USE INFORMATION AND AIR MONITORING RECOMMENDATION FOR CHLORPYRIFOS IN CALIFORNIA

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1. INTRODUCTION

An addendum (DPR, 2013) to the California Department of Pesticide Regulation's (CDPR) original request (DPR, 2011) to the Air Resources Board (ARB) for monitoring Chlorpyrifos and chlorpyrifos oxygen analog breakdown product in 2013 was submitted. Due to its use on many crops makes this organophosphate a high priority for risk assessment (CDPR, 2013).

This recommendation contains general information regarding the physical and chemical properties of the pesticide active ingredient chlorpyrifos and its reported historical uses in California after evaluating 2009-2011 pesticide use data (CalPIP, 2013) The CDPR provides this information to assist the California Air Resources Board (CARB) in its selection of appropriate locations for conducting pesticide air monitoring operations.

2. CHEMICAL DESCRIPTION

Chlorpyrifos (CAS number: 2921-88-2) is a colorless to white crystalline solid and is the common name for the chemical with IUPAC name of *O*, *O*-diethyl *O*-3,5,6-trichloro-2-pyridyl-phosphorothioate (Figure 1). Chlorpyrifos has a mild mercaptan (thiol) odor, similar to the smell of sulfur compounds found in rotten eggs, onions, garlic and skunks. Chlorpyrifos is moderately toxic and chronic exposure has been linked to neurological effects, developmental disorders, and autoimmune disorders.

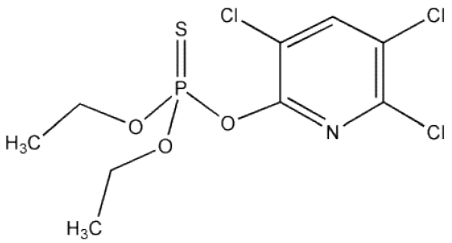

Figure 1. Chemical structure of chlorpyrifos.

2.1 Physical and Chemical Properties

The chemical and physical properties and some identifiers of Chlorpyrifos can be found in Table 1. Chlorpyrifos belongs to the chlorinated organophosphate (OP) chemical family. The value of K_{oc} has been shown to vary depending upon soil type and environmental conditions (DPR, 2010; IUPAC, 2013). Thus, its value ranges from 360-31000 ml/g (Table 1). The water solubility of chlorpyrifos is low. The CDPR determined that pesticides with a water solubility greater than 3 mg/L could be classified as having the potential to leach (Johnson, 1991). Thus, chlorpyrifos' potential to leach to groundwater is low, but contamination of groundwater would still be a possibility due to other environmental and soil factors. Typically, pesticides with high vapor pressure

(greater than 10^{-6} mm Hg) can readily volatilize. Based on its vapor pressure, chlorpyrifos can be classified as having moderate air pollution potential. Thus, chlorpyrifos is capable of volatilization and can potentially drift away from the application site.

Table 1. Physical and Chemical Properties of Chlorpyrifos (National Pesticide Information Center [NPIC], 2009; US EPA, 2002, Russell et al., 1978; The International Union of Pure and Applied Chemistry [IUPAC], 2013)

Common Name	Chlorpyrifos Dursban, Empire 20, Equity, Whitmire PT 270, Lorsban,
Chemical name (IUAPC)	*O*,*O*-diethyl *O*-3,5,6-trichloro-2-pyridyl phosphorothioate
CAS Registry Number	2921-88-2
Chemical Formula	$C_9H_{11}Cl_3NO_3PS$
Molecular Weight	350.59 g/mol
Physical form	white crystalline or irregularly flaked solid
Water Solubility	0.0014 g/L (25 ^oC) (Graebing and Chib, 2004) 0.00105 g/L (20 ^oC)
Density	1.398 g/cm^3 (43.5 ^oC) 1.49 g/cm^3 at (27 ^oC)
Octanol/water partition coefficient, Log K_{ow}	4.70 (Graebing and Chib, 2004; DPR, 2010)
Aqueous Photolysis Half-life	29.6 days (IUPAC, 2010)
Hydrolysis Half-life	35-78 days (pH 7.0; 25 ^oC) (Howard, 1991) 72.1 days (pH 7.0; 25 ^oC) DPR (2010) 72.8 days (pH 5.0; 25 ^oC) DPR (2010)
Vapor Pressure	1.87 x 10^{-5} mmHg (25 ºC)
Boiling Point	108 ^oC
Melting Point	41.5-42.5 ^oC
K_{oc}	Ranges from 360 ml/g to 31000 ml/g, depending on soil type and environmental conditions
Henry's Law Constant	4.2 x 10^{-6} atm·m^3/mol at 25 ºC and 6.7 x 10^{-6} atm·m^3/mol

3. ENVIRONMENTAL FATE

3.1 Fate in air

Henry's law constant, vapor pressure and volatilization are all interrelated for determining the fate of a pesticide in air. The best measure to describe a pesticide's fate in air is its half-life. The half-life is the time takes ½ amount of chemical to volatilize into the gas phase from any surface (Linde, 1994). The half-life of chlorpyrifos due to volatilization is 72 hours (Lyman et al., 1990). In their recent study, Hayward et al. (2010) found that the half-life of chlorpyrifos is 14 hours indicating that it is degraded more quickly in air and shows a much shorter atmospheric residence time. Howard (1991) reported that the degradation half-life of chlorpyrifos in air due to photolysis is 6.34 hours.

3.1.1 Air Monitoring Studies in California

The extensive use of chlorpyrifos on crops could result in detectable air concentrations due to its moderate volatility and drift from its application site. An initial study was conducted to determine the levels of chlorpyrifos in ambient air collected at residential sites in Salinas, Monterey County (Sawa, 1985). In this study, Sawa (1985) found very low levels of Chlorpyrifos (minimum detectable levels between 0.009-0.035 µg/m^3). Stein and White (1993) studied aerial movement of chlorpyrifos outside of the application area during a two week period during summer months in Fresno and Monterey counties. The maximum detected concentrations of chlorpyrifos were 0.0011 µg/m^3 and 0.0263 µg/m^3 for Fresno and Monterey counties, respectively. Mongar et al. (1998) reported the results of application and ambient air monitoring in Tulare County for chlorpyrifos during peak use period in May and June. Application site concentrations during seven sampling periods ranged from 2.6 – 47.2 µg/m^3 for the east side, 0.16-25.4 µg/m^3 for the south side, and 0.25-27.7 µg/m^3 for north of the field. The observed maximum ambient air concentrations from five different locations ranged from 0.0389 – 0.815 µg/m^3 (Mongar et al., 1998). Segawa et al. (2003) reported results of an ambient air monitoring study conducted at five locations in 2000 in Lompoc, Santa Barbara County, to determine concentration levels of 31 pesticides and their breakdown products. The highest air concentrations for 24 h, 14 days, and 10 weeks were 0.0151, 0.00405, and 0.00191 µg/m^3, respectively. A recent study conducted in Parlier, Fresno County, by Wofford et al. (2009) indicated that the insecticide chlorpyrifos was among the pesticides found most often. The results showed that the highest 1-day concentration was 0.150 µg/m^3 and the 14-day average concentration was 0.0961 µg/m^3 for chlorpyrifos.

3.2 Fate in water

Chlorpyrifos has a half-life of 14 days in an aqueous environment due to hydrolysis (McEwen and Stephenson, 1979). However, Howard (1991) reported half-lives ranges for chlorpyrifos in water at pH 7.0 and 25 ^{o}C from 35 to78 days due to hydrolysis.

Moreover, the degradation half-life of chlorpyrifos in water is 22 days due to photolysis (Howard, 1991).

3.3 Fate in soil

According to Tomlin (2000), the degradation half-life of chlorpyrifos in soil is 94 days. Other researchers also found that soil half-life ranged from 14 to 84 days in the field and under lab conditions (Chapman and Harris, 1980; Pike and Getzin, 1981). Furthermore, Graebing and Chib (2004) investigated soil photolysis of chlorpyrifos in a moisture and temperature controlled environment. They found that the irradiated half-life of chlorpyrifos on moist soil was 10 days, compared to 14 days on air-dry soil. When non-irradiated conditions were introduced, the half-life of chlorpyrifos was 18 and 30 days, respectively, for moist and air-dry conditions in sandy soil. Menon et al. (2004) studied the dissipation of chlorpyrifos in sandy loam and loamy sand soils. They found that chlorpyrifos showed moderately stable properties with half-lives of 13 and 17 days in loamy sand and sandy loam soils, respectively. Furthermore, they concluded that the rapid dissipation from soil post application might be caused by low sorption and its low organic matter content whereas fast dissipation from top soil might be the result of volatilization and photochemical degradation. In aerobic soils, the soil half-lives of chlorpyrifos ranged from 11 to 141 days in seven soils ranging in texture from loamy sand to clay and with soil pHs from 5.4 to 7.4. In anaerobic soils, the half-life was 15 days in loam and 58 days in clay soil (US EPA, 1989).

4. POTENTIAL HEALTH EFFECTS

Chlorpyrifos is an insecticide. Rat, rabbit, and mouse developmental toxicity studies on file at DPR did not indicate clear developmental toxicity. Signs of fetal toxicity (decreased ossification, retarded growth, decreased body weight) occurred only at or above dose levels causing clear maternal toxicity. A rat developmental neurotoxicity study had a No-Observed-Effect-Level (NOAEL) of 1 mg/kg for decreased pup survival and growth (Szabo et al., 1988). In addition to the Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA) toxicity studies, there is an extensive database of chlorpyrifos studies in the open literature. Several of these studies, including some human epidemiology studies, suggest adverse effects on neurologic and behavioral development (Nolan et al., 1984). In 2008, the Developmental and Reproductive Toxicant Identification Committee considered chlorpyrifos as a developmental toxin, but did not identify it as one. In a 2009 revised risk assessment scoping document, US EPA states, "Prenatal developmental toxicity in rats and rabbits and the rat reproduction studies provided no evidence of increased susceptibility of the fetuses or offspring. The developmental neurotoxicity study also did not provide clear indications of increased *quantitative* susceptibility in the offspring, although there were concerns for *qualitative* susceptibility in the offspring. However, the DNT study together with a growing body of studies in the open literature suggests that gestational and early postnatal exposure to pups may result in persistent alterations as indicated by various assessments of the animals when they reach adulthood". The US EPA maintained the same critical studies and points of departure used in the 2001 Interim Reregistration Eligibility Decision

(IRED) (US EPA, 2002). The IRED addressed short-term inhalation using a subchronic rat inhalation study. Rats were exposed 6 hours per day, 5 days per week. The highest dose level was 297 µg/m^3, and no effects were seen at any dose level, making 297 µg/m^3 a health-protective NOAEL. For an acute screening level, the 297 µg/m^3 is adjusted by 6/24 to give a 24-hour NOAEL of 74 µg/m^3 and a human (woman 13+ years) equivalent NOEL of 326 µg/m^3. In addition to the conventional uncertainty factor of 100X, US EPA applied an Food Quality Protection Act (FQPA)-safety factor of 10X to address the potential impacts of chlorpyrifos on neurological development. This would lead to an acute RfC or screening level of 326 ng/m^3 (including the FQPA factor).

5. CHLORPYRIFOS USE PROFILE IN CALIFORNIA

5.1 Chlorpyrifos use by county

The cumulative annual use of chlorpyrifos in California during 2009-2011 was obtained from the Pesticide Use Reporting Database (PUR). The results of annual use by counties are given in Table 2. Table 2 shows that the total use of chlorpyrifos increased from 1,240,475 lbs (2009) to 1,293,299 lbs (2011). Based on the sum of three years' (2009-

Table 2. Annual chlorpyrifos use by county and year in California during 2009-2011.

County	2009	2010	2011	Average†	Sum‡
			lbs ai		
Kern	281,686	227,656	218,387	281,686	727,730
Fresno	174,904	227,151	257,586	174,904	659,641
Tulare	143,961	191,678	244,843	143,961	580,483
Kings	52,262	110,738	124,261	52,262	287,261
Stanislaus	69,400	64,710	56,473	69,400	190,583
San Joaquin	71,823	58,685	39,984	71,823	170,492
Imperial	45,309	49,387	71,022	45,309	165,718
Monterey	50,011	49,728	38,286	50,011	138,024
Merced	57,736	41,392	34,033	57,736	133,162
Madera	36,824	29,334	23,527	36,824	89,686
Ventura	33,226	34,170	18,829	33,226	86,225
Glenn	22,582	34,385	20,376	22,582	77,343
Sutter	24,175	23,699	27,000	24,175	74,874
Butte	26,056	22,217	24,721	26,056	72,994
Santa Barbara	29,869	24,192	15,915	29,869	69,976
Solano	14,560	14,983	6,832	14,560	36,374
Tehama	14,142	11,457	8,176	14,142	33,775
Yuba	12,111	8,899	12,740	12,111	33,749

Table 2. continued.

County	2009	2010	2011	Average†	Sum‡
			lbs ai		
Colusa	10,560	8,935	8,751	10,560	28,245
Riverside	12,674	6,407	7,685	12,674	26,767
Yolo	9,470	9,057	6,465	9,470	24,992
San Luis Obispo	8,541	5,880	2,694	8,541	17,115
Sacramento	8,929	4,269	2,966	8,929	16,164
San Benito	3,338	1,738	2,828	3,338	7,903
Sonoma	1,939	4,197	1,323	1,939	7,459
San Bernardino	1,379	2,720	1,841	1,379	5,940
Napa	4,923	897	112	4,923	5,932
San Diego	1,642	1,499	2,260	1,642	5,402
Placer	2,185	1,846	1,363	2,185	5,394
Shasta	1,055	2,403	1,441	1,055	4,899
Modoc	3,060	0	1,644	3,060	4,704
Santa Cruz	1,262	1,193	1,714	1,262	4,170
Santa Clara	1,038	1,637	1,448	1,038	4,123
Lassen	728	224	2,602	728	3,554
Siskiyou	2,332	719	379	2,332	3,429
Contra Costa	1,496	430	971	1,496	2,897
San Mateo	964	1,200	637	964	2,802
Los Angeles	1,304	1,114	0	1,304	2,418
Orange	465	410	462	465	1,336
Calaveras	306	349	171	306	826
Lake	120	92	263	120	475
Mendocino	95	92	21	95	209
Mono	0	0	182	0	182
Amador	14	68	51	14	133
Alameda	0	29	34	0	63
Del Norte	14	3	0	14	16
Humboldt	4	4	4	4	12
Average§	26,393	27,274	27,517		
Sum¶	1,240,475	1,281,876	1,293,299		3,815,650

†Average yearly use by county.
‡Total use (2009-2011) by county.
§ Average use by year.
¶ Total use by year and grand total for California (2009-2011)

2011) use, Kern County recorded the overall highest use of chlorpyrifos (19 % of total statewide use). Kern County is followed by Fresno (17 %), Tulare (15 %), Kings (7.5 %), and Stanislaus counties (4.9 %). Table 3 lists the monthly use of chlorpyrifos within the years of 2009 through 2011 for the top ten counties. The general trend of significant use occurred between the months of January and August. However, the amount of use changed within given years but the peak use of chlorpyrifos was generally during the months of July and August in all counties (Table 3). The highest average use of chlorpyrifos was 20,451 lbs and 22,179 lbs in the months of July and August ,respectively, by all top ten counties,

5.2 Chlorpyrifos use by commodity and county

The total amount of chlorpyrifos used (and corresponding percentages) on treated acres in the top ten commodities/agricultural crops in California from 2009 through 2011 are given in Table 4. Although the highest chlorpyrifos use (823,990 lbs) in almond crop with 21.6 % of statewide use, the applied area (406,315 ac) for almond crop was the second highest in the state. After the almond crop, rank of commodities/agricultural crops' use of chlorpyrifos, in descending order, is as follows: Alfalfa (14 %), Walnut (13.6 %), Orange (13 %), Cotton (9.1 %), Grapes (8.9 %), Broccoli (3.5 %), Corn (2.8 %), Lemon (2.5 %), and Sugarbeet (2.2 %). A summary of chlorpyrifos use on the primary commodities/agricultural crops in the top five counties is presented in Table 5. Chlorpyrifos was used predominantly on almonds in three of the top five counties (Kern, Fresno, and Stanislaus). Meanwhile, oranges and cotton received the highest chlorpyrifos application in Tulare and Kings counties, respectively. Interestingly, almonds took fourth place in chlorpyrifos use in both counties (Table 5).

5.3 Chlorpyrifos use by method of application

Chlorpyrifos was mostly applied by ground application (67.1 %) in California between 2009 and 2011 (Table 6). Aerial application (32.3 %) ranks second in methods of application of chlorpyrifos in statewide use. The average applied amount of chlorpyrifos for both ground and other methods of application (41 and 42 lbs ai, respectively) were close. The average applied chlorpyrifos amount was 50 lbs ai in the aerial application. However, the average field size was smaller in ground (22 acre) than in aerial (57 acre) and other types (52 acres) of application methods. Therefore, ground application produced the highest average application rate (1.8 lbs ai/ac); the application rate for aerial and other types of application methods were quite similar to one another (Table 6).

5.3.1 Distribution of Chlorpyrifos use

Figure 2 depict the distribution of the total amount of active ingredient used (lbs), area treated with chlorpyrifos, and application rates (lbs ai/acre) for individual applications in the top ten counties in California between 2009 and 2011. There was almost no difference with respect to chlorpyrifos use within given years except at the 95th percentile level (Figure 2A).

Table 3. Monthly chlorpyrifos use by county and year (2009-2011) for the top ten counties in California.

County	Year	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec
		lbs ai											
Kern	2009	24391	12980	43043	7093	36898	13007	22361	4679	1479	5943	518	109294
	2010	18856	10473	25502	4897	41395	9484	42644	22610	22981	13456	8984	6376
	2011	37800	8601	26366	13144	25566	10795	21444	38306	19245	7224	1749	8147
Fresno	2009	13641	5384	11884	2001	5604	5352	75883	35737	16370	2370	392	286
	2010	11345	5749	8965	1805	20683	11717	58042	65281	35003	5282	1757	1522
	2011	15214	6301	9200	2075	8033	11015	30725	117643	46145	8466	2268	501
Tulare	2009	5873	3137	17104	8934	21960	21903	39370	12385	8057	4900	158	180
	2010	5436	3551	19461	3610	13397	29483	50267	42838	14276	7712	1463	185
	2011	4308	3294	17157	4409	22162	35137	60259	62193	22122	12850	734	217
Kings	2009	0	192	2484	1050	7397	4198	14153	17350	4823	616	0	0
	2010	816	76	2153	312	5798	6673	31182	49339	13997	330	0	62
	2011	556	155	3123	980	1118	5774	21135	66704	22139	2156	150	271
Stanislaus	2009	5962	2539	2525	2981	16611	6013	21144	6504	1252	2401	543	926
	2010	4769	1530	1518	878	9251	10178	21033	7405	1897	2203	2859	1188
	2011	656	4541	1152	583	9626	6949	11504	15177	3625	1563	855	242
San Joaquin	2009	177	8	13693	1616	6191	4398	19728	11042	4686	7877	2394	12
	2010	4590	1277	7008	3727	1603	5472	9578	16153	2195	5151	1933	0
	2011	38	679	3611	614	5465	1973	8335	10669	6858	1599	113	30

Table 3. continued.

County	Year	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec
		lbs ai											
Imperial	2009	5338	7398	4256	141	1538	1464	400	279	4212	14659	2407	3218
	2010	2727	1632	3758	2025	1536	85	43	608	12335	20560	3139	940
	2011	4996	6130	5163	985	222	648	1074	3138	9202	25545	5734	8185
Monterey	2009	2305	6514	7315	2691	3985	5628	6653	5316	1212	1234	4343	2815
	2010	2650	6177	5450	2915	4648	6239	6907	4768	1173	1251	5233	2318
	2011	1886	3283	4095	2556	3721	4586	5761	5254	2106	817	1973	2247
Merced	2009	37	2699	28685	1733	4495	4055	4592	5380	3714	2155	191	0
	2010	875	395	2820	1104	2826	2811	8604	11099	3048	6668	1142	0
	2011	178	176	4316	3754	3256	1527	6303	6417	2332	594	3064	2115
Madera	2009	0	81	4403	284	3737	3597	8605	8857	1996	2525	2741	0
	2010	306	607	1506	36	3788	3500	4313	7541	2465	2955	2319	0
	2011	75	517	1297	971	2432	1744	4199	4702	1715	3821	2054	0
Average		5860	3536	9634	2663	9831	7847	20541	22179	9755	5829	2040	5043

Table 4. Top ten commodities/agricultural crops based on total use (mass of active ingredient), corresponding percentage, and acres treated in California (2009-2011).

Commodity	Total use	Percentage	Area applied
	lbs ai	%	Acre
Almond	823,990	21.6	406,315
Alfalfa	535,920	14.0	1,121,517
Walnut	519,824	13.6	281,843
Orange	496,081	13.0	147,715
Cotton	345,663	9.1	372,735
Grapes	340,639	8.9	181,971
Broccoli	132,885	3.5	97,717
Corn	106,006	2.8	131,798
Lemon	95,730	2.5	29,913
Sugarbeet	82,161	2.2	123,557

Table 5. Chlorpyrifos use by year and average annual value for the top ten 0 commodities/agricultural crops in the top five counties.

County	Crop	Year			Average
		2009	2010	2011	
			lbs ai		lbs ai
Kern	Almond	173,083	70,210	186,265	143,186
	Alfalfa	18,977	41,109	151,484	70,523
	Grapes	51,414	51,819	66,073	56,435
	Orange	23,722	33,438	78,333	45,164
	Tangerine	6,821	8,343	51,269	22,144
	Cotton	125	8,217	26,130	11,491
	Lemon	3,083	6,524	8,649	6,086
	Sorghum	732	268	8,081	3,027
	Onion	348	1,515	6,703	2,855
	Wheat	235	1,847	5,968	2,683
Fresno	Almond	73,669	84,179	180,183	112,677
	Cotton	13,864	33,684	194,741	80,763
	Orange	21,529	42,313	82,804	48,882
	Alfalfa	24,202	21,522	57,747	34,490

Table 5. continued.

County	Crop	Year 2009	Year 2010	Year 2011	Average
		lbs ai			lbs ai
Fresno	Grapes	15,128	14,950	34,715	21,598
	Tangerine	2,989	5,204	17,554	8,583
	Peach	7,344	6,392	8,900	7,545
	Walnut	2,364	2,773	12,137	5,758
	Corn	3,827	3,399	8,142	5,123
	Nectarine	3,233	3,101	7,637	4,657
Tulare	Orange	66,374	87,329	314,092	155,931
	Alfalfa	13,317	36,629	92,272	47,406
	Walnut	17,225	11,422	41,235	23,294
	Almond	8,309	12,638	41,157	20,702
	Corn	4,402	8,848	42,322	18,524
	Grapes	12,594	12,977	19,095	14,889
	Tangerine	5,193	5,503	14,334	8,343
	Lemon	1,863	4,279	10,749	5,630
	Nectarine	3,104	2,381	5,018	3,501
	Wheat	4,447	1,280	4,484	3,404
Kings	Cotton	22,020	70,216	217,037	103,091
	Alfalfa	10,938	20,677	62,113	31,243
	Walnut	10,948	7,050	12,888	10,295
	Almond	3,031	8,094	5,884	5,669
	Corn	3,044	2,704	6,679	4,142
	Sorghum	718	1,068	3,716	1,834
	Grapes	1,014	446	825	762
	Wheat	440	75	1,394	636
	Onion	0	0	1,045	348
	Nectarine	0	36	262	99
Stanislaus	Almond	23,837	23,916	53,688	33,814
	Corn	65,737	4,056	21,332	30,375
	Walnut	23,949	25,212	41,581	30,247
	Grapes	5,663	5,035	5,815	5,505
	Alfalfa	3,311	2,382	6,139	3,944
	Sweet potato	889	729	6,129	2,583
	Citrus Fruits	0	952	3,338	1,430

Table 5. continued.

County	Crop	Year 2009	2010	2011	Average
		lbs ai			lbs ai
Stanislaus	Peach	1,199	866	0	688
	Apple	907	791	183	627
	Outdoor grown plants	20	187	603	270

Table 6. Statewide chlorpyrifos use by method of application in 2009-2011.

Application method	Total Number	Sum Applied Amount	Average Applied Amount	Sum Applied Area	Average Area	Average Rate
		lbs ai		ac		lbs ai/ac
Ground	55,407	2,257,671	41	1,231,927	22	1.8
Aerial	21,693	1,085,502	50	1,235,480	57	0.9
Other	454	19,283	42	23,511	52	0.8
Sum	77,554	3,362,455		2,490,918		

Similar patterns can be observed in the cumulative distribution of treated area whereas there are small discrepancies between years at the 90th percentile level (Figure 2B). The application rate of chlorpyrifos differentiates slightly at the 95th percentile level between years (4.0 lbs ai/ac in 2009, 5.1 lbs ai/ac in 2010, and 5.6 lbs ai/ac in 2011) (Figure 2C). For grapefruit, lemons, oranges and other citrus fruits, the recommended maximum label application rate for chlorpyrifos is 6 lbs ai/acre.

6. AIR MONITORING RECOMMENDATIONS

Using recent pesticide use report information for 2009-2011, CPDR suggests that the CARB monitors one ground application (67 %) on site for chlorpyrifos and its oxygen analog. Based on a preliminary assessment of the toxicology data, CDPR requests targeting to the concentration level of 0.03 µg/m^3 as the quantitation limits for chlorpyrifos and the chlorpyrifos oxygen analog (CDPR, 2013).

6.1 Application site monitoring

Table 4 indicates that almost 81 % of Chlorpyrifos use was on the orchards, cotton, and grapes. The selection of county and time of monitoring can be made based on the data

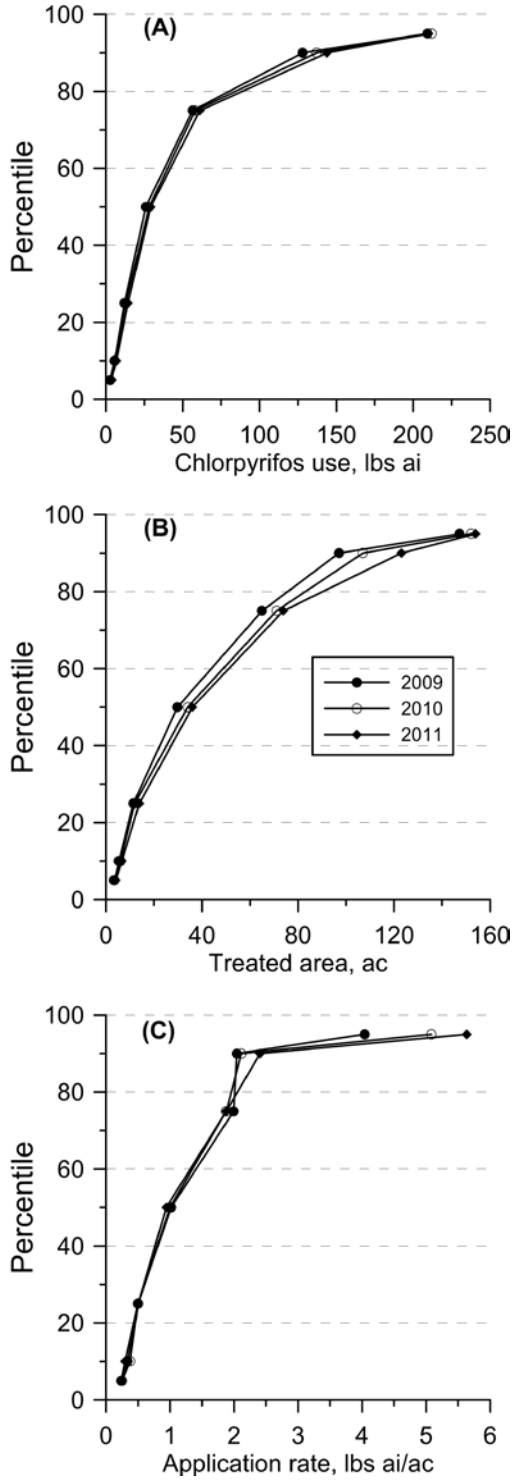

Figure 2. Cumulative frequency plot of chlorpyrifos for (A) amount applied (lbs ai), (B) treated area (ac) per application, and (C) rate of application, vs. percentile by year (2009–2011) in California's top ten counties.

provided in Tables 3 and 4. The CDPR suggests that ground application should be chosen as the method of application in the monitoring study with an application rate of 2-3 lbs ai/ac to a treated field of between 20-40 acres in size.

A minimum of eight samplers should be positioned around the application site, one on each side of the site and one at each corner. A ninth replicate sampler should be collocated at one position. Ideally, samplers should be placed a minimum of 20 m from the application area. CDPR recommends that CARB coordinate with the County Agricultural Commissioner for site selection. If a site is located on private property, permission from the property owner must be obtained before monitoring. Air samples should be taken before, during, and after application and for three daytime/overnight sampling periods. The start and end of the application should occur during daylight hours. Table 7 denotes the recommended sampling periods for collecting air monitoring samples before (pre-application), during (application), after application (post-application), and for three day time/overnight sampling periods.

Table 7. Sampling periods recommended for air monitoring an onsite.

Sampling periods	Start time	End time
1. Pre-application	12-24 h prior to application	Prior to application start
2. Application	Start of application	Until 1 h before sunset
3. Post-application	1 h before sunset	1 h after sunrise†
	1 h after sunrise	1 h before sunset
	1 h before sunset	1 h after sunrise†
	1 h after sunrise	1 h before sunset
	1 h before sunset	1 h after sunrise†

† All overnight samples must include the period from one hour before sunset to one hour after sunrise.

Moreover, the field spikes and trip blanks should be prepared in the laboratory and run in the field with the samples for quality assurance. When CARB prepares the monitoring reports, CDPR requests the following information to be included accurately (use GPS coordinates if applicable with World Geodetic System [WGS84] of 1984):

1) A record of the application site, including topographic features.
2) A record of the positions of the monitoring equipment with respect to the application site, including the exact direction and distance of the samplers from the edge of the application site.
3) A record of pesticide application, including application dosage or quantity of pesticide applied, application starting and ending time, method and application rate, etc.

4) A drawing of the monitoring site showing the precise location of the meteorological equipment, trees, buildings, and other obstacles with respect to North (identified as either true or magnetic North).
5) Meteorological data collected at 5-minute intervals including wind speed and direction, humidity, air temperature and comments regarding degree of cloud cover.

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