

Adsorption, Desorption, and Mobility of Chlorsulfuron in Soils

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Laboratory and greenhouse studies were conducted to determine adsorption and movement of chlorsulfuron [2-chloro-*N*-[[4-methoxy-6-methyl-1,3,5-triazin-2-yl]amino]carbonyl]benzenesulfonamide in four soils. Organic carbon of the soils varied from 0.16 to 1.42% and the clay fraction ranged from 3.8 to 31.5%. Freundlich *K* values indicated that organic carbon was the predominant adsorbent for chlorsulfuron in the soils studied. The herbicide showed low affinity for clay. The *R_f* values calculated from soil thin-layer chromatography closely correlated with the mobility of chlorsulfuron leached with 16.8 cm of water over a 14-day period in hand-packed soil columns. In the soil thin-layer chromatography, chlorsulfuron mobility was positively and negatively correlated with pH and organic carbon, respectively. Results indicated that chlorsulfuron could be mobile in low organic matter and nonacidic soils.

Chlorsulfuron [2-chloro-*N*-[[4-methoxy-6-methyl-1,3,5-triazin-2-yl]amino]carbonyl]benzenesulfonamide has shown good selectivity in small grains and is highly active at low rates (10-40 g/ha) against a wide range of broad-leaf weeds (Levitt et al., 1981; Palm et al., 1980). It is applied preemergence or postemergence and is absorbed by both roots and foliage of plants.

Adsorption and desorption are involved in determining the ease by which herbicides move through the soil profile, also their plant availability and microbial degradability, thus persistence. Organic pesticides adsorb on both organic and inorganic surfaces depending upon the chemical properties of the adsorbents and adsorbates involved (Weber, 1972). Basic pesticides were strongly adsorbed by soil organic matter (Weber et al., 1969) and clay minerals (Weber, 1970). Acidic pesticides were adsorbed in moderate amounts on organic matter and in relatively low amounts on clay minerals (Carringer and Weber, 1974). The new herbicide chlorsulfuron is a weak acid (pK_a 3.8) and thus may possibly be expected to behave in a manner similar to that of other acidic pesticides.

The distance a herbicide moves vertically in the soil is also important in determining its efficacy as well as its potential for crop damage and environmental pollution. This movement of soil herbicides in the soil profile is dependent upon soil factors such as pH (Bailey et al., 1968; Tolbert et al., 1965), clay, and organic matter (Tolbert et al., 1965). Since chlorsulfuron is a relatively new herbicide, there is very little information on either its adsorption or mobility in different soil types. It was the purpose of this study to determine the adsorption-desorption and mobility of chlorsulfuron in four soil types.

MATERIALS AND METHODS

Soils. The four soils selected for this study are agricultural soils in Virginia, representing a range of organic matter, clay content, and soil pH levels. They are Acredale silt loam (Typic Ochraqualfs, fine silty, mixed, thermic), Cullen clay loam (Typic Hapludults, clayey, mixed, thermic), Roanoke sandy loam (Typic Ochraqualfs, clayey, mixed, thermic), Kenansville loamy sand (Arenic Hapludults, loamy, siliceous, thermic). Soil samples from the top 15 cm of the Ap horizon were collected, air-dried, and sieved through a 2-mm screen. The composition and physical characteristics of these soils are presented in Table I.

Adsorption and Desorption. The soil adsorption-desorption techniques used for chlorsulfuron were similar to those employed by other workers (Abernathy and Davidson, 1971; Obrigawitch et al., 1981). Commercially formulated chlorsulfuron and ^{14}C -phenyl-labeled chlorsulfuron were combined to obtain initial herbicide solution concentrations of 1, 4, 8, and 12 ppm. Adsorption isotherms were determined by placing 1 g of air-dried soil and 10 mL of each concentration of [^{14}C]chlorsulfuron (sp act. 6.0 $\mu\text{Ci}/\text{mg}$) into weighed 50-mL sealed stainless-steel centrifuge tubes. Each treatment was replicated three times with each soil. The samples were shaken on a rotator at 24-27 °C for 24 h, a period that preliminary studies showed was sufficient to attain equilibrium. Afterward, samples were centrifuged at 1200 rpm for 20 min. A 0.5-mL aliquot was removed from each tube, placed in 10 mL of scintillation fluid, and counted with a liquid scintillation counter. The scintillation fluid consisted of 120 g of naphthalene, 4 g of 2,5-diphenyloxazole (PPO), and 50 mg of 1,4-bis(5-phenyloxazol-2-yl)benzene (POPOP) made to 1:1 volume with *p*-dioxane. Quenching was checked by the channel ratio method, with no sample requiring correction for quenching. The resulting radioactivity in solution was compared to 0.5-mL aliquots of the concentration standards. Differences between amounts of ^{14}C found in standard solutions and the supernatant of samples were considered to be the amounts adsorbed.

Desorption was determined on the same samples used for adsorption. Desorption was achieved by removing a known quantity of the supernatant from the centrifuged samples and then replacing the removed liquid with herbicide-free 0.01 N CaCl_2 solution. Two successive desorption extractions were made. Each time, tubes and contents were shaken and centrifuged as described above and a 0.5-mL aliquot was removed and counted at the end of a 24-h equilibration period. Two desorptions were conducted. Adsorption was described by the Freundlich equation

$$X = KC^{1/n}$$

where X = adsorbed amount ($\mu\text{g}/\text{g}$), K and n = constants, and C = equilibrium concentration ($\mu\text{g}/\text{mL}$).

The logarithmic form of the above equation was fitted by the method of least squares to the set of experimental data. Constants K and n were calculated, and linear regression analysis was performed to determine the degree of fit of the Freundlich to the observed data points.

Soil Thin-Layer Chromatography. An autoradiographic procedure described by Helling (1971) was followed. A 3- μL droplet of [^{14}C]chlorsulfuron (0.06 μCi) was spotted 2 cm from the bottom of 15 cm \times 20 cm glass

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Table I. Chemical and Physical Characteristics of the Four Soils Studied

soil	particle size distributn, %			pH	OC, %	CEC, mequiv/100 g	bulk density, g/cm ³
	sand	silt	clay				
Acredale silt loam	26.4	50.8	22.8	4.6	1.42	234.0	0.93
Cullen clay loam	41.4	27.1	31.5	5.6	0.24	13.9	1.12
Roanoke sandy loam	55.2	35.1	9.7	6.4	0.35	10.6	1.25
Kenansville loamy sand	83.7	12.5	3.8	6.9	0.16	3.2	1.48

Table II. Freundlich Constants of Chlorosulfuron in the Four Soils

soil	K	1/n
Acredale silt loam	2.4	0.87
Cullen clay loam	1.1	0.75
Roanoke sandy loam	2.0	0.71
Kenansville loamy sand	1.0	0.78

plates. The lower 5 mm of each plate was immersed in 0.01 N CaCl₂ solution and allowed to develop to a distance of approximately 12 cm. Each soil plate was then air-dried for 48 h and exposed to X-ray film. Four replications were made for each soil, with R_f values being calculated for each treatment.

Soil Column Leaching Study. Soil columns, 35 mm long, of polyvinyl chloride (PVC) pipe (inside diameter 9.7 cm) were prepared in the same manner as described by Weber and Whitacre (1982). Silicone sealer was applied to a cup that was later attached to the bottom of each column. A bead of silicone sealer was applied at 5-cm increments to the inside of the columns to prevent movement of water and chemical down the side walls. Silicone sealer was applied to each of the column halves and the halves were joined and taped together. A hole was drilled in the cupped end of each column and fitted with a tubing covered with nylon mesh. Acredale silt loam (2188 g/column), Cullen clay loam (2628 g/column), Roanoke sandy loam (2932 g/column), and Kenansville loamy sand (3478 g/column) were packed in the columns after quartz sand had been first added to fill the bottom cup. Each soil column was saturated by putting it into a tank and increasing the volume of water in the tank every 24 h, for 1 week, until it topped the columns. Then, each column was allowed to drain free for a period of 24 h. Chlorosulfuron, equivalent to 40 g/ha, was added to the top of each column. Water with 0.01 N CaCl₂ was applied dropwise from burets supported over each column, 1.2 cm/day applied for 2 weeks. After the 2-week leaching period, the columns were allowed to drain overnight. The columns were then split vertically, and mustard (*Brassica kaber* L.) seeds were planted in the columns in each 5-cm-depth increment. After 3 weeks, the shoot growth was harvested and the fresh weight was recorded. Each soil was replicated three times, and the experiment was repeated twice.

RESULTS AND DISCUSSION

Soil Adsorption-Desorption Study. The greatest amount of chlorsulfuron was adsorbed by Acredale silt loam soil followed by Roanoke sandy loam, Cullen clay loam, and Kenansville loamy sand soils (Table II). Correlation coefficient (r) values were calculated for percent organic carbon and clay vs. the Freundlich adsorption constant (k) for the four soils. Percent organic carbon vs. k resulted in $r = 0.87$, and percent clay vs. k resulted in $r = 0.09$. These correlation coefficients showed that organic carbon is more important than the clay fraction for chlorsulfuron adsorption. Chlorsulfuron is a weak acid with pK_a 3.8. This moderate affinity to organic matter and the relatively low adsorption to clay are similar to results reported for other acidic pesticides (Carringer and Weber,

Table III. Freundlich Equation Parameters for Desorption of Chlorsulfuron

soil	values	init chlorsulfuron concn, µg/mL			
		1	4	8	12
Acredale silt loam	K	0.31	0.81	1.57	1.93
	1/n	0.38	0.47	0.41	0.41
Cullen clay loam	K	0.23	0.61	0.71	1.09
	1/n	0.31	0.35	0.40	0.40
Roanoke sandy loam	K	0.30	0.98	1.58	1.41
	1/n	0.31	0.34	0.34	0.34
Kenansville loamy sand	K	0.41	0.44	0.57	0.84
	1/n	0.34	0.36	0.36	0.37

Table IV. Movement of [¹⁴C]Chlorsulfuron in Four Soils

soil	R_f value ^a
Acredale silt loam	0.36 a
Cullen clay loam	0.74 b
Roanoke sandy loam	0.93 c
Kenansville loamy sand	0.94 c

^a Values followed by the same letter are not significantly different at the 5% level according to Duncan's multiple-range test.

1974). A direct implication, therefore, was that chlorsulfuron applied to soil with low organic matter might be susceptible to redistribution within the soil profile. In another study (Mersie and Foy, 1985), organic matter was highly correlated with chlorsulfuron phytotoxicity while no significant relationship was observed between clay content and chlorsulfuron toxicity. The higher adsorption of chlorsulfuron to organic carbon observed in this study may explain the above phytotoxic response. All 1/n values were less than 1.0, which is the result of decreased adsorption as the adsorptive sites became occupied. The resultant adsorption isotherms, if plotted, would thus be of the L-type. This is similar to the results obtained by Kozak and Weber (1983) and by Grover (1975) for phenylurea herbicides.

The desorption data can also be described by the Freundlich equation as shown by Van Genuchten et al. (1974). The Freundlich parameters for each initial herbicide concentration and soil type are given in Table III. The desorption distribution coefficients were not constant for a given soil type but increased as the adsorbed herbicide concentration prior to desorption increased. The 1/n value was also a function of the maximum quantity of herbicide adsorbed prior to desorption. The desorption k values for Acredale silt loam and Roanoke sandy loam were consistently higher than that of Kenansville loamy sand and Cullen clay loam at the three higher concentrations. This indicates that chlorsulfuron might not be tightly retained by soils with low organic matter contents.

Soil Thin-Layer Chromatography. The difference in the mobility of chlorsulfuron in the four soil types is apparent from the autoradiogram (Figure 1). In Kenansville loamy sand soil, chlorsulfuron migrated with the water front, whereas in the heavier textured soils (Cullen clay loam and Roanoke sandy loam) chlorsulfuron exhibited less movement from the origin. The R_f values from the soil thin-layer chromatography (Table IV) showed that chlorsulfuron moved 2.6 times greater distance in Ken-

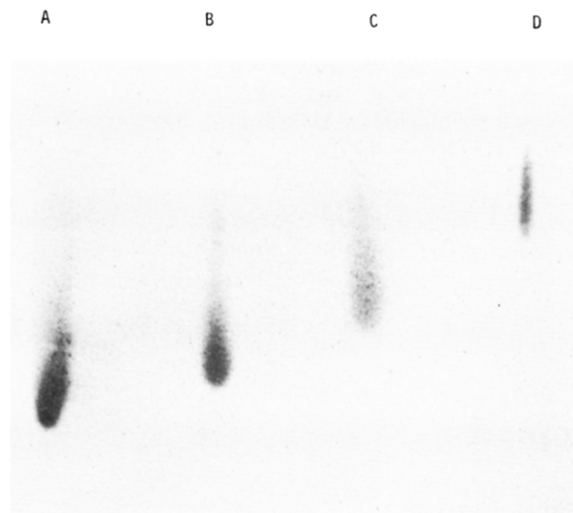


Figure 1. Autoradiogram showing the movement of chlorsulfuron on four soil thin-layer chromatograms: (A) Acredale silt loam; (B) Cullen clay loam; (C) Roanoke sandy loam; (D) Kenansville loamy sand.

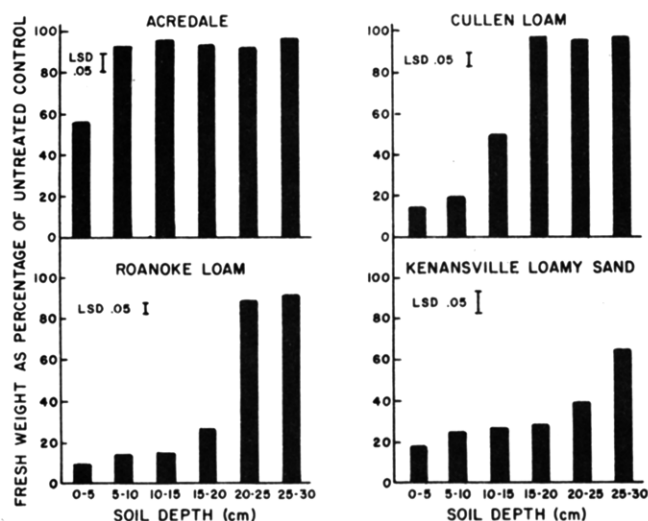


Figure 2. Mustard bioassay of chlorsulfuron in soil column sections.

ansville loamy sand than in Acredale silt loam soil. Regression analysis of R_f values and pH, organic carbon, and clay contents were performed. R_f values were highly correlated with pH ($r = 0.97$) and organic carbon ($r = 0.93$), whereas no such strong relationship was observed with clay content ($r = -0.61$). The high positive correlation between pH and R_f values indicates that the herbicide could be more mobile in neutral and alkaline than in acidic soils.

Soil Column Leaching Study. The presence of herbicide in segments of the soil columns was indicated by reduced growth of mustard compared with mustard in segments from untreated columns (Figure 2). The distribution of chlorsulfuron in the four soil types is also shown by mustard bioassay in the split soil leaching columns (Figure 3). In Acredale silt loam soil, chlorsulfuron remained in the upper 5-cm segment. Chlorsulfuron distribution in Kenansville loamy sand soil was relatively uniform throughout the columns. The movement of chlorsulfuron in the other two soils was intermediate between these two extremes. The depths to which chlorsulfuron moved in the four soil columns were in the same order as the R_f values in Table IV. The least movement of chlorsulfuron observed in the Acredale silt loam soil would be anticipated from the adsorption values. But,



Figure 3. Mustard bioassay showing the distribution of chlorsulfuron in split soil leaching columns of the four soil types. From left to right: Acredale silt loam, Cullen clay loam, Roanoke sandy loam and Kenansville loamy sand. Front is the top of the column while the far end is the bottom.

adsorption values did not substantiate the lower mobility in the less adsorptive Cullen clay loam soil compared to that of the Roanoke sandy loam soil.

The relationship between leachability and adsorption is not fully understood, but mass flow and diffusion have been reported as mechanisms by which pesticides move in soil (Letey, 1974). Since diffusion occurs slowly over several months (Lavy, 1970), mass flow is the mechanism primarily responsible for bulk pesticide transport. During the course of this study it was observed that water flow through the Cullen clay loam soil was very slow, and it has been pointed out by Kohnke (1968) that water conductivity is least in fine-textured soils and greatest in coarse-textured soils under saturated-flow conditions. During this slow drainage in Cullen clay loam soil, the rate of uptake of chlorsulfuron by mustard roots might have been reduced as a result of low concentration. Furthermore, chlorsulfuron is more soluble in alkaline (27 900 ppm at pH 7) than in acidic solutions (300 ppm at pH 5). Both Acredale silt loam and Cullen clay loam have pH lower than 6; this acidic condition reduces the solubility of chlorsulfuron, thereby decreasing its entrance into solution as well as its availability to mustard. The results indicate that, in addition to adsorption, lower net movement of soil moisture and low pH could reduce the mobility of chlorsulfuron in soil. The laboratory and greenhouse studies demonstrated that chlorsulfuron was not strongly adsorbed to soil colloids and was mobile in soils containing low organic matter. As observed from the desorption data, chlorsulfuron should be highly available for plant uptake. On soils with low organic matter, coarse texture, and high pH, chlorsulfuron could be leached into or below the weed root zone, resulting in a loss of herbicidal efficacy.

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LITERATURE CITED

- Abernathy, J. R.; Davidson, J. R. *Weed Sci.* 1971, 19, 517.
 Bailey, G. W.; White, J. L.; Rothberg, T. *Soil Sci. Soc. Am. Proc.* 1968, 32, 222.
 Carringer, R. D.; Weber, J. B. *Proc. South. Weed Sci. Soc.* 1974, 27, 332.
 Grover, R. *Can. J. Soil Sci.* 1975, 55, 127.
 Helling, C. S. *Soil Sci. Soc. Am. Proc.* 1971, 35, 743.
 Kohnke, H. "Soil Physics"; McGraw-Hill: New York, 1968; p 58.
 Kozak, J.; Weber, J. B. *Weed Sci.* 1983, 31, 368.
 Lavy, T. L. *Weed Sci.* 1970, 18, 53.
 Letey, J.; Farmer, W. J. In "Pesticides in Soil and Water"; Guenzi, W. D., Ed.; Soil Science Society of America Inc.: Madison, WI, 1974; pp 67-69.

- Levitt, G.; Ploeg, H. L.; Weigl, C. R., Jr.; Fitzgerald, D. J. *J. Agric. Food Chem.* 1981, 29, 416.
- Mersie, W.; Foy, C. L. *Weed Sci.* 1985, 33, 564.
- Murray, D. S.; Santelmann, P. W.; Davidson, J. M. *J. Agric. Food Chem.* 1975, 23, 578.
- Obrigawitch, T.; Hons, F. M.; Abernathy, J. R.; Gibson, J. R. *Weed Sci.* 1981, 29, 332.
- Palm, H. L.; Riggleman, J. D.; Allison, D. A. *Proc. Br. Crop. Prot. Conf.-Weeds.* 1980, 1, 1.
- Tolbert, R. E.; Fletchall, O. H. *Weeds* 1965, 13, 46.
- Van Genuchten, M. T.; Davidson, J. M.; Wierenga, P. J. *Soil Sci. Soc. Am. Proc.* 1974, 38, 29.
- Weber, J. B. *Residue Rev.* 1970, 32, 93.
- Weber, J. B. *Adv. Chem. Ser.* 1972, No. 111, 55.
- Weber, J. B.; Whitacre, D. M. *Weed Sci.* 1982, 30, 579.
- Weber, J. B.; Weed, S. B.; Ward, T. M. *Weed Sci.* 1969, 17, 417.

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Loss of MCPA from Simulated Spray Droplets

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MCPA [(4-chloro-2-methylphenoxy)acetic acid], as its dimethylamine (DMA) salt, dissipated from individual microliter droplets of spray solution suspended in sunlight and moving air in a wind tunnel with a half-life of 3.9 h, compared with 4.6 h for MCPA/DMA deposits on glass surfaces. Photolysis was the major dissipative force in both cases, with MCPA volatilization playing a minor role. Identification and quantitation of six photoproducts revealed very similar composition of both residues, although the principal product, 4-chloro-*o*-cresol, volatilized rapidly from the droplets as shown by analysis of the effluent air. This technique confirms that MCPA loss from small droplets such as spray or rain entails conversion to the chlorocresol and subsequent volatilization; conventional methods provide the same conclusion.

The majority of pesticides are applied as sprays, either by aerial means or by ground-rig, and enter the environment in the form of small droplets. The diameters of these droplets vary from below 10 μm to over 1 mm, depending on the type of application, the formulation viscosity, and numerous other physical factors (Matthews, 1979). The smaller droplets are prone to "drift" from the intended application site, a serious problem with many pesticides including phenoxy herbicides such as MCPA [(4-chloro-2-methylphenoxy)acetic acid] (Crosby et al., 1981).

The environmental movement and transformations of MCPA have been studied in both the laboratory and the field (Soderquist and Crosby, 1975; Loos, 1975; Crosby and Bowers, 1985), but no previous investigation of the breakdown of any pesticide within aqueous spray droplets has been reported. Indeed, very little has been established regarding the chemical influences imposed upon drifting droplets, previous investigations having centered around the physical changes occurring as droplets evaporate.

Whytlaw-Gray and Patterson (1932) studied the evaporation of very small (1- μm radius) droplets of several pure substances and showed that the decrease in surface area was linear with time. For droplets containing a mixture of solutes, however, the rate of surface area decrease slowed toward the end of the evaporation, as the concentration of the less volatile component increased. Ranz and Marshall (1952) and Charlesworth and Marshall (1960) reported similar results for droplets containing dissolved solids in moving air. Langstroth et al. (1950) examined the evaporation of 1-mm-diameter droplets of nine pure substances of various volatilities, supported from a fine thermocouple in still air, and showed that their surface

temperature was lower than their internal temperature. They also noted that convection occurred within the droplets, even in still air.

The chemical microenvironment of an airborne droplet appears to be unique: a maximum surface-to-volume ratio, maximum exposure to oxygen and other gaseous reagents, and full exposure to direct sunlight. The possibility exists that the fate of agricultural chemicals in spray drift, or of any chemical in fog or raindrops, could be markedly different from that observed in bulk solutions or surface coatings. The purpose of this investigation was to determine the fate of MCPA in individual microliter "spray droplets" and compare it with that observed in bulk solutions and solid deposits.

EXPERIMENTAL SECTION

Chemicals. MCPA dimethylamine salt was obtained as a 589 g/L (4 lb of MCPA/gallon) commercial aqueous formulation (Dow Chemical Co.). This solution was diluted 1:40 with water to obtain the recommended field spray concentration of 14.7 mg/mL (0.10 lb of MCPA/gallon). Analysis of the starting material showed it also to contain traces of two contaminants, (2-methylphenoxy)acetic acid and (2,4-dichloro-6-methylphenoxy)acetic acid (Crosby and Bowers, 1985).

Amberlite XAD-4 macroreticular resin was cleaned before use by wetting it with HPLC grade methanol, washing with 1 N NaOH followed by 1 N HCl, and then extracting in a Soxhlet extractor with methanol for 2 h, acetonitrile for 2 h, and finally diethyl ether overnight.

4-Chloro-*o*-cresol (III), 5-chlorosalicylaldehyde (IV), and *o*-cresol (V) (Aldrich Chemical) were used without further purification.

(4-Chloro-2-methylphenoxy)-*N,N*-dimethylacetamide (VII). One gram of MCPA was refluxed for 3 h with 4 mL of thionyl chloride, the mixture evaporated to

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