

USE AND RECOMMENDED AIR MONITORING OF THE PESTICIDE ACTIVE INGREDIENT CARBARYL IN CALIFORNIA

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1 INTRODUCTION

This recommendation includes summary information regarding the physical and chemical properties of the pesticide active ingredient (ai) carbaryl, its environmental fate, and summary statistics on historical carbaryl use (2007–2009) on agricultural commodities in the state of California. The use information has been obtained from the Pesticide Use Report (PUR) system adopted by the California Department of Pesticide Regulation (CDPR). In 1990 the CDPR implemented a full pesticide use reporting system, requiring all pesticide users to report the agricultural use of any pesticide to their county agricultural commissioner, who subsequently forwards this information to the CDPR. Following a revision process, the CDPR compiles and publishes the use information in the annual PUR. In the PUR system, any agricultural crop is considered as a commodity upon which chemicals can be applied to control for pests. The CDPR provides the current information to assist the California Air Resources Board (CARB) in selecting appropriate locations for conducting pesticide air monitoring samplings.

Carbaryl was first introduced in 1951 and is a member of the carbamate group of pesticides, which includes insecticides, herbicides, and fungicides that are moderately to highly toxic to mammals. It is one of the most widely used pesticides in agriculture due to its broad spectrum of insect control (Shealy et al., 1997; Ware and Whitacre, 2004, p. 59), and is a substitute for some organochlorine insecticides (e.g., DDT), because of its high efficiency and relatively lower persistence in the environment (Ribera et al., 2001). Once carbaryl is introduced into the environment it may be degraded into secondary byproducts or metabolites, generally more polar, soluble and somewhat less toxic than the parent molecules (Cheesman et al., 2007). It may also be mineralized into inorganic forms, such as CO₂ and water and inorganic nitrogen (Nkedi-Kizza and Brown, 1998). Hydrolysis, photolysis, and biolysis have been recognized as key processes controlling carbaryl environmental fate and transport. Residual levels of carbaryl in the environment are generally not believed to be hazardous to humans, although their fate and transport remain unclear (Shealy et al., 1997; Bollag and Liu, 1972).

Carbaryl is used in a variety of applications including agricultural crops, forests, and non-crop uses (e.g., residential uses, horticultural nurseries and greenhouses, ornamental plants, and pets). In agricultural applications, carbaryl is applied to control pests on more than 120 crops including fruit crops (e.g., orange, lemon, tangerine, cherry, apple, peach, nectarine, banana, mangoes, olive, and pecan, and strawberries), vegetables (e.g., tomatoes, lettuce, potatoes), cereals (e.g., rice), grasses (e.g., alfalfa), vines, cotton, and forestry productions (Kuhr and Dorough, 1976; Hastings et al., 2001; Ware and Whitacre, 2004; Gunasekara et al., 2008). Several trade names are associated with carbaryl and the most common one is Sevin®. It is available in granules, powders, pellets, dispersions, and suspension formulations (Ware and Whitacre, 2004). It can be applied through different air and ground (i.e., ground-based equipment) application methods (Kuhr and Dorough, 1976; Ware and Whitacre, 2004). (Throughout this report, I always refer to the “amount” or “use of carbaryl” as the mass of the active ingredient carbaryl in pounds [lbs]).

2 ENVIRONMENTAL FATE BRIEF

Carbaryl enters the environment due to human activities and, depending on environmental conditions, may be transferred into soil, i.e., the pedosphere, atmosphere, and/or biosphere (i.e., soil fauna, plants, humans, etc.) through different pathways. For example, it can reach the groundwater in solution as runoff or deposition as aerial mist (Kuhr and Dorough, 1976), or can be uptaken and metabolized by plants (Kuhr, 1970; Castelo-Grande et al., 2010). Knowledge of carbaryl's physical and chemical properties allows to better explaining and predicting its behavior in the environment. Given the objectives of this recommendation, the focus of this brief section will be primarily on the fate of carbaryl in air.

Figure 1. The chemical structure of carbaryl (Sevin®).

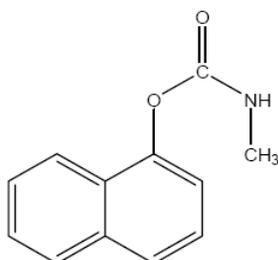


Table 1. Selected physical and chemical properties of carbaryl (C₁₂H₁₁NO₂)[†].

Property	Value / Description
Pure physical state	White crystal
Molecular weight (g/mol)	201.22
Melting point (°C)	142.2
Vapor pressure (mmHg at 25 °C)	1.36×10^{-6}
Henry's law constant (atm m ³ g/mol at 20 °C)	1.27×10^{-5}
Octanol-water partition coefficient (log K _{ow})	2.31–2.81
Organic-carbon normalized partition coefficient (log K _{oc})	2.02–2.59
Water solubility (mg/L at 20 °C)	104
Hydrolysis half life (d at 27 °C)	1500 (pH 5)
	15 (pH 7)
	0.15 (pH 9)
Photolysis half life	51.66 h (absorbance $\lambda = 257.5$ nm, concentration on glass plates = 6.7 $\mu\text{g}/\text{cm}^2$)
	~ 45 h (buffered solution, $\lambda > 280$ nm)

[†] See Montgomery (1997) for further details.

2.1 FATE IN AIR

Carbaryl (1-naphthyl-N-methyl carbamate, Figure 1) is a low molecular weight compound that is not readily volatilized due to its low vapor pressure (Table 1). It generally volatilizes in minimal or zero quantities from aqueous solutions as indicated by its low Henry's law constant. It may become airborne because of its sorption to particulates or as a spray drift immediately following application. It has low tendency to adsorption onto soil particles. When pesticides are sprayed using different application methods (e.g., aircraft, ground air blast, etc.), particles are accelerated by the spray airflow through the contributor, and lose their momentum almost instantly upon leaving the air flow due to high air resistance and their low mass. Those particles that do not immediately encounter foliage surfaces, ground cover, or soil surface have a tendency to drift, following distribution patterns that depend on weather conditions (Currier et al., 1982). It has been shown that carbaryl is generally rapidly degraded in the atmosphere and unlikely to cause persistent pollution, although knowledge on possible hazards posed by its by-products to humans and the environment remains unknown (Sun et al., 2005).

2.1.1 Spray Application Studies

Studies on carbaryl air concentration following application underscore that the variability in the data depends on the distance from the application point, weather conditions (i.e., wind speed and direction), and time since application. In general, carbaryl concentration peaks during the application and decreases to non-detectable levels within few hours thereafter. Environmental monitoring studies (Table 2) indicate that carbaryl remains detectable in air for about 47 h after application (Walters et al., 2003).

Results from a study after aerial spraying at 2,250 g/ha in a Vermont orchard showed detectable air concentrations within 3.5 km downwind from the source site after spraying under moderate wind conditions (8–12 km/h) (Currier et al., 1982). During the application, the highest overall concentration was 82.8 $\mu\text{g}/\text{m}^3$ detected at 12.2 m upwind of the site. The highest downwind concentration was 28.8 $\mu\text{g}/\text{m}^3$ sampled at 3.5 km away from the site. One hour after the application, the highest detected concentration was 17.6 $\mu\text{g}/\text{m}^3$ observed at 1.4 km downwind away from the site. All concentrations decayed to $< 2 \mu\text{g}/\text{m}^3$ two hours after application.

In a past helicopter spray application study conducted by the staff of CDPR (Segawa et al., 1982), air concentrations were determined by conducting helicopter samplings at 55-m and 15-m height from the ground, as well as at different ground-level sampling intensities, over a county park in Tulare County, CA. The aim was to determine the efficacy of aerial pesticide application against the spread of the European gypsy moth (*Lymantria dispar* [L.]), and quantify potential hazardous effects to humans due to pesticide drift. During the 55-m height application, carbaryl concentrations ranged 0–8.0 $\mu\text{g}/\text{m}^3$: Carbaryl average concentration was 0.2 $\mu\text{g}/\text{m}^3$ and non detectable at 80 m and 550 m downwind from the application site, respectively. Similarly during the 15-m height application, carbaryl concentrations ranged 0.4–6.2 $\mu\text{g}/\text{m}^3$, and a concentration of 4.5 $\mu\text{g}/\text{m}^3$ was detected at 310 m downwind.

2.1.2 Ambient Monitoring Studies

Carbaryl is generally detected less frequently in ambient monitoring studies compared to studies conducted during pesticide application. During July and August 2007, the CARB conducted a routine monitoring of ambient air for methomyl and carbaryl in Fresno, Tulare, and Kings Counties, CA. These pesticides are commonly used to control a wide range of insects. Carbaryl concentrations in all samplers ($n = 182$) were less than the method detection limit of 0.68 ng/m^3 (Adler, 2008).

Similarly during 2000, the CDPR monitored the ambient air concentration of carbaryl applied to control the glassy-winged sharpshooter (*Homalodisca coagulata* Say) in urban areas of five California cities, i.e. Porterville, Fresno, Rancho Cordova, Brentwood, and Chico. To prevent the insect from moving into vineyards, the State of California had been spraying urban trees, shrubs, and garden fruits and vegetables with carbaryl. The highest concentration was $1.2 \text{ }\mu\text{g/m}^3$, much lower than the $51.7 \text{ }\mu\text{g/m}^3$ limit, established by the CDPR as a health screening level (Walters et al., 2003).

Carbaryl was also detected at concentrations $< 1 \text{ }\mu\text{g/m}^3$ in the Alsace region, northeastern France, and in its vicinity during the summers of 1993 and 1994 (Sanusi et al., 2000). Sanusi and coworkers compared ambient air concentrations in order to assess the atmospheric contamination of various ecosystems, i.e. rural, urban, and mountainous areas. They observed an increasing contamination level from the control site (average of $0.28 \text{ }\mu\text{g/m}^3$) in the Vosges Mountains near Aubure (1100 m a.s.l.) to the rural site near Colmar ($0.348 \text{ }\mu\text{g/m}^3$, at $\sim 100 \text{ m a.s.l.}$) and the urban site within the historic center of Strasbourg ($0.577 \text{ }\mu\text{g/m}^3$, at $\sim 100 \text{ m a.s.l.}$).

2.2 FATE IN WATER

Carbaryl is moderately soluble in water, and its solubility increases with temperature (Table 1). It is among the most frequently detected pesticides in water systems, i.e., streams and ground water, due to its large use, mobility, and persistence, although it is degraded through both biotic and abiotic mechanisms. In a long-term study conducted in 51 major hydrologic systems across the USA by the USGS during 1992–2001, carbaryl was one of the four insecticides most commonly detected in urban streams. Residues at low concentrations have been detected in surface waters adjacent to both agricultural and urban areas of some 42 states (Gilliom et al., 2006). Similarly, carbaryl was among the 10 most frequently detected pesticides in rainfall samples collected during the 2003–2004 growing seasons in four agricultural watersheds in Maryland, Indiana, Nebraska, and California (Vogel et al., 2008).

2.3 FATE IN SOIL

When carbaryl enters a soil's system, it can be transported in solution or as colloidal particle, it can evaporate or be uptaken by plants, be adsorbed onto soil particles, degrade into intermediate products, or mineralize under the action of soil microorganisms. It is generally believed that both hydrolysis and biolysis are the main pathways of carbaryl degradation in soil (Bollag and Liu, 1972; Wolfe et al., 1978). Sorption, microbial degradation, mineralization, hydrolysis, and photolysis are all mechanisms that prevent or reduce carbaryl leaching into the groundwater.

Nkedi-Kizza and Brown (1998) investigated sorption, degradation, and mineralization of carbaryl as single or as part of a multiple pesticide systems (i.e., carbaryl combined with other pesticides in a mixture), in two soil types of varying soil organic carbon concentrations (ranging 2.0–15.2 g/kg) and depths (0–30 cm and 31–60 cm depth increments). These authors found that surface soil horizons, rich in organic matter, had greater carbaryl sorption capacity than organic-poor, subsurface horizons. They estimated linear average sorption coefficients (K_d) ranging 4.42–5.07 L/kg and 0.44–0.9 L/kg for top and subsurface horizons, respectively; degradation half lives ranging 8–18 d and 6–18 d for single and multiple systems, respectively; and mineralization half lives ranging 1.5–4 yr in top soils and 2–5 yr in subsoils for both systems (Nkedi-Kizza and Brown, 1998).

3 DEGRADATION

The behavior of carbaryl in the environment has been studied to understand the effect of environmental factors contributing to its transformation into less hazardous products or degradation. To quantify the rate of carbaryl degradation, researchers have attempted to extrapolate the half life computed under laboratory, controlled conditions (i.e., temperature, pH, solution composition, organism growth, etc.) to more variable, less predictable environmental conditions (Aly and El-Dib, 1971; Wolfe et al., 1978; Fisher and Lohner, 1986; Armbrust and Crosby, 1991; Arroyo et al., 2004).

Carbaryl's degradation may occur through both biotic and abiotic processes, and the magnitude of degradation varies depending on whether carbaryl degradation occurs in an air's, soil's, or water's system. As a consequence, there is also a high variability in the by-product suit resulting from carbaryl degradation. One commonly measured metabolite is 1-naphthol. The formation of 1-naphthol has been reported as one of the main by-products derived from carbaryl degradation in aqueous solutions (Wolfe et al., 1978; Miller and Chin, 2002), soil (Chapalamadugu and Chaudhry, 1991; Menon and Gopal, 2003), and in the human body (Shealy et al., 1997).

Carbaryl degradation in air and soil does occur and its byproducts are generally considered less toxic (Nkedi-Kizza and Brown, 1998). These processes are poorly understood, because it is generally more difficult to design studies on the influence of individual environmental factors in air and soil than it is in aqueous samples. Thus, knowledge of the major soil and air byproducts is still lacking (Brahmia and Richard, 2003; Sun et al., 2005).

3.1 ABIOTIC

3.1.1 Hydrolysis

In the scientific community, there is general agreement that the behavior of aqueous carbaryl in the environment (i.e., in ground or surface water systems as well as in soil solution) is strongly dependent on temperature and pH. These factors have a major influence on the rate of carbaryl hydrolysis (Aly and El-Dib, 1971; Wolfe et al., 1978; Chapman and Cole, 1982; Miller and Chin, 2002).

For example, Aly and El-Dib (1971) conducted laboratory experiments using distilled water to investigate the effect of experimental conditions, i.e., temperature and alkalinity, on carbaryl hydrolysis and degradation. Results and calculations by these authors showed that the increase in the rate of carbaryl hydrolysis for each 10 °C increase (i.e., Q_{10}) is about 2.9; and that carbaryl was relatively stable to hydrolysis at pH ranging 3.0–6.0 but degraded at higher pHs. The half-life was found to be 10.5 d, 1.8 d, 2.5 h, and 15 min at pH 7, 8, 9, and 10, respectively.

Wolfe et al. (1978) confirmed these findings by performing lab experiments on the hydrolysis, photolysis, and biolysis of carbaryl and other two carbamate pesticides, using both distilled and natural waters that were collected from ponds near Athens, Georgia, USA (pHs were 6.7 and 7.2). They reported a hydrolysis half-life of 0.15 d at pH 9 and 27 °C.

In similar laboratory studies, Chapman and Cole (1982) measured half-lives of 300, 2, and 0.27 wk in aqueous buffer solutions at pH 4.5, 7.0, and 8.0, respectively. Their work focused also on the persistence of carbaryl in solids and soils. They showed that there are strong limitations when attempting to extrapolate half-lives estimated for aqueous solutions to mixed media, such as soils.

3.1.2 Photolysis

Both direct and indirect photolysis, that is, sensitized photolysis, are considered important pathways of carbaryl degradation, whose intensity depends on complex interactions with other environmental factors that may or may not favor carbaryl photolysis (Wolfe et al., 1978; Samanidou et al., 1988; Mabury and Crosby, 1996; Miller and Chin, 2002).

For example, Samanidou et al. (1988) conducted laboratory studies comparing the rate of degradation of carbaryl and other carbamates in aqueous samples aerated with an oxygen stream and under sun light and UV light. They used natural waters from the Vasilios Lake, Axios River, and Thermaikos Gulf (Northern Greece), which typically receive pesticide leachates from the surrounding agricultural areas. They showed that carbaryl degradation was complete after approximately two and four days in sea and lake samples, respectively; whereas it remained incomplete for the river samples (with 5 % carbaryl remaining) seven days after the experiment start. They explained the lower rate of degradation in river and lake samples compared to the sea samples, speculating that the high concentration of suspended matter in river and lake waters influences the adsorption of sunlight, and consequently the photodegradation of carbaryl and other carbamates. The rate of degradation was two-fold higher when samples were exposed under artificial UV light.

Table 2. Comparison among carbaryl maximum concentrations reported in air monitoring studies (See text for further details).

Method and height of application	U.S State or Country/ Commodity	Carbaryl upper limit concentration (ng/m ³)	Type of monitoring or study and sampling height	Reference
Ground and Aerial	California/Agricultural areas with high use of methomyl and carbaryl near small urban areas/centers	< 0.68	Ambient	(Adler, 2008)
Ground with truck-mounted application equipment	California/Residential and commercial properties, highways, and parks	1.12	Ambient	(Walters et al., 2003)
Aerial with Helicopter/boom, 13.7 m swath, at 76 m	California/County park area with forest of valley oak plus mixed species (pine, sequoia, and mulberry trees)	7.95	Spray application study / Helicopter samplings at ground level, 15 m, and 50 m	(Segawa et al., 1982)
Aerial with agricultural aircraft/boom, 16.8 m swath, at 6.1–7.6 m	Vermont/ Apple orchard	82.8	Ambient at 4.89 m	(Currier et al., 1982)
Spraying operations	Vosges Mountains, France/Nonpopulated	0.28	Ambient	(Sanusi et al., 2000)
	5 km from Colmar, France/Rural	0.348	Ambient	(Sanusi et al., 2000)
	Strasbourg, France/Urban	0.577	Ambient	(Sanusi et al., 2000)

Similarly, results on photolysis rates by Wolfe et al. (1978) showed that carbaryl in aqueous solutions exposed to sunlight was rapidly degraded, whereas the carbaryl solutions used as dark controls showed no decomposition. These authors estimated a half life of 45 h for carbaryl in distilled water at pH 5.5 under a June midday sunlight (lat. 34°N).

Miller and Chin (2002) conducted experiments using water samples (pH range 7.65–8.09) collected from a 30-ha wetland on the south shore of Lake Erie, OH during June, August, and September of 1998. In their study, they attempted to elucidate the role of natural organic matter and nitrate, as naturally occurring photosensitizers, in the degradation of carbaryl. They quantified the influence of three components contributing to carbaryl degradation: the (1) base-promoted (i.e., by the presence of hydroxyl ions which causes high pH), (2) light-promoted (i.e., direct photolysis), and (3) photosensitizer-promoted component (i.e., due to naturally occurring photosensitizers in natural waters). Their results showed that it was possible to delineate the photolytic contribution of natural organic matter and nitrate, as photosensitizers, only when the influence of the base-promoted component (ranging 46–73 % of the overall reaction at natural pH) was limited by lowering the natural water pHs (pH ~ 4.3). In the pH-adjusted samples, the light promoted reactions accounted for 87–98 %. Based on results from the pH-adjusted samples, these authors concluded that that photo-enhanced degradation was both seasonally and spatially dependent. Nitrate and dissolved organic matter were primary constituents responsible for the formation and reaction of hydroxyl radicals with carbaryl.

3.2 BIOTIC

Several studies have been conducted to analyze the influence of different organisms on carbaryl's fate and transport. Depending on the specific metabolic pathways, carbaryl can be decomposed and/or transformed into various by-products or bioaccumulated by a vast array of organisms. These include soil and aquatic microorganisms, e.g., soil fungi (Bollag and Liu, 1972), insects and plants (Kuhr, 1970), rats (Padilla et al., 2007), and humans (Montgomery, 1997). Authors who reviewed this subject include Paris and Lewis (1973) who focused on the chemical and microbial degradation of carbaryl in aquatic systems, Gunasekara et al. (2008) on the effects of carbaryl on aquatic and terrestrial organisms, and Cheesman et al. (2007) on the potential use of enzymatic bioremediation of carbamate compounds, including carbaryl.

The magnitude of microbial activity that relates to pesticide degradation is generally much greater in soil than it is in water (Chapman and Cole, 1982). Although hydrolysis and photolysis have long been considered the dominant mechanisms of carbaryl degradation (Aly and El-Dib, 1971; Aly and El Dib, 1972; Wolfe et al., 1978; Miller and Chin, 2002), researchers have shown that enzymatic bioremediation, which enhances microbial degradation with the addition of detoxifying enzymes to clean up residues in contaminated environments, is a promising bioremediation strategy for aqueous systems and soils (Chapalamadugu and Chaudhry, 1991; Cheesman et al., 2007).

Two selected studies show evidence of carbaryl degradation by aquatic and soil microbes. Aly and El Dib (1972) studied the biodegradation of added carbaryl in Nile River waters under controlled temperature, pH, and oxygen conditions. Samples were maintained at temperature of 25 ± 2 °C, pH of 7.2 with buffer addition, and under aerobic

conditions. After the initial carbaryl addition, carbaryl concentration decreased progressively with time, i.e., 89 % of the added amount of carbaryl (4.75 mg/L) degraded in six days. Results also showed that 1-Naphthol, which appeared as a degradation product, did not derive only from the chemical hydrolysis of carbaryl, but was produced primarily by the biological activity of microorganisms present in river water.

Chapalamadugu and Chaudhry (1991) isolated two bacterial cultures of the genus *Pseudomonas* spp (isolates “50552” and “50581”) from soils with a history of carbaryl application and from an abandoned pesticide disposal site. They studied the degradation of carbaryl and 1-naphthol by these isolates individually (i.e., the 50581 bacterium was associated with carbaryl, while 50552 with 1-naphthol) and in combination. During the experiments, they maintained aerobic conditions at 30°C, monitored bacterial activity with labeled [¹⁴C]carbaryl and [¹⁴C]1-naphthol as the sole source of carbon, and measured the ¹⁴CO₂ evolved at various intervals. When the two bacterial isolates were kept separated during the experiment, the 50552 completely metabolized 1-naphthol to CO₂, whereas the 50581 first hydrolyzed carbaryl to 1-naphthol and then converted it into a brown-colored compound. This compound could not be degraded. However, when the isolates were combined in a unique bacterial consortium, the added carbaryl was completely catabolized to CO₂, indicating that the isolated bacteria individually or as a consortium may be used for detoxification of certain industrial and agricultural wastes.

4 AIR MONITORING RECOMMENDATIONS

The current recommendations to develop a sampling design and monitor carbaryl air concentrations are based on the most recent trends (2007–2009) in pesticide use in California. The risk assessment for this pesticide by the CDPR is currently in progress, and air monitoring will provide data needed for a complete evaluation of the exposure. The CDPR requests that the CARB monitor one application on site without conducting any ambient monitoring at this time. Based on a preliminary assessment of the toxicology data, CDPR requests a target quantification limit of 0.04 µg/m³ for carbaryl (CDPR, 2011).

4.1 CARBARYL USE IN CALIFORNIA

According to the PUR, the cumulative annual use of carbaryl in California during 2007–2009 decreased from 136,953 lbs (in 2007) to 122,083 (2008) and 126,587 lbs (2009) (Table 3). The overall highest uses (2007–2009) were in Fresno (19.8 % of total statewide use), Tulare (16.7 %), and Kern Counties (16.6 %). The other counties with lower uses (~ ½) over the same period were Kings (8.4 %), Sacramento (6.6 %), and San Joaquin (4.7 %).

Table 3. Annual carbaryl use by county and year in California during 2007–2009.

County	2007	2008	2009	Average†	Sum‡
	lbs ai			lbs ai	
Fresno	26,572	26,200	23,634	25,469	76,406
Tulare	27,389	20,704	16,185	21,426	64,279
Kern	15,407	23,957	24,686	21,350	64,049
Kings	8,339	11,046	12,881	10,755	32,266
Sacramento	11,733	7,225	6,430	8,463	25,388
San Joaquin	8,545	3,922	5,723	6,063	18,190
Yolo	5,821	2,038	5,170	4,343	13,029
Merced	2,257	5,639	2,564	3,487	10,460
Stanislaus	2,175	1,873	3,872	2,640	7,920
Monterey	2,990	2,709	1,789	2,496	7,489
Sutter	3,795	2,125	1,488	2,469	7,408
Ventura	1,899	2,993	1,579	2,157	6,472
Glenn	2,396	1,201	2,295	1,964	5,892
Riverside	1,635	1,417	2,694	1,915	5,746
Solano	1,298	755	3,149	1,734	5,202
Colusa	1,920	472	2,642	1,678	5,034
San Benito	2,860	503	1,649	1,671	5,012
Contra Costa	1,327	1,486	762	1,192	3,576
Santa Cruz	1,492	1,287	509	1,096	3,288
Madera	1,232	610	1,444	1,096	3,287
Siskiyou	537	0	1,553	1,045	2,091
Butte	1,231	1,054	55	780	2,339
Orange	405	887	791	694	2,083
Siskiyou	537	0	1,553	1,045	2,091
Butte	1,231	1,054	55	780	2,339
Orange	405	887	791	694	2,083
Alpine	515	0	290	402	805
San Diego	563	96	482	380	1,141
Tehama	504	428	173	368	1,105
Los Angeles	365	342	216	308	923
Santa Barbara	164	17	637	273	818
Santa Clara	330	369	81	260	780
El Dorado	166	61	262	163	488
San Bernardino	29	31	378	146	438
San Luis Obispo	37	90	292	140	419
Yuba	284	109	24	139	417
Sonoma	223	120	2	115	345
Imperial	175	0	50	113	225
Shasta	210	22	42	91	274
Mendocino	36	133	77	82	246
Placer	3	86	3	31	92

Table 3 continued.

County	2007	2008	2009	Average†	Sum‡
	lbs ai			lbs ai	
Mariposa	43	0	16	29	59
Tuolumne	29	0	0	29	29
Lassen	9	49	5	21	63
Napa	0	25	11	18	36
Lake	14	0	2	8	15
Average§	3,261	3,300	3,014		
Sum¶	136,953	122,083	126,587		385,622§

† Average yearly use by county.

‡ Cumulative use (2007–2009) by county.

§ Average use by year.

¶ Totals by year and grand total for California (2007–2009).

The period of pesticide high use, with average across all top 10 counties and years > 100 lbs, occurred between March and October; whereas the low-use period, with average use < 100 lbs, was during November–February (Table 4). The monthly maximum use varied among counties and was highest during the month of April (2,052 lbs). Instead, the monthly maximum, in average for 2007–2009 by county, occurred between March and May for all counties, except for Tulare (in August) and Sacramento County (October).

Table 4 Monthly carbaryl use by county and year (2007–2009) for the top ten counties in California.

County	Year	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec
		lbs ai											
Fresno	2007	0	0	6,569	6,805	3,275	2,105	2,125	3,155	1,956	261	323	0
	2008	16	0	5,564	8,183	4,362	609	3,038	2,036	2,392	0	0	0
	2009	0	0	3,469	8,492	4,246	2,061	2,844	1,685	838	0	0	0
Tulare	2007	0	0	36	0	3,235	3,664	8,724	5,692	1,308	4,656	27	48
	2008	0	0	156	88	5,649	3,703	3,540	5,272	1,419	838	40	0
	2009	0	344	1,360	216	1,376	4,776	2,300	3,856	702	820	435	0
Kern	2007	0	0	3,763	1,964	1,753	1,670	1,426	1,994	2,045	791	0	0
	2008	0	0	3,261	1,793	4,016	3,846	5,755	1,615	2,829	830	11	0
	2009	0	0	4,401	4,337	3,912	4,923	3,498	3,584	30	0	0	0
Kings	2007	0	0	5,101	1,505	0	1,102	605	27	0	0	0	0
	2008	0	264	4,706	2,607	2,189	662	0	464	155	0	0	0
	2009	0	0	4,393	5,813	2,140	468	0	67	0	0	0	0
Sacramento	2007	0	0	5	469	901	420	347	255	1,164	7,821	350	0
	2008	0	0	18	728	610	280	324	216	172	3,963	914	0
	2009	0	0	6	599	889	402	235	332	126	3,611	230	0
San Joaquin	2007	30	0	509	2,046	2,989	1,767	333	649	222	0	0	0
	2008	0	0	26	2,136	589	404	467	298	0	0	0	0
	2009	0	0	20	1,809	382	669	257	1,800	751	24	12	0

Table 4 continued.

County	Year	lbs ai											
		Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec
Yolo	2007	0	0	256	1,444	1,912	859	971	19	114	245	0	0
	2008	0	0	312	322	70	460	358	412	0	105	0	0
	2009	0	0	552	2,546	907	614	445	0	0	105	0	0
Merced	2007	0	16	193	688	355	125	416	180	284	0	0	0
	2008	0	0	700	1,645	2,551	252	239	223	30	0	0	0
	2009	2	6	102	1,123	383	344	144	260	188	12	0	0
Stanislaus	2007	0	0	235	770	436	461	114	10	150	0	0	0
	2008	0	1	0	746	897	53	177	0	0	0	0	0
	2009	0	0	0	1,009	1,444	1,180	114	45	80	0	0	0
Monterey	2007	379	166	660	996	42	173	0	0	36	537	1	0
	2008	0	0	72	386	847	700	12	15	476	202	0	0
	2009	1	0	198	301	450	69	8	415	187	0	16	144
Average†		14	27	1,555	2,052	1,760	1,294	1,294	1,152	588	827	79	6

† Monthly average in California during 2007–2009.

4.2 CARBARYL USE BY COMMODITY AND COUNTY

The top ten commodities/agricultural crops in California (2007–2008), in descending order of carbaryl use, were Tomato for Processing (23.9 % of total statewide use), Orange (18.8 %), Apple (7.2 %), Pistachio (6.1 %), Pear (4.7 %), Cantaloupe (4.2 %), Olive (2.9 %), Lemon (2.7 %), Peach (2.5 %), and Melon (2.4 %) (Table 5).

Table 5. Top 10 commodities/agricultural crops ranked in descending order based on carbaryl (mass of active ingredient) use and corresponding percentage in California (2007–2009).

Commodity (use)	Total use lbs ai	Percentage %
Tomato, Processing	92,286	23.9
Orange	72,378	18.8
Apple	27,955	7.2
Pistachio	23,677	6.1
Pear	18,004	4.7
Cantaloupe	16,121	4.2
Olive	11,095	2.9
Lemon	10,252	2.7
Peach	9,652	2.5
Melon	9,294	2.4

Similar summary data split by the top five counties are presented in Table 6. Carbaryl was used, in decreasing order, primarily on Tomato for Processing (46 % of the countywide use during 2007–2009), Cantaloupe (18 %), and Orange (6 %) in Fresno County; mainly on Orange (70 %) and less on Pistachio (9 %), and Nectarine (7 %) in Tulare County; on Orange (34 %), Pistachio (13 %), and Apple (11 %) in Kern County; almost entirely on Tomato for Processing (82 %), Pistachio (10 %), and Nectarine (2 %) in Kings County; and on Pear (69 %), Corn for Human Consumption (14 %), and Apple (6 %) in Sacramento County.

Table 6. Carbaryl use by year and average annual value for the top 10 commodities/crops in the top five counties in California.

County	Site	2007	2008	2009	Average
		lbs ai			lbs ai
Fresno	Tomato, Processing	10,347	12,726	12,452	11,842
	Cantaloupe	5,517	3,603	4,346	4,489
	Orange	1,670	2,456	691	1,605
	Pistachio	2,887	744	500	1,377
	Tomato	815	1,241	1,137	1,064
	Apple	48	1,027	1,406	827
	Peach	529	1,121	522	724
	Lettuce, Head	605	931	390	642

Table 6 continued.

County	Site	2007	2008	2009	Average
		lbs ai			lbs ai
Fresno	Watermelon	407	567	811	595
	Nectarine	513	841	187	513
Tulare	Orange	20,642	13,996	10,444	15,027
	Pistachio	877	1,328	3,375	1,860
	Nectarine	1,829	1,699	777	1,435
	Peach	632	1,426	189	749
	Lemon	1,183	284	0	489
	Plum	383	330	428	381
	Olive	113	108	720	313
	Cherry	516	342	0	286
	Tangerine	184	355	94	211
	Grapefruit	271	145	146	187
	Kern	Orange	4,860	6,023	11,087
Pistachio		3,423	4,646	215	2,761
Apple		1,878	1,498	3,817	2,398
Lemon		240	3,657	1,215	1,704
Tomato, Processing		159	688	3,673	1,507
Cherry		651	819	2,388	1,286
Plum		168	2,219	509	965
Peach		1,141	872	0	671
Grapefruit		781	495	614	630
Tangerine		180	690	557	476
Kings	Tomato, Processing	5,896	8,333	12,296	8,842
	Pistachio	1,620	1,530	125	1,092
	Nectarine	79	475	18	191
	Tomato	140	356	0	165
	Alfalfa	435	0	0	145
	Peach	118	51	216	128
	Melon	51	57	74	61
	Corn (Forage - Fodder)	0	0	119	40
	Apple	0	114	0	38
	Pecan	0	80	0	27
	Sacramento	Pear	8,873	4,756	3,781
Corn, Human Consumption		1,222	1,082	1,142	1,149
Apple		435	439	566	480
Tomato, Processing		353	444	465	420
Cherry		120	264	413	266
Grape, Wine		542	0	0	181
Corn, Field, Dent (Grain Crop)		0	140	21	54

Table 6 continued.

County	Site	2007	2008	2009	Average
		lbs ai			lbs ai
Sacramento	Tomato	120	1	32	51
	Christmas Tree	0	89	0	30
	Uncultivated Ag	44	0	0	15

4.3 CARBARYL USE BY METHOD OF APPLICATION

The most common methods of application in California during 2007–2009 were, in descending order, Ground application (74 % of statewide use), Aerial application (25 %), and Other methods (2 %) (Table 7).

Table 7. Carbaryl use by method of application during 2007–2009 in California.

Application method†	N‡	Sum	Average	Area sum	Average area	Average rate
		— lbs ai —		ac	ac	lbs ai/ac
Aerial	1,154	94,525	82	69,644	60	1.5
Ground	6,585	283,743	43	226,092	34	1.9
Other	72	6,586	91	2,773	39	2.6
Sum	7,811	384,854		298,509		

† Applied aerially, using ground-based equipment, or other application methods.

‡ N, Number of applications (A subset of observations [n = 17] were excluded because their method of application was not reported).

4.4 CARBARYL USE BY LABEL

The most common trade names of commercial carbaryl insecticides used in aerial applications in California during 2007–2009 included Sevin 5 Bait, Red-Top Sevin 5 pellets (available as Pellet/Tablet/Cake/Briquet), Sevin Brand XLR Plus Carbaryl Insecticide (as a suspension), Gowan Sevin Bait (Granular/Flake), Sevin 80S (Powder), Clean Crop Carbaryl Bait (Granular/Flake), Sevin XLR (Emulsifiable concentrate), First Choice Carbaryl Cutworm Bait, Sevin Brand 80WSP Carbaryl Insecticide (Withdrawn) (Soluble Powder), and Drexel Carbaryl 4L (Flowable Concentrate).

4.5 RATE OF APPLICATION BY YEAR

Patterns of carbaryl use, rate of application, and area treated with carbaryl per application were generally similar, for the majority of applications, among years (Figure 2). There were relatively large differences in cumulative frequency distribution for carbaryl mass and rate of application above the 75th percentile (i.e., the upper limit below which 75 % of the applications occurred in a given year). The carbaryl masses corresponding to the 75th percentile were 80.1 lbs, 77.5 lbs, and 77.5 lbs for 2007, 2008, and 2009, respectively. Similarly, the rates of application (75th percentiles for 2007, 2008, and 2009) were 2.5, 2.0,

and 2.0 lbs/ac in 2007, 2008, and 2009, respectively, while the areas of application were 73 ac, 75 ac, and 78.5 ac, respectively.

4.6 GENERAL RECOMMENDATIONS

The CDPR suggests that either an air or ground application is selected with an application rate greater than 2 lbs/ac, i.e. approximately the 75th percentile for 2007–2009, and a field size greater than 40 ac, i.e. approximately the 50th percentile. The county and time of monitoring should be selected based on data provided in Tables 3–4. 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 co-located at one position. Ideally, samplers should be placed a minimum of 20 m from the application area. The CDPR recommends that the CARB coordinate with the county agricultural commissioners 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 for three overnight sampling periods (Table 8). The start and end of the application should occur during daylight hours.

Table 8. Sampling periods recommended for air monitoring an onsite, soil application of carbaryl as fumigant.

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†

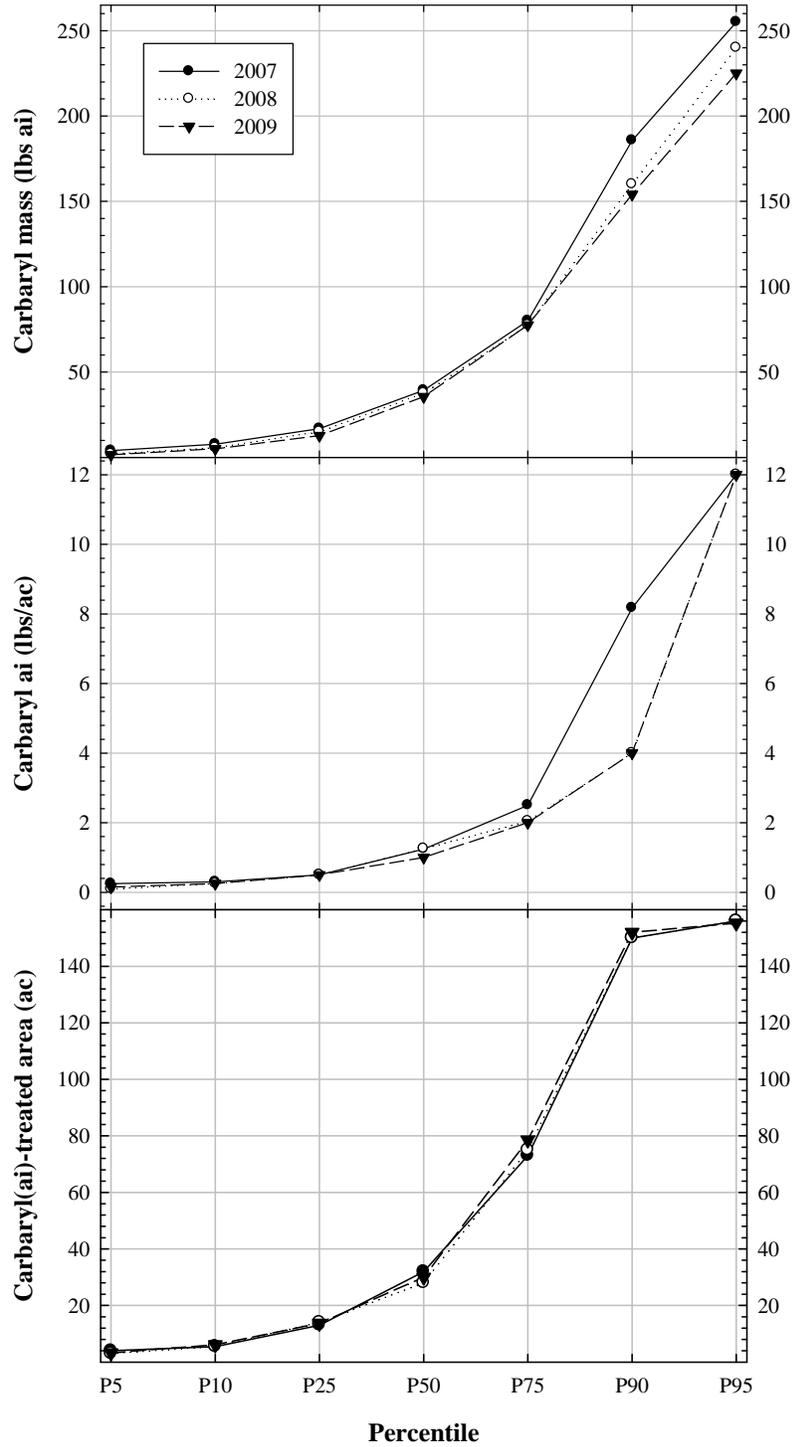
† All overnight samples must include the period from one hour before sunset to one hour after sunrise.

The CDPR requests that the monitoring report includes the following accurate information:

1. The application site, including topographic features
2. 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. Pesticide application, including application dosage or quantity of pesticide applied, application starting and ending time, method and application rate, etc.

4. Drawings 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, if applicable.

Figure 2. Cumulative frequency plot of carbaryl mass, rate of application, and carbaryl-treated area per application vs. percentile (P) by year (2007–2009) in California top 10 Counties.



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