

Chlorimuron Ethyl Sorption and Desorption Kinetics in Soils and Herbicide-Desiccated Cover Crop Residues

Krishna N. Reddy,* Martin A. Locke, Stephen C. Wagner, Robert M. Zablotowicz,
Lewis A. Gaston, and Reid J. Smeda

Southern Weed Science Laboratory, Agricultural Research Service, U.S. Department of Agriculture,
P.O. Box 350, Stoneville, Mississippi 38776

Interaction between a herbicide and plant residue on the soil surface in plant residue management systems such as no-tillage or cover crop is of interest in terms of environmental fate of the herbicide. This study was designed to evaluate sorption and desorption of chlorimuron ethyl {ethyl 2-[[[(4-chloro-6-methoxy-2-pyrimidinyl)amino]carbonyl]amino]sulfonyl]benzoic acid} in herbicide-desiccated rye (*Secale cereale* L.) and hairy vetch (*Vicia villosa* Roth) residues and soils collected from a field. Sorption was determined by reacting 0.5 g of soil or plant residue with 6 mL of [¹⁴C]chlorimuron ethyl solution at five concentrations (0.06–12.04 μmol L⁻¹) for 72 h. Freundlich K_f was highest in hairy vetch (6.33) followed by rye (3.95) and soils from no cover crop or beneath plant residue (0.81–1.03). The N values (0.88–0.95) for soils and plant residues indicated nearly linear sorption. Time course sorption data analyzed by an equilibrium/kinetic model indicated that sorption was initially rapid (within 1 h), followed by a negligible increase in soil or a slow increase in rye and hairy vetch residue. Chlorimuron ethyl K_f increased with increased decomposition of plant residue. The K_f for rye and hairy vetch residues sampled at 11 weeks after soybean planting increased by 54 and 49%, respectively, compared with residues sampled at planting. CaCl₂-desorbable chlorimuron ethyl in two consecutive 24-h cycles ranged from 54 to 65% in soils and from 42 to 49% of that sorbed in plant residues. Two additional 24-h cycles with methanol/(NH₄)₂CO₃ did not completely desorb the remaining chlorimuron ethyl. Under field conditions, plant residues can apparently intercept and temporarily retain chlorimuron ethyl.

Keywords: Herbicide; chlorimuron; rye; hairy vetch; cover crop; plant residue; sorption; desorption; no-tillage

INTRODUCTION

Crop production involving plant residue management systems such as reduced tillage and cover crops require alternative weed management strategies. A no-tillage with a cover crop system is of current interest in the context of recent legislation that links farm subsidies with soil conservation practices and the renewed emphasis on integrated weed management programs to reduce herbicide use. A cover crop based on a no-tillage system involves planting winter cover crops in the fall. Rye (*Secale cereale* L.) and hairy vetch (*Vicia villosa* Roth) are winter annuals used as cover crops in most areas of the United States. They produce substantial vegetative biomass before the crop is planted the following spring, before which time the cover crops are usually desiccated with a herbicide and left standing, flattened, or mowed to form a mulch on the soil surface before successive crops are seeded.

Cover crop residues on the soil surface can influence weed populations. Plant residues suppress weed germination and emergence of many weeds (Teasdale et al., 1991; Liebl et al., 1992; Teasdale and Daughtry, 1993) by altering the light, temperature, and moisture conditions under the mulch (Teasdale and Mohler, 1993). Small grain and legume residues have been shown to release allelochemicals that suppress germination and growth of weed species (Putnam, 1988; White et al., 1989). Plant residue left on the soil surface reduces soil erosion as well as nutrient and pesticide

loss in runoff, conserves soil moisture, and may also offer other benefits such as improved physical properties of soil, increased soil organic carbon (Blevins and Frye, 1993), and enhanced microbial populations and soil enzyme activities (Wagner et al., 1995a).

Despite the negative impact of cover crop residue on weed germination and emergence, often adequate weed control may not be achieved and may require post-emergence herbicide applications to prevent weed populations from increasing to a severe level of infestation. Herbicide intercepted by crop residues must reach the soil beneath the residue to prevent weed seedling development. Herbicide intercepted by residue is washed off and/or released to soil upon rainfall. The extent of washoff and/or release may vary, depending upon time and amount of rainfall following herbicide application and on the nature of any interaction between herbicide and plant residue. Several workers have reported that plant residues intercepted and retained a significant portion of applied herbicides (Banks and Robinson, 1982; Ghadiri et al., 1984; Banks and Robinson, 1986).

Herbicide interaction with plant residue has practical implications in terms of herbicide release to soil for target plant uptake. Herbicide binding can be weak or strong depending on the type and degree of decomposition of cover crop residue. Increased herbicide retention by plant residue not only reduces the amount reaching the soil (affecting weed control) but also prolongs herbicide persistence. The latter could provide season-long weed control from herbicide desorbed from plant residues over a period of time. However, the residues persistent beyond the crop season have potential to injure rotational crops including vegetables (Johnson

* Author to whom correspondence should be addressed.

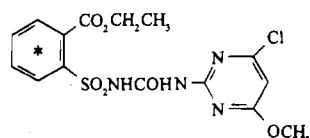


Figure 1. Structure of chlorimuron ethyl. An asterisk indicates ^{14}C -[U]-phenyl label.

and Talbert, 1993). Herbicide retention by plant residue can also minimize herbicide runoff and leaching losses.

Chlorimuron ethyl (Figure 1) is used extensively for pre- and post-emergence broadleaf weed control in soybean [*Glycine max* (L.) Merr.]. It is a weak acid with a $\text{p}K_a$ of 4.2. Water solubility and the octanol/water partition coefficient of chlorimuron ethyl change with pH; water solubilities are 11 and 1200 mg L^{-1} and octanol/water partition coefficients are 320 and 2.3 at pH 5 and 7, respectively (Beyer et al., 1988; Weed Science Society of America, 1994). Chlorimuron ethyl sorption in soil increased with increased organic carbon and decreased with increased soil pH (Goetz et al., 1989; Reddy et al., 1995). However, the magnitude of chlorimuron ethyl sorption and retention by cover crop residues has not been reported.

Information on herbicide interaction with plant residue and soil is needed as plant residue management systems become more widely used. The objectives of this research were to characterize chlorimuron ethyl sorption and desorption in rye and hairy vetch residue. The sorptive characteristics of plant residues were compared with those of soils beneath plant residue and no cover crop soil. Effects of decomposition of plant residue on chlorimuron ethyl sorption were also studied.

MATERIALS AND METHODS

Herbicide. Technical grade (98.7% purity) and ^{14}C -labeled (^{14}C -[U]-phenyl labeled, specific activity 2168.2 kBq mg^{-1} , 99% purity) chlorimuron ethyl were obtained from DuPont Agricultural Products, Wilmington, DE, and used without further purification. Herbicide stock solutions were prepared in acetone and stored in darkness at 0 °C until used. Appropriate volumes of ^{14}C -labeled and technical grade stock solutions were diluted with 0.01 M CaCl_2 as required.

Cover Crop Residues and Soils. A soybean field study under nonirrigated conditions was established in 1993 on a Dundee silt loam (fine-silty, mixed, thermic Aeric Ochraqualf: 25% sand, 49% silt, 26% clay) soil near Stoneville, MS. This soil had been under soybean production and had no history of chlorimuron ethyl for at least 4 years. The experimental area was under a conventional tillage system (subsoil, disking, cultivation) during 1992 and 1993, but was converted to a no-tillage system following soybean harvest in 1993. The treatments consisted of no cover crop, rye cover crop, and hairy vetch cover crop, each replicated four times. Rye and hairy vetch were planted in the fall of 1993, desiccated with paraquat (1,1'-dimethyl-4,4'-bipyridinium ion), and flattened at soybean planting in spring of 1994. Soybean was seeded directly into cover crop residues and received only a post-emergence application of sethoxydim {2-[1-(ethoxyimino)butyl]-5-[2-(ethylthio)propyl]-3-hydroxy-2-cyclohexen-1-one} during midseason. Since differences in soil characteristics between cover crop and no cover crop systems are more apparent in the surface layer than in lower depths (Wagner et al., 1995a), soils from the surface 2 cm were used in the studies. Surface 2 cm soils were collected from no cover crop (1.36% organic carbon and pH 6.44) soils as well as soils beneath cover crop residues (1.46% organic carbon and pH 6.44 in rye soil; 1.53% organic carbon and pH 6.38 in hairy vetch soil) at planting in 1994. Cover crop residues were collected at 0, 3, 6, and 11 weeks after planting. The samples were pooled from four replications. Soils were sieved (2 mm), and cover crop residues were chopped to 2–3 cm long and stored at 4 °C.

Chlorimuron Ethyl Sorption Kinetics. Chlorimuron ethyl sorption kinetics were measured on 0.5 g (oven-dry equivalent) of field moist soil or plant residue collected at planting. Six milliliters of technical grade and ^{14}C -labeled chlorimuron ethyl solution was added to a 25-mL glass centrifuge tube and sealed with a Teflon-lined cap. The chlorimuron ethyl concentration used was 2.40 $\mu\text{mol L}^{-1}$ with about 110 Bq mL^{-1} . Samples were shaken on a rotary shaker for 1, 24, 48, 72, 96, and 144 h in a cold room (4 °C) to minimize microbial activity. After shaking, samples were centrifuged at 5900g for 10 min. Two 1-mL aliquots of the supernatant were counted for radioactivity using a liquid scintillation spectrometer. All volumes were determined by weight for increased accuracy. The difference between initial and final solution concentrations (micromoles per liter) was attributed to sorption (micromoles per kilogram). Each treatment was replicated three times. This study was conducted in two sets. One set of tubes with soil or plant residue was exposed to chloroform fumigation in a glass desiccator for 72 h preceding sorption. Chloroform fumigation gives a near-complete kill of microbes and is used to determine soil biomass (Jenkinson and Ladd, 1981). The other set of tubes with soil or plant residue was used as a control (nonfumigated).

[^{14}C]Chlorimuron ethyl sorption kinetics were described using a three-site equilibrium/kinetic model (Gaston and Locke, 1994), similar to those of Amacher et al. (1988) and Boesten et al. (1989).

$$S_1 = k_e C^N \quad (1a)$$

$$dS_2/dt = k_f C^N - (k_r + k_{ir})S_2 \quad (1b)$$

$$dS_3/dt = k_{ir}S_2 \quad (1c)$$

The subscript numbers refer to sorption sites, C ($\mu\text{mol L}^{-1}$) is solution concentration, S_j ($\mu\text{mol kg}^{-1}$) are sorbed concentrations, k_e is the coefficient for instantaneous equilibrium, k_f ($\text{L kg}^{-1} \text{h}^{-1}$) is the forward rate constant, k_r (h^{-1}) is the reverse rate constant, k_{ir} (h^{-1}) is the rate constant for irreversible sorption, and the exponent N accounts for nonlinearity. Equations 1a–1c were expressed in finite difference form and optimized values for parameters obtained using a least-squares procedure. Although the model contains five parameters, this number was reduced to three by using values for N and K_f (assumed equal to $k_e + k_f/k_r$) obtained from the (apparent) equilibrium sorption studies discussed below.

Chlorimuron Ethyl Sorption. A batch equilibrium technique was employed to characterize sorption of chlorimuron ethyl. As described above for the sorption kinetics study, 0.5 g (oven-dry equivalent) of soil or plant residue collected at planting was reacted with 6 mL of technical grade and/or ^{14}C -labeled chlorimuron ethyl solution. Chlorimuron ethyl concentrations were 0.06, 0.23, 1.19, 2.40, and 12.04 $\mu\text{mol L}^{-1}$ with about 50–116 Bq mL^{-1} . Samples were shaken for 72 h, centrifuged, and counted for radioactivity as described for the sorption kinetics study. Each treatment was replicated four times with no chloroform fumigation.

The distribution of herbicide between sorbed and solution phases was best described by the Freundlich equation, $S = K_f C^N$, where S is the amount of herbicide sorbed ($\mu\text{mol kg}^{-1}$) and C is the solution concentration ($\mu\text{mol L}^{-1}$). K_f and N are empirical constants, where K_f is the Freundlich coefficient (L kg^{-1}) and the exponent N is a dimensionless parameter commonly less than unity. Nonlinear regression techniques used to derive K_f and N minimized the weighted residual sum of squares (SAS Institute Inc., 1991). The linearized K_d (distribution coefficient) values were also calculated.

Chlorimuron Ethyl Desorption. Desorption was measured on samples equilibrated with initial chlorimuron ethyl concentrations of 1.19 and 12.04 $\mu\text{mol L}^{-1}$. After an initial 72-h sorption and centrifugation, the desorption was induced by a successive replacement of 70–80% of the supernatant with herbicide-free desorbing solution. The samples were re-equilibrated on a rotary shaker for 24 h in a cold room (4 °C). After shaking, samples were centrifuged at 5900g for 10 min

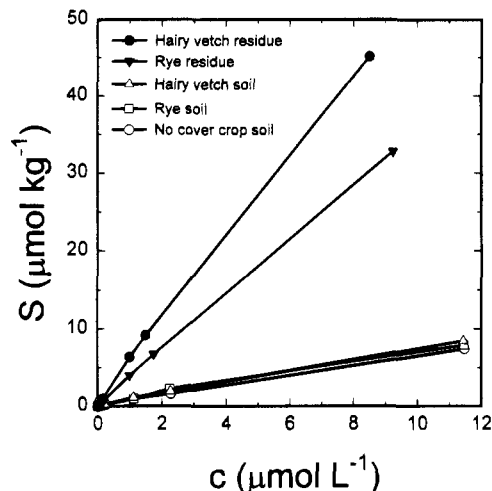


Figure 2. Freundlich isotherms that describe chlorimuron ethyl sorption in rye and hairy vetch residue and soils collected at soybean planting.

Table 1. Parameter Coefficients for Chlorimuron Ethyl Sorption in Soils and Herbicide-Desiccated Cover Crop Residues at Planting

soil/plant residue		Freundlich sorption parameter ^a		
		K_f , L kg ⁻¹	N , dimensionless	K_d , L kg ⁻¹
no cover crop	soil	0.81 (0.02)	0.91 (0.01)	0.78 (0.04)
rye	soil	0.92 (0.02)	0.91 (0.02)	0.93 (0.03)
	rye residue	3.95 (0.07)	0.95 (0.01)	3.96 (0.10)
hairy vetch	soil	1.03 (0.02)	0.88 (0.01)	1.09 (0.04)
	hairy vetch residue	6.33 (0.14)	0.92 (0.02)	6.02 (0.14)

^a Values in parentheses are asymptotic standard errors.

and two 1-mL aliquots of supernatant were counted for radioactivity as described earlier. Of the four desorption cycles, the first and second were desorbed with 0.01 M CaCl₂ and the third and fourth with methanol/2 M (NH₄)₂CO₃ (3:1 v/v). Following the methanol/2 M (NH₄)₂CO₃ desorption, the soil samples were air-dried and plant residue samples were oven-dried (55 °C for a week). Duplicate subsamples of 0.2 g of soil or 0.1 g of plant residue were mixed with 0.3 g of cellulose and combusted using a Packard Oxidizer 306 (Packard Instruments Co., Downers Grove, IL) to determine undesorbed ¹⁴C. The ¹⁴CO₂ released during combustion was trapped in Carbo-Sorb and Permafluor, and radioactivity was quantified using a liquid scintillation spectrometer. Desorbable and undesorbed data were expressed as percent of [¹⁴C]-chlorimuron ethyl sorbed.

Effect of Age of Plant Residue on Chlorimuron Ethyl Sorption. Rye and hairy vetch cover crop residues collected at 0, 3, 6, and 11 weeks after soybean planting were used to assess the effect of residue decomposition on chlorimuron ethyl sorption. Chlorimuron ethyl sorption was characterized using a batch equilibrium technique as described in the sorption study.

RESULTS AND DISCUSSION

Chlorimuron Ethyl Sorption. Sorption was well described by the Freundlich equation. Model parameters for the sorption isotherms of Figure 2 are given in Table 1. The Freundlich coefficient, K_f , was lowest (0.81) in soil from no cover crop (Table 1). The soil beneath rye residue (0.92) and hairy vetch residue (1.03) had slightly higher K_f values than no cover crop soil. Overall, chlorimuron ethyl sorption in rye ($K_f = 3.95$) and hairy vetch ($K_f = 6.33$) residue was 4–6 times higher than in the three soils. The N values for

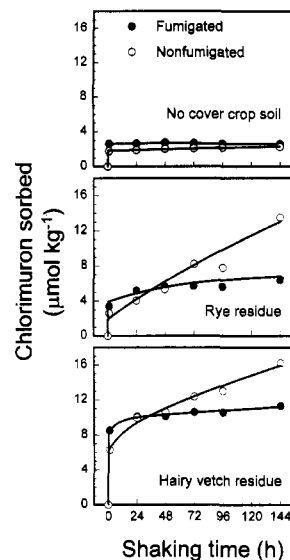


Figure 3. Effect of shaking time on chlorimuron ethyl sorption in fumigated and nonfumigated rye and hairy vetch residue and soil from no cover crop collected at planting. Predicted values were calculated from eqs 1a–1c. Solid lines of predicted values run through observed values depicted as either open or solid circles with the exception of fumigated soil. In fumigated soil, the line represents observed values as sorption appears to be instantaneous with no apparent kinetic behavior.

chlorimuron ethyl sorption were greater than 0.88 in soils and plant residues, indicating near linearity. Accordingly, K_d values were almost identical to their respective K_f values (Table 1).

Chlorimuron ethyl sorption was weak, and the differences in sorption were smaller among the three soils as evidenced by their low K_f values and sorption isotherms (Table 1 and Figure 2). Apparently, these soils had minor differences in organic carbon content (1.36–1.53%) and pH (6.38–6.44). However, a similar trend was observed for fluometuron under no-tillage system by Brown et al. (1994). Fluometuron sorption was greater in hairy vetch soil ($K_d = 2.96$) than in no cover crop soil ($K_d = 2.23$), which they attributed to the higher organic carbon accumulated over a period of 11 years in hairy vetch soil (2.5%) as compared to no cover crop soil (2.0%). High organic carbon content and soil pH close to the pK_a (4.2) tend to increase sorption of chlorimuron ethyl (Goetz et al., 1989; Reddy et al., 1995) and chlorsulfuron (Shea, 1986). Rye and hairy vetch residues were more sorptive than the underlying soils. This trend is similar to the sorption of metribuzin (Dao, 1991), benzene, ethylbenzene, 1,2,3-trichlorobenzene (Boyd et al., 1990), alachlor, acifluorfen, 2,4-D (Locke et al., 1994), and fluometuron (Locke et al., 1995) in various plant residues. Plant residues contain cellulose, hemicellulose, lignin, and protein as well as soluble substances, such as sugars, amino sugars, organic acids, and amino acids which constitute a major fraction of organic carbon (Paul and Clark, 1989; Waggoner, 1989). Higher sorptive capacity may have been due, in part, to a greater carbon content of plant residues. Entrapment or physical absorption within cell wall structures such as cellulose microfibrils embedded in a lignin-hemicellulose matrix may also account for the higher sorptive capacity (Dao, 1991).

Chlorimuron Ethyl Sorption Kinetics. Chlorimuron ethyl sorption in soil during a 1–144-h shaking indicated that sorption increased very rapidly during the first hour (Figure 3). Sorption in fumigated soil

Table 2. Parameters for the Equilibrium/Kinetic Model^a

parameter	soil nonfumigated	rye		hairy vetch	
		fumigated	nonfumigated	fumigated	nonfumigated
k_e , L kg ⁻¹	0.870 ± 0.020	1.900 ± 0.300	0.90 ± 0.40	4.900 ± 0.200	3.40 ± 0.40
k_f , L kg ⁻¹ h ⁻¹		0.030 ± 0.020	0.05 ± 0.04	0.150 ± 0.080	0.15 ± 0.05
k_{ir} , h ⁻¹	0.002 ± 0.001	0.001 ± 0.005	0.10 ± 0.50	0.006 ± 0.002	0.03 ± 0.01

^a Standard errors (±).

Table 3. Desorption of Chlorimuron Ethyl from Cover Crop Residues and Soils after 72 h of Sorption with 1.19 or 12.04 μmol L⁻¹ Chlorimuron Ethyl^{a,b}

chlorimuron ethyl concn, μmol L ⁻¹	soil/plant residue		desorbed			
			CaCl ₂ , ^c %	methanol/(NH ₄) ₂ CO ₃ , ^d %	undesorbed, %	total recovered, %
1.19	no cover crop	soil	61 ab	28 b	14 a	103 a
		rye	soil	65 a	24 bc	16 a
	rye	residue	42 d	27 b	2 b	71 c
		soil	54 bc	17 c	15 a	86 bc
	hairy vetch	soil	54 bc	17 c	15 a	86 bc
		residue	49 cd	38 a	8 b	95 ab
12.04	no cover crop	soil	59 a	21 c	16 ab	96 a
		rye	soil	60 a	20 c	17 a
	rye	residue	46 b	28 b	5 c	79 a
		soil	58 a	19 c	16 ab	93 a
	hairy vetch	soil	58 a	19 c	16 ab	93 a
		residue	45 b	46 a	2 c	93 a

^a Percent of [¹⁴C]chlorimuron ethyl sorbed. ^b Means within a column for each concentration followed by the same letter do not differ significantly at the 5% level as determined by Fisher's lsd test. ^c Total chlorimuron ethyl desorbed in first and second 24-h desorptions with CaCl₂. ^d Total chlorimuron ethyl desorbed in third and fourth 24-h desorptions with methanol/(NH₄)₂CO₃ following CaCl₂ desorption.

showed no kinetic behavior at the time scale of this experiment, achieving maximum sorption within 1 h of reaction time. The kinetics of sorption in the nonfumigated soil were also very rapid. In this case, however, the data were adequately described if reversible kinetics were ignored and only the instantaneous and irreversible sorption components of the equilibrium/kinetic model considered, i.e., the two-site analogue defined by eqs 1a and 1c, the latter written as $dS_2/dt = k_{ir}S_1$. Parameter estimates are given in Table 2. In a different study, Reddy et al. (1995) observed nearly maximum chlorimuron ethyl sorption within 72 h in conventional tillage and no-tillage soils of Dundee silt loam.

Fumigated rye and hairy vetch residues exhibited sorption trends similar to those of soil (Figure 3). Although chlorimuron ethyl sorption in fumigated and nonfumigated rye and hairy vetch residues was somewhat similar up to 48 h, thereafter sorption was greater in nonfumigated residues. In the same experimental site, microbial activities and populations were several-fold greater in rye and hairy vetch residue than in no cover crop soil (Wagner et al., 1995a). As a result, sorption should have been lower in nonfumigated residues due to a greater microbial degradation/mineralization of chlorimuron ethyl than in fumigated residues. However, less than 0.5% of chlorimuron ethyl applied was mineralized in rye and hairy vetch residue as compared to 14% in no cover crop soil under nonfumigated conditions (Wagner et al., 1995b). Higher sorption in nonfumigated residue may have been due to chlorimuron ethyl bioaccumulation in microbial cells in addition to the actual sorption by plant residue. Bioaccumulation of herbicide metolachlor in microbial cells has been reported (Liu et al., 1989). They observed that about 80% of metolachlor from liquid medium was taken up and accumulated in microbial cells over a period of 7 days. Furthermore, metolachlor absorbed by microbial cells was strongly bound and only 4% was released into deionized water after shaking for 3 h. Under fumigated conditions, chloroform competition for sorption sites may have been negligible as volatile fumigant was removed prior to sorption. Apparently, chlorimuron

ethyl sorption in fumigated residues represents actual sorption by residues in addition to any sorption by microbial biomass killed during fumigation. The equilibrium/kinetic model (eqs 1a–1c), however, was applicable to fumigated and nonfumigated rye and hairy vetch residue. Among differences due to fumigation, values for the instantaneous equilibrium coefficient k_e were larger in the fumigated samples. Also, values for k_{ir} were smaller in fumigated samples. Uncertainty was fairly high in all estimates, particularly for k_f and k_{ir} values.

Chlorimuron Ethyl Desorption. The amount of chlorimuron ethyl desorbed with either CaCl₂ or methanol/(NH₄)₂CO₃ for 1.19 and 12.04 μmol L⁻¹ initial concentrations is shown in Table 3. At a concentration of 1.19 μmol L⁻¹, the amount of CaCl₂-desorbable chlorimuron ethyl in two 24-h desorptions ranged from 54 to 65% in three soils and from 42 to 49% in plant residues. Overall, the amount desorbed by CaCl₂ in the first step was higher than the amount desorbed in the second step (data not shown). Methanol/(NH₄)₂CO₃ was used to maximize desorption following CaCl₂ desorption. Methanol/(NH₄)₂CO₃ solution has been reported to extract 95% of chlorimuron ethyl from soil (Fuesler and Hanafey, 1990). However, not all remaining chlorimuron ethyl was desorbed with methanol/(NH₄)₂CO₃ (Table 3). Undesorbable amounts were higher in soils (14–16%) than in plant residue (2–8%). Total recovery of chlorimuron ethyl ranged from 71 to 105% among soils and plant residues. A similar desorption trend was observed for 12.04 μmol L⁻¹ concentration. We have no explanation for a low total recovery of chlorimuron ethyl from rye residue.

Under field conditions, any plant residue on the soil surface at the time of herbicide application can reduce the amount of herbicide reaching the soil, thereby affecting weed control. The amount of herbicide washoff from plant residue to soil is primarily a function of time and amount of rainfall received after herbicide application. Ghadiri et al. (1984) reported that 50 mm of rainfall in 3 weeks washed off 63% of applied atrazine from wheat stubble to soil. Less than 45% of applied

Table 4. Sorption Parameter Coefficients for Chlorimuron Ethyl As Affected by Age of Cover Crop Residues

cover crop	age of residue, weeks after planting	Freundlich sorption parameter ^a		
		K_f , L kg ⁻¹	N , dimensionless	K_d , L kg ⁻¹
rye	0	3.95 (0.07)	0.95 (0.01)	3.96 (0.10)
	3	3.97 (0.16)	0.99 (0.02)	3.98 (0.16)
	6	4.61 (0.19)	0.93 (0.02)	4.66 (0.22)
	11	6.10 (0.11)	0.86 (0.01)	5.63 (0.32)
hairy vetch	0	6.33 (0.14)	0.92 (0.02)	6.02 (0.14)
	3	7.26 (0.21)	0.95 (0.01)	7.48 (0.26)
	6	8.22 (0.11)	0.97 (0.01)	8.38 (0.14)
	11	9.42 (0.28)	0.93 (0.02)	9.85 (0.36)

^a Values in parentheses are asymptotic standard errors.

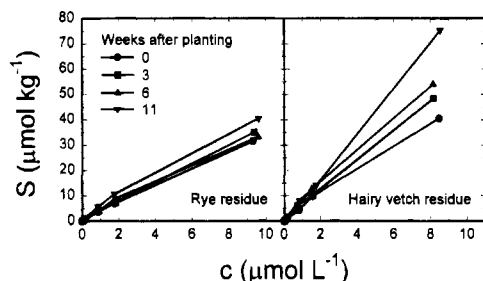


Figure 4. Chlorimuron ethyl sorption isotherms for rye and hairy vetch residue as affected by decomposition.

metribuzin reached the soil from wheat straw after 3 mm of rainfall or more was applied (Banks and Robinson, 1982). In a different study, Banks and Robinson, (1986) reported that only 15–20% of applied acetochlor, alachlor, and metolachlor was washed off from wheat straw by a sprinkler irrigation of 13 mm. Since the amount of chlorimuron ethyl desorbed in two successive steps by CaCl_2 in rye and hairy vetch residue ranged from 42 to 49% of that sorbed, much may be retained by plant residue.

Effect of Age of Plant Residue on Chlorimuron Ethyl Sorption. Sorption isotherms for rye and hairy vetch residues as affected by decomposition are shown in Figure 4. The K_f values progressively increased from 3.95 at planting to 6.10 at 11 weeks after planting in rye residue (Table 4). Chlorimuron ethyl sorption in hairy vetch was higher than in rye; however, similar to rye, K_f values progressively increased, from 6.33 at planting to 9.42 at 11 weeks after planting. The increased sorption of chlorimuron ethyl in both rye and hairy vetch residues with increased decomposition of residue may partly be attributed to alterations in physical and chemical composition. Physical disintegration of residue over time increases the surface area for herbicide sorption compared to fresh plant residue at planting. Dao (1991) reported a 2.5-fold higher metribuzin sorption in ground wheat straw (passed through a 1-mm sieve) than in 2.5-cm lengths of wheat straw, and he attributed increased sorption to increased surface area for herbicide interaction. Degradation of cellulose and lignin–cellulose complexes of cell walls exposes additional binding surfaces for herbicide sorption (Dao, 1991). In a study with metribuzin and *S*-ethylmetribuzin, Dao (1991) observed increased sorption with increased length of field-weathering of wheat straw.

Greater chlorimuron ethyl sorption in hairy vetch than rye residue may have been due to differences in the physical state and chemical composition of plant residues. Hairy vetch residue consisted of thin stems and branches, whereas rye had thicker stems. Consequently, hairy vetch had a greater surface area for herbicide sorption. Differences in chemical composition

include higher N and lignin content in hairy vetch residue and higher cellulose and hemicellulose in rye residue (Wagger, 1989). Higher chlorimuron ethyl sorption in hairy vetch may be attributed to functional groups (amino, amine, amide, phenolic OH, alcoholic OH, and carboxylic) associated with N and lignin content (Stevenson, 1982; Paul and Clark, 1989). In contrast, cellulose and hemicellulose (polymers of glucose in a semicrystalline state and various polymers of hexoses, pentoses, and sometimes uronic acids, respectively; Stevenson, 1982; Paul and Clark, 1989) may not provide as many interaction sites as N and lignin but could provide occluded space for physical entrapments (Dao, 1991).

Conclusions. The results of this study show that chlorimuron ethyl sorption was affected by plant residues. Chlorimuron ethyl sorption was greater in rye and hairy vetch residues than in soil from no cover crop or soils beneath plant residue. Chlorimuron ethyl sorption increased with increased length of decomposition of plant residue, and hairy vetch had greater affinity for chlorimuron ethyl than rye residue. Less than 65% of chlorimuron ethyl was desorbed in two consecutive steps of a 24-h period with CaCl_2 . Under field conditions, any plant residue on the soil surface at the time of chlorimuron ethyl application can intercept and retain herbicide. The amount retained by plant residue may vary, depending upon the degree of residue decomposition and amount of rainfall received. Partial retention of herbicide by plant residues may retard lateral and downward movement of herbicide, thus reducing off-site movement and subsequent adverse impact on the environment. Alternatively, the herbicide retained by plant residues could desorb with time and could provide season-long weed control.

ACKNOWLEDGMENT

We are grateful to DuPont Agricultural Products, Wilmington, DE, for supplying technical and radiolabeled chlorimuron ethyl. We thank Mr. R. Earl Gordon for laboratory assistance.

LITERATURE CITED

- Amacher, M. C.; Selim, H. M.; Iskander, I. K. Kinetics of chromium(IV) and cadmium retention in soils; a nonlinear multireaction model. *Soil Sci. Soc. Am. J.* **1988**, *52*, 398–408.
- Banks, P. A.; Robinson, E. L. The influence of straw mulch on the soil reception and persistence of metribuzin. *Weed Sci.* **1982**, *30*, 164–168.
- Banks, P. A.; Robinson, E. L. Soil reception and activity of acetochlor, alachlor, and metolachlor as affected by wheat (*Triticum aestivum*) straw and irrigation. *Weed Sci.* **1986**, *34*, 607–611.
- Beyer, E. M., Jr.; Duffy, M. J.; Hay, J. V.; Schlueter, D. D. Sulfonylureas. In *Herbicides: Chemistry, Degradation, and*

- Mode of Action*; Kearney, P. C., Kaufman, D. D., Eds.; Dekker: New York, 1988; pp 117-189.
- Blevins, R. L.; Frye, W. W. Conservation tillage: an ecological approach to soil management. *Adv. Agron.* **1993**, *51*, 33-78.
- Boesten, J. J. T. I.; van der Pas, L. J. T.; Smelt, J. H. Field test of a mathematical model for non-equilibrium transport of pesticides in soil. *Pestic. Sci.* **1989**, *25*, 187-203.
- Boyd, S. A.; Xiangcan, J.; Lee, J. Sorption of nonionic organic compounds by corn residues from a no-tillage field. *J. Environ. Qual.* **1990**, *19*, 734-738.
- Brown, B. A.; Hayes, R. M.; Tyler, D. D.; Mueller, T. C. Effect of tillage and cover crop on fluometuron adsorption and degradation under controlled conditions. *Weed Sci.* **1994**, *42*, 629-634.
- Dao, T. H. Field decay of wheat straw and its effects on metribuzin and S-ethyl metribuzin sorption and elution from crop residues. *J. Environ. Qual.* **1991**, *20*, 203-208.
- Fuesler, T. P.; Hanafey, M. K. Effect of moisture on chlorimuron degradation in soil. *Weed Sci.* **1990**, *38*, 256-261.
- Gaston, L. A.; Locke, M. A. Predicting alachlor mobility using batch sorption kinetic data. *Soil Sci.* **1994**, *158*, 345-354.
- Ghadiri, H.; Shea, P. J.; Wicks, G. A. Interception and retention of atrazine by wheat (*Triticum aestivum* L.) stubble. *Weed Sci.* **1984**, *32*, 24-27.
- Goetz, A. J.; Walker, R. H.; Wehtje, G.; Hajek, B. F. Sorption and mobility of chlorimuron in Alabama soils. *Weed Sci.* **1989**, *37*, 428-433.
- Jenkinson, D. S.; Ladd, J. N. Microbial biomass in soil: measurement and turnover. In *Soil Biochemistry*; Paul, E. A., Ladd, J. N., Eds.; Dekker: New York, 1981; pp 415-471.
- Johnson, D. H.; Talbert, R. E. Imazaquin, chlorimuron, and fomesafen may injure rotational vegetables and sunflower (*Helianthus annuus*). *Weed Technol.* **1993**, *7*, 573-577.
- Liebl, R.; Simmons, F. W.; Wax, L. M.; Stoller, E. W. Effect of rye (*Secale cereale*) mulch on weed control and soil moisture in soybean (*Glycine max*). *Weed Technol.* **1992**, *6*, 838-846.
- Liu, S.-Y.; Zheng, Z.; Zhang, R.; Bollag, J.-M. Sorption and metabolism of metolachlor by a bacterial community. *Appl. Environ. Microbiol.* **1989**, *55*, 733-740.
- Locke, M. A.; Zablotowicz, R. M.; Gaston, L. A.; Smeda, R. J. Sorption of herbicides to cover crop residues. *Agronomy Abstracts*; ASA: Madison, WI, 1994; p 50.
- Locke, M. A.; Zablotowicz, R. M.; Gaston, L. A. Fluometuron interactions in crop residue-managed soils. In *Proceedings—Southern Conservation Tillage Conference for Sustainable Agriculture*; Kingery, W. L., Buehring, N., Eds.; Mississippi State University: Mississippi State, MS, 1995; pp 55-58.
- Paul, E. A.; Clark, F. E. *Soil Microbiology and Biochemistry*; Academic Press: New York, 1989; 275 pp.
- Putnam, A. R. Allelopathy: problems and opportunities in weed management. In *Weed Management in Agroecosystems: Ecological Approaches*; Altieri, M. A., Liebman, M., Eds.; CRC Press: Boca Raton, FL, 1988; pp 77-88.
- Reddy, K. N.; Zablotowicz, R. M.; Locke, M. A. Chlorimuron adsorption, desorption, and degradation in soils from conventional tillage and no-tillage systems. *J. Environ. Qual.* **1995**, *24*, 760-767.
- SAS Institute, Inc. *SAS System for Regression*, 2nd ed.; SAS Institute: Cary, NC, 1991.
- Shea, P. J. Chlorsulfuron dissociation and adsorption on selected adsorbents and soils. *Weed Sci.* **1986**, *34*, 474-478.
- Stevenson, F. J. *Humus Chemistry: Genesis, Composition, Reactions*; Wiley: New York, 1982; 443 pp.
- Teasdale, J. R.; Daughtry, C. S. T. Weed suppression by live and desiccated hairy vetch (*Vicia villosa*). *Weed Sci.* **1993**, *41*, 207-212.
- Teasdale, J. R.; Mohler, C. L. Light transmittance, soil temperature, and soil moisture under residue of hairy vetch and rye. *Agron. J.* **1993**, *85*, 673-680.
- Teasdale, J. R.; Beste, C. E.; Potts, W. E. Response of weeds to tillage and cover crop residue. *Weed Sci.* **1991**, *39*, 195-199.
- Wagger, M. G. Time of desiccation effects on plant composition and subsequent nitrogen release from several winter annual cover crops. *Agron. J.* **1989**, *81*, 236-241.
- Wagner, S. C.; Zablotowicz, R. M.; Locke, M. A.; Smeda, R. J.; Bryson, C. T. Influence of herbicide-desiccated cover crops on biological soil quality in the Mississippi Delta. In *Proceedings—Southern Conservation Tillage Conference for Sustainable Agriculture*; Kingery, W. L., Buehring, N., Eds.; Mississippi State University: Mississippi State, MS, 1995a; pp 86-89.
- Wagner, S. C.; Zablotowicz, R. M.; Reddy, K. N.; Locke, M. A.; Smeda, R. J. Chlorimuron mineralization in soils under herbicide-desiccated rye and vetch cover crops. *WSSA Abstracts*; Weed Science Society of America: Champaign, IL, 1995b; p 77.
- Weed Science Society of America. *Herbicide Handbook*; Weed Science Society of America: Champaign, IL, 1994; 352 pp.
- White, R. H.; Worsham, A. D.; Blum, U. Allelopathic potential of legume debris and aqueous extracts. *Weed Sci.* **1989**, *37*, 674-679.

Received for review March 30, 1995. Accepted July 10, 1995.
JF950182U

® Abstract published in *Advance ACS Abstracts*, September 1, 1995.