond, walnut, alfalfa, and wine grapes, accounting for 83% of the total use in the region (Table 3). Applications occurred mainly in March during spring and from May to September during summer (Fig. 3). Most applications were implemented via ground spray except for those on alfalfa, of which 63% was applied via aerial spray (Table 3). Both EC and LC formulated products were used, with EC being the most dominant type (Table 4). Very few granular products were applied in this region (Table 4).

In the Sacramento Valley region, 35 sites were monitored for chlorpyrifos from 2006 to 2010. A total of 352 samples were taken, 0.6% of which exceeded the target concentration (Table 1). Between 2006 and 2010, over 773,000 lbs of chlorpyrifos were used, accounting for 12% of use in the entire state. Chlorpyrifos was mainly used on walnut, almond and alfalfa, accounting for 96% of the total use in the region (Table 3). Applications occurred mainly in March during spring and from May to September during summer (Fig. 3). Almost all the applications were by ground spray using EC formulated products except for alfalfa, on which 63% of the applications were by air (Table 3 and 4).

Table 3. Chlorpyrifos use by application method, 2006-2010.

Region	Crop	Total (lbs)	Ground (%)	Aerial (%)	Other (%)	Major* Irrigation
Tulare	Almond	1,194,140	83	17	0	drip/micro
	Orange	647,130	99	0	1	drip/micro
	Alfalfa	521,801	10	90	0	gravity
	Cotton	476,993	12	88	0	gravity
	All Crops	3,898,613	68	31	0	
San Joaquin	Almond	453,072	88	12	0	drip/micro
	Walnut	309,647	97	3	0	drip/micro gravity
	Alfalfa	233,398	37	63	0	gravity
	Grapes, Wine	126,826	100	0	0	drip/micro
	All Crops	1,354,356	79	21	0	
Sacramento	Walnut	497,586	85	15	0	drip/micro sprinkler
	Almond	191,882	93	7	0	drip/micro
	Alfalfa	54,797	33	67	0	gravity
	All Crops	773,087	83	17	0	
Salinas	Broccoli	153,695	99	0	1	sprinkler drip/micro
	Grapes, Wine	72,971	100	0	0	drip/micro
	Cauliflower	37,324	99	0	1	sprinkler drip/micro
	All Crops	284,541	99	0	1	
Imperial	Sugarbeet	128,883	20	76	4	gravity
	Alfalfa	89,456	31	68	1	gravity
	Corn	12,281	49	37	14	gravity
	All Crops	239,728	26	71	3	
Santa Maria	Broccoli	86,061	98	2	0	sprinkler drip/micro
	Grapes, Wine	19,707	100	0	0	drip/micro
	Strawberry	15,891	100	0	0	sprinkler drip/micro
	Cauliflower	10,915	100	0	0	sprinkler drip/micro
	All Crops	138,524	99	1	0	
Pajaro	Apple	8,762	100	0	0	sprinkler drip/micro
	Cabbage	4,059	99	0	0	sprinkler
	Corn	3,123	93	7	1	drip/micro
	All Crops	33,613	95	5	0	

*Source : California Department of Water Resources statewide irrigation methods survey of 2010. (DWR, 2012). Major types refer to the type of irrigation used in greater than 50% of the irrigated crop land. If none of the irrigation method was >50%, the top two types, which normally accounted for 30-50% of the irrigated crop land were listed.

In summary, the three regions in the Central Valley accounted for 90% of chlorpyrifos applied statewide. Top use crops include trees (almond, walnut, orange), vines (wine grapes), alfalfa and cotton. On tree crops, dormant uses had been reduced significantly with the remaining uses

occurred mainly in March during spring and from May to September during summer. Most of the applications were made by ground spray using EC formulated products. For those crops, most of the land was equipped with low volume irrigation such as micro/mini sprinkler and drip (Table 3). For wine grapes, chlorpyrifos was applied in spring and fall via ground spray using EC and LC formulated products. Most of the wine grapes were irrigated using drip or micro sprinkler (Table 3). For alfalfa, chlorpyrifos was applied mostly in March, July and August. Most of the applications were by aerial spray using EC formulated products. Gravity irrigation such as flood and furrow were commonly practiced in alfalfa. Figure 3 shows that monthly use of chlorpyrifos mirrors the monthly percentage of exceedances, with highest exceedances occurring during summer month (Fig. 3).

Table 4: Chlorpyrifos use by formulation 2006-2010

Region	Crop	Total (lbs)	EC (%)	LC (%)	GR (%)	Other (%)
Tulare	Almond	1,194,140	76	23	0	0
	Orange	647,130	76	24	1	0
	Alfalfa	521,801	95	5	0	0
	Cotton	476,993	94	6	0	0
	All Crops	3,898,613	82	17	1	0
San Joaquin	Almond	453,072	91	9	0	0
	Walnut	309,647	85	15	0	0
	Alfalfa	233,398	97	3	0	0
	Grapes, Wine	126,826	54	46	0	0
	All Crops	1,354,356	83	13	3	0
Sacramento	Walnut	497,586	92	8	0	0
	Almond	191,882	90	10	0	0
	Alfalfa	54,797	92	8	0	0
	All Crops	773,087	91	9	0	0
Salinas	Broccoli	153,695	39	14	47	0
	Grapes, Wine	72,971	86	14	0	0
	Cauliflower	37,324	20	4	74	2
	All Crops	284,541	50	13	36	1
Imperial	Sugarbeet	128,883	48	35	17	0
	Alfalfa	89,456	76	23	0	0
	Corn	12,281	52	36	12	0
	All Crops	239,728	59	30	10	0
Santa Maria	Broccoli	86,061	2	0	98	0
	Grapes, Wine	19,707	84	16	0	0
	Strawberry	15,891	92	8	0	0
	Cauliflower	10,915	10	0	90	0
	All Crops	138,524	26	4	69	0
Pajaro	Apple	8,762	88	12	1	0
	Cabbage	4,059	39	0	60	1
	Corn	3,123	9	1	90	0
	All Crops	33,613	52	12	32	4

* EC: emulsifiable concentrates; LC: liquid concentrates; GR: granular/flake

Regions with low use and high exceedance frequencies (Salinas, Santa Maria, Pajaro, and Imperial)

In the Salinas Valley region, 21 sites were monitored for chlorpyrifos from 2006 to 2010. A total of 236 samples were taken, 26.7% of which exceeded the target concentration of 0.04 ug/L (Table 1). All the sites with exceedances were located in the Lower Salinas Valley basin. A total of 284,541 lbs of chlorpyrifos were used in the region between 2006 and 2010. Chlorpyrifos was mainly used on broccoli, wine grapes and cauliflower (Table 3 and 4). Use of chlorpyrifos on broccoli alone accounted for about 54% of the total chlorpyrifos use in the area. Chlorpyrifos was used throughout the year with the majority of applications occurring in spring and summer (Fig. 3). Almost all the applications were by ground spray (Table 3). In this region, both EC and granular products were popularly used. On broccoli and cauliflower, a higher percentage of applied chlorpyrifos was formulated as granular, while on wine grapes EC products were the major formulation.

In the Imperial Valley region, 15 sites were monitored for chlorpyrifos from 2006 to 2010. A total of 72 samples were taken, 30.6% of which exceeded the target concentration of 0.04 ug/L (Table 1). Exceedances occurred in 9 of the 15 sites. Between 2006 and 2010, over 230,000 lbs of chlorpyrifos were used in this valley. Chlorpyrifos was mainly used on sugarbeet, alfalfa and corn, accounting for 96% of the use in the entire valley (Table 3). Applications occurred mostly in months from September to March (Fig. 3). Unlike Salinas Valley, chlorpyrifos was applied more often via aerial application than ground application. More than half of the use was from EC formulated products with 30% from LC and 10% from granular products (Table 4).

In the Santa Maria Valley region, 19 sites were monitored for chlorpyrifos from 2006 to 2010. A total of 84 samples were taken, 57% of which exceeded the target concentration (Table 1). Exceedances occurred in 15 of the 19 sites. Between 2006 and 2010, over 138,000 lbs of chlorpyrifos were used in this valley. Chlorpyrifos was mainly used on broccoli, wine grapes, strawberry and cauliflower, accounting for 96% of the use in the entire valley (Table 3). Almost all the applications were by ground spray (Table 3). In this region, both EC and granular products were popularly used. On broccoli and cauliflower, over 90% of applied chlorpyrifos was formulated as granular, while on wine grapes and strawberry, EC products were the majority.

In the Pajaro Valley region, 21 sites were monitored for chlorpyrifos from 2006 to 2010. A total of 68 samples were taken, 13% of which exceeded the target concentration (Table 1). Exceedances occurred in all the monitoring sites. Between 2006 and 2010, over 33,000 lbs of chlorpyrifos were used in this valley. The top use crops include apple, cabbage and corn (Table 3). Almost all the applications were by ground spray (Table 3). In this region, both EC and granular products were popularly used. On apple, 88% of applied chlorpyrifos was formulated as EC. On corn, however, over 90% of applied chlorpyrifos was formulated as granular. On cabbage, 60% of applied chlorpyrifos was from granular compared to 39% from EC products.

The above four regions used only 10% of the statewide chlorpyrifos use, however, they had the highest frequencies of chlorpyrifos detections and exceedances. Over 50% of the detections and 57% of exceedances for chlorpyrifos were from samples taken in these four regions. The four regions shared some similarities in chlorpyrifos use patterns. The top use sites were mainly non-tree crops: vegetables, wine grapes, corn and alfalfa. Except for Imperial Valley, where chlorpyrifos was mostly applied via aerial application, the rest of the three regions were

dominated by ground application. While all EC, LC and granular products had been used, EC and granular products were most popular. Unlike the regions in the Central Valley, where almost no granules were used, these four regions used a significant amount of granular products. Macro sprinkler and gravity irrigation were commonly used on vegetable crops (Table 3). Chlorpyrifos exceedance frequencies in each month follow closely with the monthly variations of pesticide use, with March having the highest use and exceedance frequencies (Fig. 3).

The differences in detection/exceedance frequencies between regions can be explained largely by the types of crops treated and their associated factors including use intensity, irrigation method and monthly application patterns. In the high detection/exceedance regions (Central Coast and Imperial), vegetable crops were the main uses of chlorpyrifos, where multiple cropping with two to three vegetables per year were common. Chlorpyrifos was often applied repeatedly on these crops within a year. This resulted in relatively higher chlorpyrifos use intensity. In contrast, in the low detection/exceedance regions, where tree crops were the main uses of chlorpyrifos, chlorpyrifos use intensity was relatively lower. Regarding irrigation method, in the low detection/exceedance regions, several of the high chlorpyrifos use crops used low volume irrigation methods (drip, micro sprinkler) (Table 3). In contrast, many of the high chlorpyrifos use crops in the high detection/exceedance areas used gravity or sprinkler irrigation. These methods generate much larger amounts of irrigation runoff. Pesticide application methods were similar between regions, with ground application being the most common type followed by aerial application. Regarding product formulation, EC, LC and granular products were commonly used, with EC formulated products being the most popular. Granular products were only used in regions with high exceedances; however, whether uses of granular products contributed to the higher detection/exceedances in those regions requires further investigation because there was limited literature on the effects of product formulation on surface runoff for chlorpyrifos. In addition, seasonal variations in chlorpyrifos exceedance mirror those in pesticide use suggesting that monthly use variations may be an important factor.

Once applied to the field, chlorpyrifos can move off-site dissolved in runoff water or attached to sediment. Factors that affect surface runoff and sediment erosion would impact chlorpyrifos runoff from agricultural fields. These factors may include climate (rainfall amount, intensity and timing relative to pesticide applications), soil characteristics, field slope, agricultural management practices (irrigation, soil erosion control efforts, pesticide formulation, application method and application rate), and the physiochemical properties of pesticides (Larson *et al.* 1991). This study suggests that application method likely was not related to the regional differences in chlorpyrifos detection/exceedances. Factors such as use intensity, irrigation method, and monthly use variations are more relevant. Therefore, further investigation into the effects of these factors may provide additional insights into this matter. Many of the key factors are crop specific. Thus, such investigation should focus on crops with high chlorpyrifos use in regions with frequent chlorpyrifos detections in surface water. In addition, studies on the use of granular products on high use crops are needed to examine the effects of granular formulation on chlorpyrifos runoff.

Acknowledgements The authors would like to thank Kean Goh, Sheryl Gill, David Duncan, John Sanders and Charles Andrews for their support and guidance on the work.

References

- California Department of Pesticide Regulation (DPR) (2012a). Surface Water Protection Program Database. <http://www.cdpr.ca.gov/docs/emon/surfwtr/surfddata.htm>
- California Department of Pesticide Regulation (DPR) (2012b). Pesticide Information Portal, Pesticide Use Report (PUR) data. Available via CDPR website: <http://calpip.cdpr.ca.gov/main.cfm>.
- California Department of Pesticide Regulation (DPR) (2005). Text of final regulations. Available online via: http://www.cdpr.ca.gov/docs/emon/dormspray/05_004final.pdf
- Corbin M, Daiss R, Judkins DR. (2009). Risks of Chlorpyrifos Use to Federally Threatened & Endangered California red-legged frog (*Rana aurora draytonii*), California tiger salamander (*Ambystoma californiense*), San Francisco garter snake (*Thamnophis sirtalis tetrataenia*), California clapper rail, (*Rallus longirostris obsoletus*), Salt marsh harvest mouse (*Reithrodontomys raviventris*), Bay checkerspot butterfly (*Euphydryas editha bayensis*), Valley elderberry longhorn beetle (*Desmocerus californicus dimorphus*), San Joaquin kit fox (*Vulpes macrotis mutica*), California freshwater shrimp (*Syncaris pacifica*), and Delta smelt (*Hypomesus transpacificus*). USEPA Office of Pesticide Program. Available online via: <http://www.epa.gov/espp/litstatus/effects/redleg-frog/chlorpyrifos/analysis.pdf>
- Ensminger, M, Bergin R, Spurlock F, Goh KS (2011). Pesticide concentrations in water and sediment and associated invertebrate toxicity in Del Puerto and Orestimba Creeks, California, 2007-2008. *Environ. Monit. Assess.* 175:573-587.
- Guo, L, Nordmark CE, Spurlock FC, Johnson BR, Li L, Lee JM, Goh KS (2004). Characterizing dependence of pesticide load in surface water on precipitation and pesticide use for the Sacramento River watershed. *Environ Sci Technol.* 38:3842-52.
- Larson J, Capel, PD, Majewski MS (1991). *Pesticides in the Hydrologic System*. Ann Arbor Press, Inc. Chelsea, MI.
- Phillips P, Scott WA, Nystrom EA (2007). Temporal changes in surface-water insecticide concentrations after the phaseout of diazinon and chlorpyrifos. *Environ.Sci.Technol.* 41: 4246-4251.
- Spurlock, F. (2004). Analysis of recent chlorpyrifos use and surface water monitoring data. Memorandum. Report. California Department of Pesticide Regulation. Environmental Monitoring Branch, Sacramento, California.
- USDA (2009) USDA Natural Resources Conservation Service. Available via NRCS website: <http://www.ca.nrcs.usda.gov/features/calwater/>
- U.S. EPA (2012). Office of Pesticide Program's Aquatic Life Benchmarks. Available online via: http://www.epa.gov/oppefed1/ecorisk_ders/aquatic_life_benchmark.htm#benchmarks

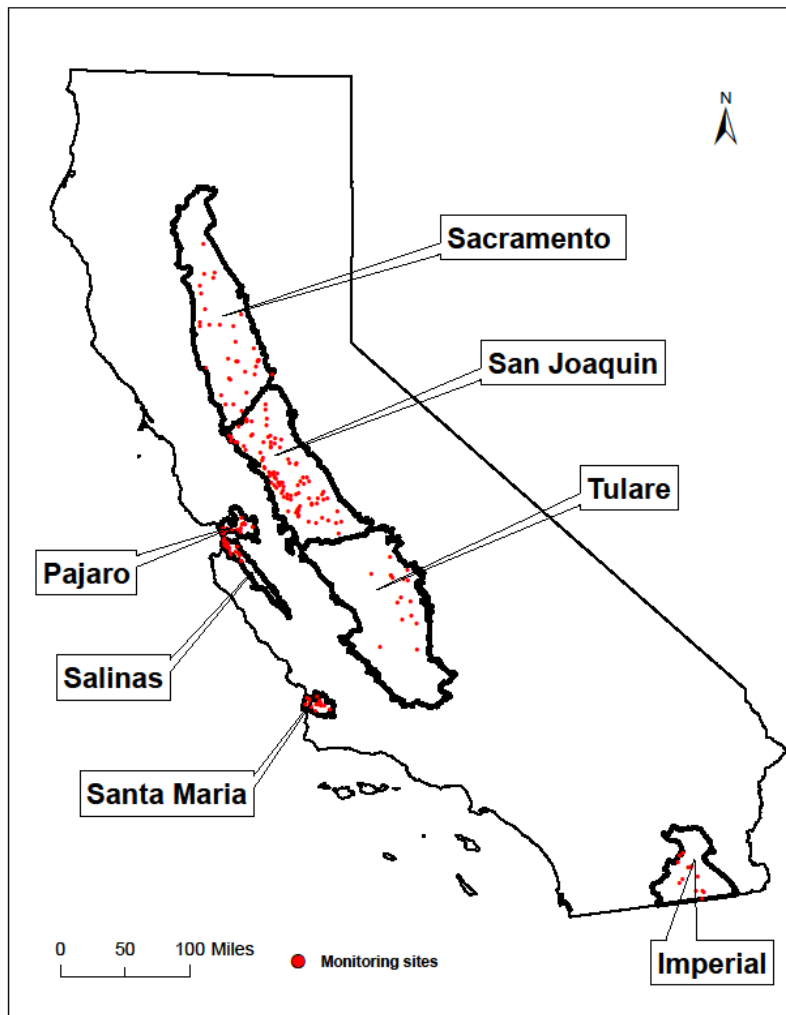


Fig. 1 Seven study regions in California, USA.

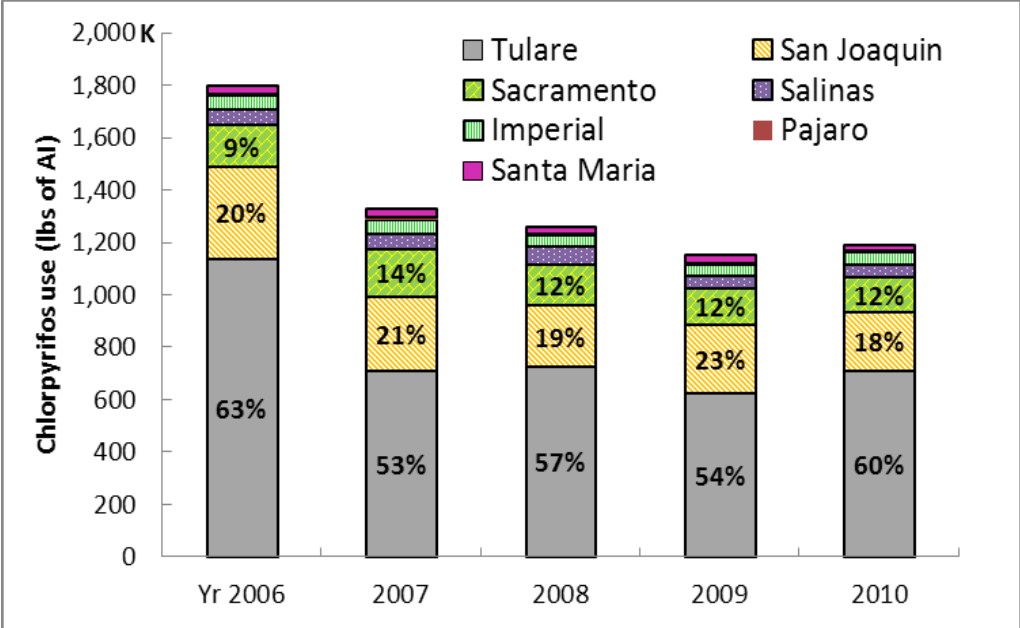


Fig. 2 Chlorpyrifos use in different regions of California by pounds of active ingredient

*Numbers are the percentage of statewide use (pounds of AI) for each region. No percentage less than 5% was shown in the graph.

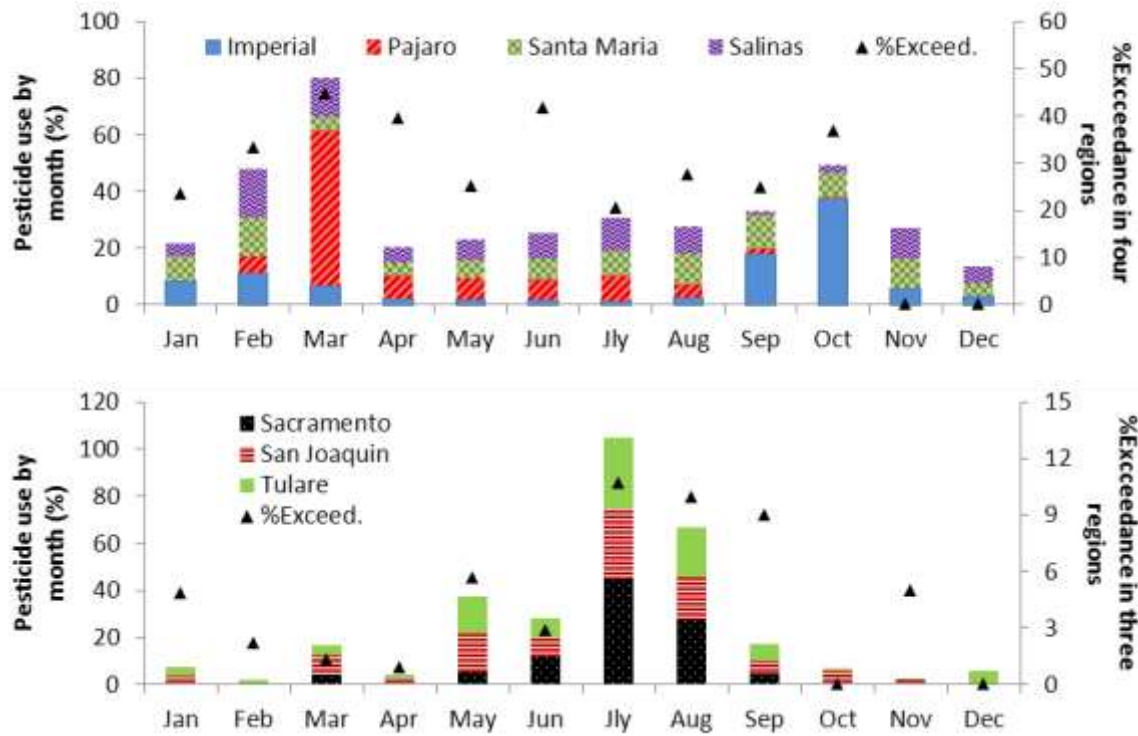


Fig. 3 Monthly average use of chlorpyrifos on in seven regions. 2006 -2010.