



Staff Report

**USE INFORMATION AND AIR MONITORING
RECOMMENDATION FOR THE PESTICIDE ACTIVE
INGREDIENT LINURON**

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USE INFORMATION AND AIR MONITORING RECOMMENDATION FOR THE PESTICIDE ACTIVE INGREDIENT LINURON

A. BACKGROUND

This recommendation contains general information regarding the physical-chemical properties and the historical uses of 3-(3,4-Dichlorophenyl)-1-methoxy-1-methylurea (linuron). The Department of Pesticide Regulation (DPR) provides this information to assist the Air Resources Board (ARB) in their selection of appropriate locations for conducting pesticide air monitoring operations.

Linuron (CAS: 330-55-2) exists as either colorless to white, odorless crystals or as a crystalline solid. Linuron has a molecular formula of $C_9H_{10}Cl_2N_2O_3$, a molecular weight of 249.10 g/mole. It has a water solubility of 75-81 mg/L at 25 °C, a Henry's Constant of 6.1×10^{-8} atm·m³/mol at 20–25 °C, and a vapor pressure of 1.5×10^{-5} mmHg at 20 °C. Linuron's solubility in many organic solvents is as follows: 1) acetone: 500 g/kg at 25 °C; 2) benzene: 150 g/kg at 25 °C; 3) ethanol: 150 g/kg at 25 °C; 4) *n*-heptane: 150 g/kg at 25 °C; and 5) xylene: 130 g/kg at 25 °C.

In soil, linuron degrades to 3,4-dichloroaniline. The soil microorganism *Bacillus sphaericus* degrades linuron to *N,O*-dimethylhydroxylamine and carbon dioxide; however *Aspergillus niger* degraded linuron to phenylmethylurea, phenylmethoxy-urea, chloroaniline, ammonia, and carbon dioxide. Linuron's soil half-life ($t_{1/2}$) is two to five months when applied at recommended label rates. When in aqueous solution and exposed to summer sunlight for two months, linuron's photodegradation products included 3-(3-chloro-4-hydroxyphenyl)-1-methoxy-1-methylurea, 3,4-dichlorophenylurea, and 3-(3,4-dichlorophenyl)-1-methylurea formed at yields of 13, 10, and 2 percent, respectively. Linuron's photolysis half-life was approximately 97 days. In a laboratory study, after 24 days of exposure to sunlight, linuron photodecomposed to a trichlorinated biphenyl (1 percent yield) with the accompanying loss of hydrogen chloride. When in a 0.5 N sodium hydroxide solution at 20 °C, linuron's hydrolysis half-life is one day. In an alkaline solution, linuron's hydrolysis yielded an aromatic amine.

Linuron's acute oral LD₅₀ is approximately 1,500 mg/kg for rats. Its LC₅₀ (96 hour) is 16 mg/L for rainbow trout and bluegill sunfish. Linuron entered the risk assessment process at DPR under the SB 950 (Birth Defect Prevention Act of 1984) based on its use rate and known oncogenic and reproductive toxicity.

B. USE OF LINURON

As of January 28, 1997, four linuron-containing products were registered for use in California. Linuron is a selective preemergence and postemergence herbicide used to control a broad spectrum of annual and broadleaf weeds.

With DPR's implementation of full pesticide use reporting in 1990, all users must report the agricultural use of any pesticide to their county agricultural commissioners, who subsequently forward this

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information to DPR. DPR compiles and publishes the use information in the annual Pesticide Use Report (PUR). Because of California's broad definition for agricultural use, DPR includes data from pesticide applications to parks, golf courses, cemeteries, rangeland, pastures, and rights-of-way, postharvest applications of pesticides to agricultural commodities, and all pesticides used in poultry and fish production, and some livestock applications in the PUR. DPR does not collect use information for home and garden use, or for most industrial and institutional uses. The information included in this monitoring recommendation reflects widespread cropland applications of linuron. Use rates were calculated by dividing the total pounds of linuron used (where linuron was applied to acreage) by the total number of acres treated.

According to the PUR, over 90 percent of California's total linuron use occurs in six counties (Table 1). Historically, cropland applications account for over 99 percent of the total amount of linuron reported used each year. Non-agricultural applications—landscape maintenance or rights-of-way—account for less than one percent of the total amount of linuron reported used each year. The information included in this monitoring recommendation reflects widespread cropland applications of linuron. Use rates were calculated by dividing the total pounds of linuron used (where linuron was applied to acreage) by the total number of acres treated.

In California, growers use linuron to control a broad spectrum of annual and broadleaf weeds in asparagus, carrots, celery, and outdoor-grown nursery crops. Linuron is also used along rights of way for weed control. Linuron has both soil and foliar activity. Labeled use rates for linuron range from 1-2 pounds of active ingredient per acre for carrots to as much as 8 pounds per acre on fern-stage asparagus. Linuron is formulated as either a dispersible granule or flowable powder; in either case, it is mixed in water and applied as a spray. Linuron-containing products include the Signal Word "Caution" on their labels.

Table 1. Annual Agricultural Use of Linuron (Pounds of Active Ingredient)

County	1995	1994	1993
Kern	39,970	36,297	37,758
Imperial	15,986	12,347	19,638
San Joaquin	7,851	6,032	5,988
Santa Barbara	6,181	6,625	7,135
Monterey	5,470	5,558	6,319
San Luis Obispo	2,989	5,034	5,155
County Totals	78,447	71,893	81,993
<i>Percent of Total</i>	92%	90%	92%
CALIFORNIA TOTAL	85,127	79,993	89,568

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According to the PUR, Kern County routinely receives the greatest applications of linuron; Kern County growers use nearly half of all the linuron reported used in California. Table 2 summarizes the total amounts and average daily rates of linuron applied in the counties of highest use—Kern and Imperial Counties—during the months of greatest use. Applications of linuron in Kern County are highest in September, when more than twice the amount is applied than during any other time of the year. The second highest use occurs in Kern County in March, followed by applications of linuron in Imperial County in November.

The application of linuron in Kern County during September may be attributed to widespread use of a single product—Du Pont Lorox DF Herbicide®[†]. DPR issued a Special Local Need (SLN) registration (820042) to allow growers the use of this product for the preharvest control of annual broadleaf weeds—Shepherd’s Purse, Hairy Nightshade, Sow Thistle, Mustard Chickweed—and annual grasses in carrots.

Table 2. Linuron Applications in Kern and Imperial Counties

		<u>1995</u>		<u>1994</u>		<u>1993</u>	
		<i>Lbs Used¹</i>	<i>Rate²</i>	<i>Lbs Used¹</i>	<i>Rate²</i>	<i>Lbs Used¹</i>	<i>Rate²</i>
Kern							
	September	13,017	1.18	11,710	1.16	12,615	1.12
	March	3,389	0.91	7,172	1.16	5,816	0.91
Imperial							
	November	3,673	0.64	3,703	0.64	3,673	0.64

¹ In pounds of active ingredient.

² Average rate (in pounds of active ingredient per acre).

The highest rates of linuron are used to treat asparagus at an average rate of 2.0 lbs per acre; however, the applications are limited and occur only a few days per year. Consequently, monitoring the use of linuron on this commodity may be difficult to arrange. The highest consistent use occurs during the month of September in Kern County, when growers apply linuron to carrots at the average rate of 1.2 lbs per acre.

[†] Du Pont Lorox DF Herbicide is a registered product of the E.I. Du Pont de Nemours & Co., Inc. Agricultural Products Department, Wilmington, Delaware.

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C. RECOMMENDATIONS

1. *Ambient Air Monitoring*

The historical trends in linuron use suggest that monitoring should occur over a 30- to 45-day sampling period in Kern County during the month of September. Three to five sampling sites should be selected in relatively high-population areas or in areas frequented by people. Sampling sites should be located near carrot growing areas. Ambient samples should not be collected from samplers immediately adjacent to fields or orchards where linuron is being applied. At each site, twenty to thirty discrete 24-hour samples should be taken during the sampling period. Background samples should be collected in an area distant to linuron applications.

Replicate (collocated) samples are needed for five dates at each sampling location. Two collocated samplers (in addition to the primary sampler) should be run on those days. The date chosen for replicate samples should be distributed over the entire sampling period. They may, but need not be, the same dates at every site. Field blank and spike samples should be collected at the same environmental conditions (e.g., temperature, humidity, exposure to sunlight) and experimental conditions (e.g., air flow rates) as those occurring at the time of ambient sampling.

2. *Application-Site Air Monitoring*

Linuron is typically used at a higher rate on fern-stage asparagus than on carrots; however, the limited number of applications made each year to asparagus may make it difficult to locate an appropriate monitoring site. Therefore, the historical trends in use suggest that application-site air monitoring should be conducted during September in Kern County in association with application to carrots. Applications of linuron to carrots during September are associated with a SLN registration; consequently, monitoring staff should ensure the SLN is still in effect prior to selecting an appropriate monitoring site. Linuron is extensively applied during this period so care should be taken to prevent nearby applications from contaminating collected samples. A three day monitoring period should be established with sampling times as follows: application + 1 hour, followed by one 2-hour sample, one 4-hour sample, two 8-hour samples and two 24-hour samples. A minimum of four samplers should be positioned, one on each side of the field. A fifth sampler should be collocated at one position. Since linuron is extensively used in the area, background samples should collect enough volume (either 12 hours at 15 liters/min, or a shorter period with a higher volume pump) to permit a reasonable minimum detection level. Ideally, samplers should be placed a minimum of 20 meters from the field. Field blank and field spike samples should be collected at the same environmental conditions (temperature humidity, exposure to sunlight) and experimental conditions (similar air flow rates) as those occurring at the time of sampling.

Additionally, we request that you provide in the monitoring report: 1) an accurate record of the positions of the monitoring equipment with respect to the field, including the exact distance that the sampler is positioned from the field; 2) an accurate drawing of the monitoring site showing the precise location of the meteorological equipment, trees, buildings, and other obstacles; 3) meteorological data collected at a

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minimum of 15-minute intervals including wind speed and direction, humidity, and air temperature, and comments regarding degree of cloud cover; and 4) the elevation of each sampling station with respect to the field, and the orientation of the field with respect to North (identified as either true or magnetic North).