Environmental Fate of Linuron

Risk Characterization

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1. Introduction

1.1 Uses and Mode of Action

Linuron [3-(3,4-dichlorophenyl)-1-methoxy-1-methylurea] is an herbicide used to control broad-leaved weeds and annual grasses, such as chickweed, prickly lettuce, lambsquarter, crabgrass and goosegrass (Kidd and James 1991; Tessenderlo Group 2008). It is used in both pre- and post-emergence control of weed growth. For pre-emergence control, linuron is incorporated into the soil and then taken up by roots of emerging weeds. For post-emergence control, residues are directly sprayed onto the foliage of the target weeds where it is adsorbed into the plant (Kidd and James 1991; Tessenderlo Group 2008). Two different formulations with linuron as the active ingredient (AI) are registered for use in California: dry flowable and liquid concentrate. Carrot crops receive roughly 80% of the linuron applications in California, while the rest of the U.S. primarily applies linuron to soybeans (Table 1; CDPR 2013; U.S. EPA 1995).

Table 1 Top three application sites for linuron (AI) in California and Nationwide

	California (Lbs. AI)		Nationwide (Lbs. AI)	
1	Carrots	40,682	Soybeans	1,400,000
2	Celery	5,528	Field Corn	95,000
3	Asparagus	1,770	Carrots	90,000

Source: US EPA 1995; CDPR 2013

1.2 Regulation

Linuron was registered with the U.S. Environmental Protection Agency (U.S. EPA) by E.I. DuPont de Nemours and Company, Inc. (DuPont) in 1966, and with California in 1985 (U.S. EPA 1995). Due to 1988 revisions to the Federal Insecticide, Fungicide and Rodenticide Act, all pesticides registered prior to November 1, 1984 must undergo reregistration by the U.S. EPA to ensure that they meet more stringent regulatory standards. During the reregistration process, linuron was placed under special review from 1984 to 1988 due to oncogenicity concerns (U.S. EPA 1995). Although the special review identified linuron as an unquantifiable Group C human carcinogen, evidence to support this claim remains limited (U.S. EPA 1995). Linuron is not currently regulated by the U.S. EPA under the Safe Drinking Water Act and there is no established drinking water Maximum Contaminant Level. In 1999, linuron was listed as having reproductive (developmental) toxicity under California's Proposition 65, the Safe Drinking Water and Toxic Enforcement Act of 1986.

U.S. EPA's reregistration eligibility decision (RED) concluded that levels of concern for ecological effects and groundwater quality were exceeded by linuron (U.S. EPA 1995). New stringent application measures, from prohibiting certain uses to reducing use rates, and label advisories were implemented to substantively reduce the amount of linuron released into the environment (U.S. EPA 1995). DuPont voluntarily cancelled certain uses in concordance with risk mitigation measures enacted by U.S. EPA (U.S. EPA 1995).

California's Pesticide Contamination Prevention Act (PCPA) requires registrants to submit mobility and persistence data, and requires the California Department of Pesticide Regulation (DPR) to use this data to identify and monitor for potential groundwater contaminants (California Food and Agricultural Code § 13141-13152). Due to qualifying physicochemical data and the fact that label language recommends soil application, linuron is placed on the Ground Water Protection List (Title 3, California Code of Regulations [3 CCR] section 6800[b]). Well sampling studies are conducted to determine if AIs from the 3 CCR section 6800(b) list have moved to groundwater.

1.3 Use in California

Table 2 Top counties in California for linuron use from 1995 – 2010

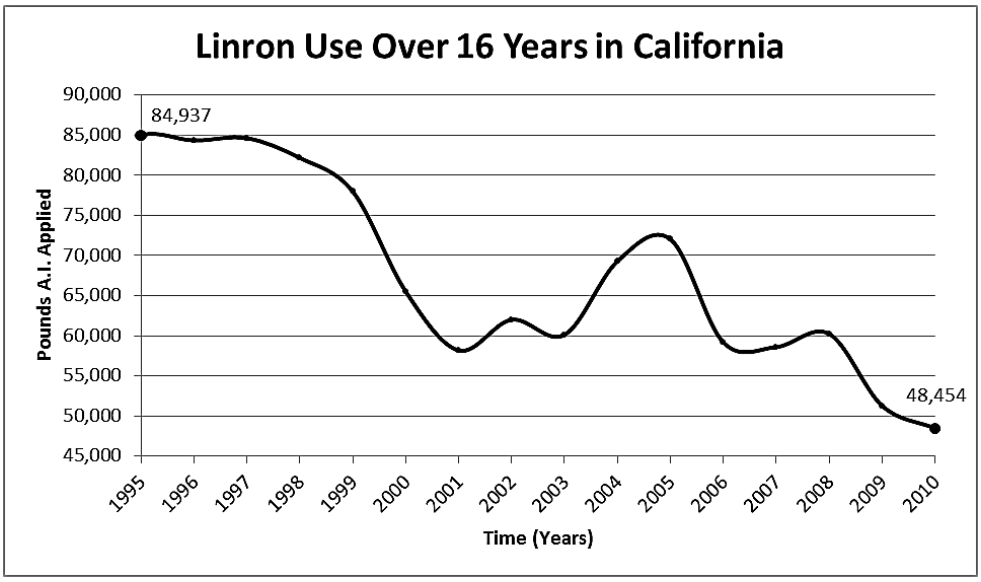
	County	Pounds Applied		County	Pounds Applied
1	Kern	429,007	5	San Joaquin	53,195
2	Imperial	214,078	6	Los Angeles	51,432
3	Santa Barbara	99,513	7	San Luis Obispo	47,293
4	Monterey	67,454	8	Ventura	41,344

Source: CDPR 2013

Linuron use in California has declined steadily over the past 16 years, from a peak in 1995 of 84,937 pounds to the recent low in 2010 of 48,454 pounds (Figure 1; CDPR 2013). Since linuron was first introduced to California in 1985, 17 different linuron products have been registered, but only two products are currently active: Linex 4L and Lorox DF. Applications in Kern and Imperial counties account for the majority of linuron use, followed by applications in the central and southern coastal counties (Table 2). While application to carrots accounts for approximately 80% of annual linuron use in California, it accounts for only 1% of the suggested herbicides for carrot production by the University of California Integrated Pest Management Program (UC

IPM). By contrast, an average of 5.2 million pounds of metam sodium, a soil fumigant, is applied annually to roughly 99% of the carrot crops (CDPR 2013; UC IPM).

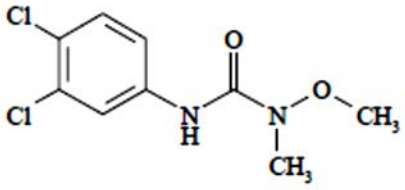
Figure 1 Total pounds of linuron applied in California over 16 years



Source: CDPR 2013

2. Physicochemical Properties

Figure 2 Chemical structure of linuron



Source: US EPA 1995

Linuron belongs to the phenylurea class of herbicides, which include diuron [3-(3,4-dichlorophenyl)-1,1-dimethylurea], an herbicide already known to contaminate groundwater (Kidd and James 1991; 3 CCR section 6800[a]. It is an odorless, colorless solid crystal that is moderately soluble in water and slightly soluble in solvents (Table 3; Kidd and James 1991). Linuron has a very low rate of volatility. The mean K_{oc} of linuron is 341, which is slightly lower than diuron's average value of 499 (Bergin 2013). Smaller K_{oc} values indicate a lower propensity to bind to organic carbon constituents of soil and, subsequently, greater potential mobility in soil water. Table 3 presents the physicochemical properties for linuron.

Table 3 Physicochemical properties of linuron

Physicochemical Properties[a]	
Chemical Name [b]	3-(3,4-dichlorophenyl)-1-methoxy-1-methylurea
Common Name [c]	Linuron
CAS Registry Number [c]	330-55-2
Molecular Formula [b]	$C_9H_{10}Cl_2N_2O_2$
Molecular Weight [b]	249.10 g · mol
Chemical Family [b]	phenylurea
Water Solubility [b]	81 mg · L (25° C)
Acetone at 25°C	500 g · kg
Benzene at 25°C	150 g · kg
Ethanol at 25°C	150 g · kg
Xylene at 25°C	130 g · kg
Heptane at 25°C	15 g · kg
Vapor Pressure [c]	1.5 E-5 mm Hg
Octanol-Water Coefficient (K_{ow}) [b]	1010
Henry's Law Constant (K_H) [d]	1.97 E-9 atm · m^3 · $mole^{-1}$
Adsorption Coefficient (K_{oc})	341 L · kg^{-1}
Distribution Coefficient (K_d) [c]	2.7 (Sandy loam) 7.7 (Silty loam)
Melting Point [c]	86 - 91°C
Physical State [b]	Solid Crystal
Color [b]	White, colorless

a. Bergin 2013
b. Kidd and James 1991
c. US EPA 1995
d. Hazardous Substances Data Bank

3. Environmental Fate

3.1 Soil

Soil conditions are important to predict the degree to which linuron will adsorb, including organic matter content, moisture content, temperature and type. Since linuron has structural and physicochemical properties similar to other pesticides known to contaminate groundwater in California, such as diuron, it is classified as a potential threat to groundwater based on persistence and mobility characteristics (Guzzella et al. 2006; U.S. EPA 1995a).

When the sorption coefficient of silty clay soils (K_d: 3.9) was compared to that of sandy loam soils (K_d: 7.0) keeping temperature and moisture content constant, it was concluded that linuron sorption is guided more by organic matter content than clay content (Berglöf et al. 2000). Zbytniewski and Buszewski (2002) examined the effect of soil organic matter content of podzolic soils at different depths (0-15 cm, 15-30 cm, 30-40 cm) on the propensity of linuron to sorb, concluding that the higher the respective percentage of soil organic matter (2.1%, 4.0%, 6.3%), the higher the respective sorption coefficient (K_d: 0.25, 6.20, 12.09). Likewise, linuron increasingly sorbed to soils that were augmented with organic matter, such as the addition of compost or humic acid to crop soils (Zbytniewski and Buszewski 2002).

Increases in the water content of the soil below the saturation point are also related to a higher sorption affinity of linuron to soils (Table 3; Berglöf et al. 2000; El Imache et al. 2009). Berglöf et al. (2000) increased water content in sandy loam soils from 8% to 18% at 40°C, resulting in increased sorption affinity (K_d: 4.0 to 11.7, respectively). The same study was conducted on silty clay soils, changing the water content from 12% to 15%, resulting in a less marked increase in sorption affinity (K_d: 3.7 to 4.0, respectively) (Berglöf et al. 2000).

Two field lysimeter studies were conducted to determine the leaching potential of linuron versus that of diuron. El Imache et al. (2009) compared relative leaching where linuron was added at a theoretical rate of 0.3 kg/ha and diuron at a higher rate at 1.3 kg/ha, reflecting their typical rates of application. Owing to greater accumulated total mass of linuron leached through the loamy clay soil with 0.15% organic carbon content, the authors concluded a greater leaching potential for linuron than for diuron. In contrast, Guzzella et al. (2006) reported greater loss of diuron in leachate than linuron in a similar lysimeter study conducted on a silty loam soil with 2.6% organic carbon content. The exact cause for these differences is not clear, but could be due to a combination of differential binding to soil and degradation by soil microbes. The amount of percolating water produced in these studies was relatively low when compared to the potential loss in irrigated agriculture, so residues were confined to the lysimeters, potentially enhancing differences due to soil processes.

3.2 Water

Water samples obtained from peripheral ditches were examined to understand the effects of linuron drift on surface water bodies. The samples revealed a high rate of mixing along the water column owing to linuron's moderate water solubility (Crum et al. 1998). Half-lives of linuron varied depending on the flow of water, ranging from 7.2 to 11.8 days when water was stagnant and 3.8 days when water was flowing at a velocity of 5 m/d (Crum et al. 1998). These rates contrasted with Stephenson and Kane's (1984) calculated half-life range of 16 to 40 days, which was attributed to differences in measurement timing and initial nominal linuron concentrations in respective mesocosms (Crum et al. 1998). Concentration dependent degradation was corroborated during an indoor microcosm experiment by Van den Brink et al. (1997), where the calculated half-life for linuron in the water compartment ranged from 11 to 49 days, with lower concentrations correlating with lower half-lives (Crum et al. 1998). Significant differences in mean temperature of up to 10ºC between the application periods in May, June and July (e.g., 13ºC, 15ºC, and 23ºC during week one, respectively) resulted in variable half-lives during the experiment (Crum et al. 1998). Widely ranging pH values (7.2 – 9.2) throughout all concentrations and application months also contributed significantly to the half-life variability (Crum et al. 1998).

According to a compilation of groundwater monitoring studies produced by the U.S. EPA's Office of Pesticide Programs from 1971 to 1991, linuron residues have been detected in samples obtained in Georgia, Missouri, Virginia, and Wisconsin, the highest of which was 5 ppb in Georgia (U.S. EPA 1992). As a result of the Ground Water Protection List listing in California, two groundwater studies to examine linuron in high use areas were conducted by DPR in 1989 and 2011, neither study revealing positive detections (CDPR 2012). Cumulative results of well studies conducted in 2011 by DPR, in 2011 by the California Department of Public Health, and from 2004 to 2011 the State Water Resources Control Board, also reported negative linuron detections in all of the 35 counties sampled, which included many of the counties where linuron use is highest (CDPR 2012). However, 5% of wells sampled (94 wells) contained detections for 3,4-dichloroaniline, a degradate of linuron, diuron, and propanil (3,4-dichloropropionanilide), with detections ranging from 0.001 – 0.541 ppb. The highest reported detection was in Butte County, an area where linuron use has never been reported (CDPR 2012). The cumulative application rates for propanil and diuron far exceed those of linuron over the past five years:

277,660 lbs (125,944 kg) for linuron compared to 3,843,789 lbs (1,743,603 kg) for diuron and 8,917,281 lbs (4,044,811 kg) for propanil, indicating a low potential for linuron as a source of degradate detections (CDPR 2012; CDPR 2013).

3.3 Air

Given linuron's extremely low vapor pressure of 1.4 E-6 mm Hg and Henry's law constant of 5.8 E-9, it is unlikely that linuron will occupy the air compartment through volatilization from the soil (Table 3). Guzzella et al. (2006) examined the fate of linuron in air by setting up a combined lysimeter and air sampling system. Of the air samples that were collected 13 days after application, 2 detected linuron with a total volatilized quantity of 2.63 E-5 $\mu g/m^2$, which were concluded to be negligible (Guzzella et al. 2006). Since volatilization is improbable due to the inherent chemical properties of linuron, the U.S. EPA did not review any studies regarding air contamination in their 1995 reregistration eligibility decision (U.S. EPA 1995).

4. Environmental Degradation

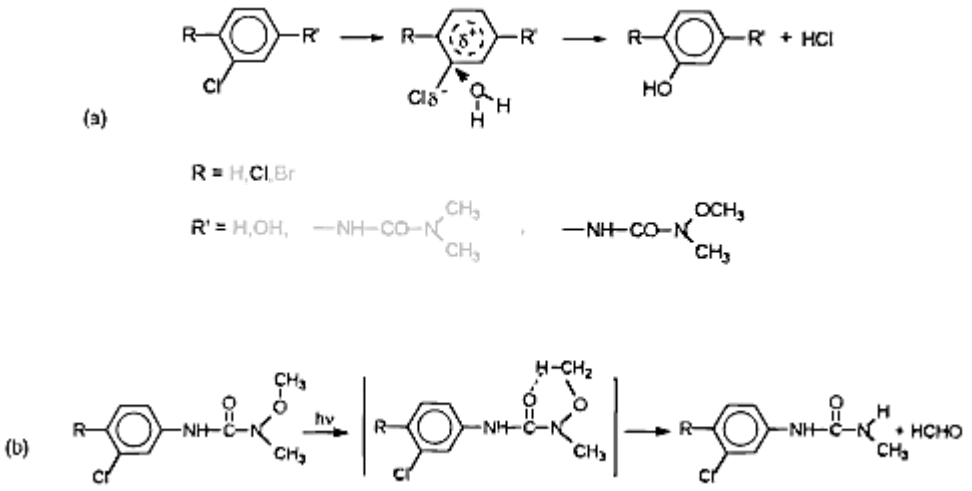
Photochemical reactions of phenylureas depend on the location (*meta* versus *para*) of the halogen(s) on the phenyl group rather than the chemical nature of the halogen that occupies those positions (Faure and Boule 1997). Phenylureas absorb ultraviolet light primarily between wavelengths of 240 nm and 250 nm, and weakly between 270 nm and 300 nm, with a molar absorption coefficient of 15,000 – 20,000 L/mol·cm at the maximum (Amine-Khodja et al. 2004). Photohydrolysis and demethoxylation compete when linuron is irradiated at various wavelengths (Figure 3; Faure and Boule 1997).

4.1 Photolysis

Linuron in aqueous solution irradiated at a wavelength of 254 nm eliminated 63% of the linuron through demethoxylation, as evidenced by the dominant presence of the intermediate species DCPMU (Rao and Chu 2009). The formation of formaldehyde (CH_2O) through a Norrish-type II reaction is indicative of successful cleavage of the N-methoxy bond (Amine-Khodja et al. 2004; Faure and Boule 1997). Although effective at degrading linuron in a laboratory setting, photolysis is not considered to be a major degradation pathway under natural conditions, as the absorption spectrum of linuron minimally overlaps with the UV light spectrum (280 – 315 nm) (Amine-Khodja et al. 2004; Rao and Chu 2009). However, when photolysis does occur, it can be

an effective means of dehalogenation of the phenyl ring, a degradation step that does not easily occur through biodegradation (Amine-Khodja et al. 2004).

Figure 3 Two abiotic degradation schemes for linuron: (a) *meta*-hydroxylation, (b) demethoxylation



Source: Adapted from Faure & Boule 1997

When exposed to sunlight, transformation of phenylureas can be slow and temporarily produce low amounts of transformation products that have been shown to be more toxic than their parent material (Bonnemoy et al. 2004). Although these are likely to be further transformed, disappearance of the parent compound and known degradates does not necessarily indicate an absence of toxicity, since photoproduct formation rates can exceed degradation rates (Amine-Khodja et al. 2004; Bonnemoy et al. 2004).

4.2 Hydrolysis

Hydrolysis is considered to be a minor degradation pathway because of the stability of linuron in the presence of sterile water, although the intermediate products are more prone to hydrolysis than the parent compound (El-Dib and Aly 1976a). Photohydrolysis-dechlorination eliminated 96.9% of the intermediate species DCPMU when irradiated at 254 nm, indicated by the presence of chloride ions in solution (Rao and Chu 2009). The methoxy group on linuron makes it more susceptible to reaction with hydroxyl radicals under ideal conditions, although the only observed environmental factors that increase the rate of hydrolysis are high alkalinity and temperature increases along the order of 10ºC, both of which are unlikely to occur in natural waters (Caux et

al. 1998; El-Dib and Aly 1976a; Kidd and James 1991). The second order hydrolytic reaction rate coefficient (k_2) is 1.19 L/mol·day (El-Dib and Aly 1976a).

4.3 Biotic Processes

Biodegradation is primarily responsible for the disappearance of linuron from soils, with a half-life range between 38 and 67 days (Dejonghe et al. 2003; Kidd and James 1991). While there are several known bacterial consortiums that can use linuron as a source of carbon and nitrogen, isolating one strain that can completely degrade linuron is much more difficult (Dejonghe et al. 2003). Generally, one strain of bacteria attacks the urea chain of the structure and a different strain breaks the phenyl ring (Dejonghe et al. 2003). Complete mineralization of linuron in laboratory and natural environments is concomitant with *Variovorax* sp. bacterial strains (Sniegowski et al. 2011).

Silty loam soils with a prior history of linuron use possess an increased capacity to mineralize linuron, even after undergoing induced stress, indicating that mineralizing-bacteria populations remain competitive when linuron is not being actively applied (Sniegowski et al. 2011). When active application to soils with no history of linuron use was stopped, mineralization capacity either slowed considerably or halted altogether, although under longer periods of linuron application, these soils could permanently develop the ability to mineralize linuron (Sniegowski et al. 2011). Differences in resilience of linuron degrading communities for the two different experimental soils could be due to higher community diversity in soils with prior linuron use, which protected the microbial community from environmental stressors, or instability associated with the xenobiotic genes that developed the ability to degrade linuron in soils with no prior linuron use (Sniegowski et al. 2011). Environmental stressors which have no apparent effect on the mineralization capacity of linuron include prolonged exposure to cold weather and the application of other pesticides in combination with linuron such as bentazon, atrazine and isoproturon (Sniegowski et al. 2011). Overall, bacterial communities that mineralize linuron were able to weather induced stressors and regain their pre-stress degradation rates or were not affected by the stressors at all (Sniegowski et al. 2011).

Biodegradation is less likely to occur in aquatic environments than in soil, as noted by El-Dib and Aly (1976b) who observed that chemical concentrations remained constant in a river for four months after application. Only after bioaugmentation with *Bacillus cereus* did linuron

concentrations noticeably decrease, as indicated by the presence of anilines in the intermediate metabolites, including 3-(3,4-dichlorophenyl) urea, 3-(3,4-dichlorophenyl)-1-1-methyl urea, and 3-(3,4-dichlorophenyl)-1-methoxy urea (El-Dib and Aly 1976b). While native microbial populations did not readily degrade linuron, the chemical itself did not appear to have toxic or inhibitory effects on bacteria when exposed to concentrations of 10 mg/L (El-Dib and Aly 1976b).

Chlorbromuron [3-(4-bromo-3-chlorophenyl)-1-methyl-1-methoxyurea], a chemical structurally similar to linuron with the *para* halogen substituted with bromine instead of chlorine, and its metabolites were found to be significantly degraded over a period of 12 days by the soil fungus *Rhizoctonia solani* (Weinberger and Bollag 1972). The proposed degradation pathway by *R. solani* is demethoxylation followed by demethylation and evidence that the resulting urea is eventually converted into an aniline (Weinberger and Bollag 1972). Biodegradation of a sampling of other phenylureas by *R. solani* was examined, revealing varying degrees of parent chemical transformation, including linuron, of which 40% of the initial 10 μg was degraded into three different metabolites (Weinberger and Bollag 1972). The transformation of all tested phenylureas affirms the active role *R. solani* plays in the biodegradation of this class of pesticides in soil (Weinberger and Bollag 1972).

5. Ecotoxicology

5.1 Vegetation

Linuron applied to soil is translocated from the root system to the leaves via the xylem, where it obstructs electron flow in photosystem II, decreasing photosynthetic efficiency (Daam et al. 2009; Kidd and James 1991). When photosynthesis is halted, plants increase their reliance on stored energy which can result in plant death. Van den Brink et al. (1997) noted that *Elodea nuttallii* biomass significantly decreased when grown in water with linuron concentrations of 50 μg/L to 150 μg/L, likely due to photosynthetic inhibition by linuron. Snel et al. (1998) found that photosynthetic inhibition reaches equilibrium after four hours, but the effect can be reversed once linuron is removed from the growth medium with plants able to fully recover after six hours (Kidd and James 1991).

5.2 Toxicity

Linuron and other phenylureas degrade into three major degradation products: DCPMU [3-(3,4-dichlorophenyl)-1-methylurea], DCA [3,4-dichloroaniline], and DCPU [3-(3,4-dichlorophenyl)urea], with DCPMU and DCA being the primary degradates for linuron (Guzzella et al. 2006; Tixier et al. 2002). Guzzella et al. (2006) found that there was a peak of DCPMU towards the beginning of linuron application, with DCA and DCPU peaking towards the end of the observation period, suggesting that DCA and DCPU are transformation products of DCPMU. Diuron studies are used as a proxy for linuron toxicity because they share several degradation products which likely follow the same degradation pathways. *Mortierella isabellina* is the only fungal strain that has been shown to completely mineralize diuron after 15 days, a majority of which occurred during the first 10 hours (Tixier et al. 2002). The fungal strains *Cunninghamella elegans, Mortierella isabellina,* and *Beauveria bassiana* are known to transform DCPMU to DCPU, although it was revealed that the rate of diuron disappearance was not proportional to the appearance of transformation products (Tixier et al. 2000). DCA was shown to be much more toxic than diuron based on the Microtox® test using the bacteria *Vibrio fischeri*, with an EC_{50} roughly 97 times lower than that of diuron (Tixier et al. 2002). These results were corroborated when DCA was exposed to the eukaryotic protozoan *Tetrahymena pyriformis*, although when tested in vivo, there were no signs of increased toxicity as compared to diuron (Tixier et al. 2000).

While the toxicity of phenylurea degradates can exceed that of the parent compound, Guzzella et al. (2006) highlighted that only 0.005% (1.89 μg) of the initial amount of parent compound applied in their soil lysimeter study transformed into DCPMU, DCPU, and DCA. Likewise, metabolites in the experimental plot were negligible in the two months following the completion of the experiment (Guzzella et al. 2006). These studies have not been conducted on soils with a history of linuron or phenylurea use, likely oversimplifying the forces that transform and degrade linuron and other phenylureas that did not reach their target site.

5.3 Invertebrates

Francis et al. (1985) studied the biomagnification effects of linuron on terrestrial food chains by quantifying concentrations of linuron in the excretions of soybean loopers that consumed the leaves of treated sorghum plants. Much of the linuron that was applied was either metabolized

completely by the sorghum plants or found in the roots rather than the stems and leaves, reducing the concentration of linuron the soybean loopers consumed (Table 4; Francis et al. 1985). Moreover, it was concluded that soybean loopers were able to metabolize linuron consumed through the sorghum leaves, reducing the concentration of linuron in their excretions (Francis et al. 1985).

Table 4 Linuron concentration locations in sorghum plants

	Linuron Concentrations (ppm)		
	1	*2*	*3*
Stems	11.72	19.69	28.00
Roots	22.08	15.00	44.46

Source: Francis et al. 1985

In microcosms chronically supplied with linuron, invertebrates did not elicit an immediate response to any concentration of linuron application, although there was a zooplankton population shift from Rotatoria-dominated to Copepoda-dominated, possibly due to the selective feeding of copepods (Cuppen et al. 1997). A decrease in the aquatic snail species *Physella acuta* at 150 µg/L, the highest concentration of linuron examined, was likely due to a decrease in food sources and oviposition sites (Cuppen et al. 1997). It should be noted that it is unlikely that these effects would be observed in drainage ditches under normal application rates of linuron, unless there is an event in which a high concentration of linuron comes into prolonged contact with a water body, resulting in a macrophyte die-off (Cuppen et al. 1997).

5.4 Vertebrates

While linuron is not intended for use against vertebrates, the potential for unintended exposure exists and potential adverse effects have been examined. The acute oral LD_{50} is 4000 mg/kg for rats, NOAEL for adults is 125 ppm and for pups is 25 ppm (U.S. EPA 2010; Wolf et al. 1999). When ingested by rats, linuron undergoes demethoxylation then hydroxylation of the benzene ring before being excreted, with metabolites being urea derivatives (Hazardous Substances Data Bank). During project number 4580-001, part of U.S. EPAs OSRI (Order Recipient Submissions), rats were fed a diet of 625 mg/kg (5 times NOAEL for adult rats), which resulted in decreased body weight, decreased fertility in successive generations of females, and decreased litter size and pup weight (U.S. EPA 2010). Moreover, in feeding studies on rats well below the

acute oral LD50 (625 mg/kg), linuron was shown to cause testicular tumor growth, which is hypothesized to be a result of endocrine disruption (Wolf et al. 1999). Due to the limited nature of these findings, U.S. EPA designated linuron as a group C carcinogen, meaning it is a possible human carcinogen (U.S. EPA 1995). California's Office of Environmental Health Hazard Assessment designated linuron as having reproductive toxicity under Proposition 65 in 1999. LD50 values generated for other species are contained in Tables 5 and 6.

Table 5 Toxicity data for vertebrates

Name	Species	Endpoint	Concentration (mg/kg)
Rats	*Rattus* sp.	LD50[a]	1,500-4,000
Dogs	*Canus lupus familiaris*	LD50[a]	500
Rabbits	--	LD50[a]	2,250
		LD50[b]	>5,000
Mallard Ducklings	*Anas platyrhynchos*	LC50[c]	3,083
Ring-Necked Pheasants	*Phasianus colchicus*	LC50[c]	3,438
Japanese Quail	*Coturnix japonica*	LC50[c]	>5,000

Source: Kidd and James 1991; (a) acute oral, (b) acute percutaneous, (c) 8 day dietary

Table 6 Toxicity data for aquatic organisms

Taxa	Name	Species	Endpoint	Min (ppb)	Median (ppb)	Max (ppb)
Crustacea	Water flea	*Daphnia magna*	EC50	120.0	240.0	1,100.0
Fish	Sheepshead minnow	*Cyprinodon variegatus*	LC50	--	890.0	--
	Channel catfish	*Ictalurus punctatus*	LC50	1,800.0	2,350.0	2,900.0
	Bluegill	*Lepomis macrochirus*	LC50	9,200.0	9,600.0	16,200.0
	Rainbow trout	*Oncorhynchus mykiss*	LC50	3,000.0	9,700.0	16,400.0

Source: Munn and Gilliom 2001

Summary

Linuron is a wide-spectrum herbicide used for both pre-emergent and post-emergent weed control. It functions by decreasing photosynthesis efficacy through electron transfer inhibition in chloroplasts, requiring plants to rely on stored energy, eventually resulting in plant death. A reregistration decision by the U.S. EPA concluded that linuron exceeded ecological and groundwater quality levels of concern in addition to labeling linuron as an unquantifiable group C carcinogen. California's Office of Environmental Health Hazard Assessment declared linuron a developmental toxicant as defined under Proposition 65. California's Department of Pesticide Regulation has classified linuron as a possible groundwater contaminant, and under the authority of the PCPA has conducted two groundwater monitoring studies for linuron in areas of high use, neither study revealing positive detections. Although linuron is similar in many ways to diuron, a known groundwater contaminant, linuron use in 2010 was only 8.3% of total diuron use for the same year, indicating that it is probably less likely to contaminate groundwater than diuron. Based on significantly lower quantities of linuron applied, it is less likely that linuron will be found in groundwater than diuron in California.

Loss of linuron to volatilization is minimal because of low vapor pressure and Henry's law constant. Biodegradation by bacterial consortiums and fungus is the primary route of disappearance in soils, with half-lives ranging between 38 and 67 days. When in contact with surface water, degradation is concentration-dependent, with half-life ranges between 7 and 49 days. While linuron does not usually undergo phototransformation, photohydrolysis has been shown to dehalogenate the phenyl ring, a step that does not easily occur via biodegradation. Linuron's water solubility is greater and its K_{oc} is lower than that of diuron, a chemical with similar properties that has been detected in groundwater. Consequently, residues of linuron have also been detected in areas of higher use in the U.S. Lysimeter studies comparing the leaching capacity of linuron with diuron note that even minor differences in experimental environmental conditions could result in linuron reaching groundwater.

Preliminary studies on the toxicity of phenylurea degradates conclude that the degradates can potentially be more toxic than their parent compounds, but toxicity tests have had mixed results when examined on organisms beyond bacteria. It has been shown that even in the case of

degradates that are much more toxic than their parent compound, the quantity detected is very low, minimizing their potential impact on the surrounding environment. Likewise, diuron and propanil share some of the same degradates as linuron, masking the source of these degradate detections. Risk mitigation measures described in the U.S. EPA's reregistration eligibility decision in 1995 reduced maximum use rates and number of annual applications for certain crops, including prohibited applications on sandy and loamy sand soils, and on soils with less than 1% organic matter. These restrictions, combined with the ongoing use reductions and the lack of groundwater detections, suggest that linuron is likely not currently a major groundwater threat in California, although based on the shared properties of linuron with chemicals known to contaminate groundwater in California and the fact that there have been detections in other states, the risk of contamination still exists.

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