SELECTIVITY AND SOIL BEHAVIOR OF CHLORSULFURON

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(ABSTRACT)

Response of barley (Hordeum vulgare L.) and wheat (Triticum aestivum L.) to root-applied chlorsulfuron (2-chloro N-[[(4-methoxy-6-methyl-1,3,5-triazin-2-yl)amino]carbonyl] benzenesulfonamide), a herbicide for use in small grains, was investigated. The results showed that, although wheat roots take up more chlorsulfuron than barley roots, barley was less tolerant to chlorsulfuron and chlorsulfuron was more mobile in barley. This study indicated that difference in uptake or translocation cannot explain the differential response of the two species to root-applied chlorsulfuron.

In an interaction study, significant chlorsulfuron antagonism on ryegrass (Lolium multiflorum Lam.) control by diclofop {(±)[-2-[4-(2,4-dichlorophenoxy)phenoxy) propanoic acid} was observed. Greenhouse experiments showed that the tolerance of corn (Zea mays L.) to chlorsulfuron and metsulfuron (2-[[[[(4-methoxy-6-methyl-1,3,5-triazin--2-yl)amino]carbonyl]amino] sulfonyl]benzoic acid) was greatly increased by seed dressing with the herbicide safener NA (1,8-naphthalic anhydride).

The soil behavior of chlorsulfuron was studied in the field, greenhouse and laboratory. In the field, corn adequately tolerated soil residues present 10 months following postemergence application of chlorsulfuron at 10 to 120 g/ha. However, at the same site and rates, residues from chlorsulfuron injured corn when sampled 2 months after application. In laboratory studies chlorsulfuron was moderately adsorbed by organic matter but showed low affinity to clay. 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 matter, respectively. The results indicated that chlorsulfuron could be mobile in low organic matter and non-acidic soils. The relationship of chlorsulfuron phytotoxicity to soil physical and chemical properties was also evaluated. Organic matter was inversely related to chlorsulfuron phytotoxicity while no such relationship to clay content was observed. The adsorption of chlorsulfuron decreased with increasing soil pH whereas desorption was greater at alkaline pH.

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TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

I. LITERATURE REVIEW

The herbicide chlorsulfuron

Chlorsulfuron (2-chloro-N-[[(4-methoxy-6-methyl-1,3,5, -triazin-2-yl] amino]carbonyl]benzenesulfonamide) belongs to a family of highly active compounds called sulfonylureas. The sulfonylureas were first reported to be highly herbicidal by Finnerty et al. (12) and were synthesized by E. I. du Pont de Nemours & Co., Inc. in the United States. The physicochemical properties and structure of chlorsulfuron are given on Table 1, page 2 and Figure 1, page 3 respectively.

Chlorsulfuron which is a forerunner of the sulfonylureas is now widely used as a 75% dry flowable granular formulation to be mixed in water containing a non-ionic surfactant. It has shown excellent crop selectivity in small grains such as wheat (*Triticum aestivum* L.), barley (*Hordeum vulgare* L.), rye (*Secale cereale* L.) and oat (*Avena sativa* L.) while controlling many broadleaf weeds and suppressing some annual grasses. An important feature of this compound is its high herbicidal activity at extremely low application rates. Recommended rates for weed control in wheat and barley are between 10 and 40 g/ha.

Although chlorsulfuron is extremely active as a herbicide, it has low mammalian toxicity. The acute oral LD_{50} for fasted male rats is 5545 mg/kg and for fasted female rats 6293 mg/kg.

Table 1. Physicochemical properties of chlorsulfuron.

Physical form	odorless, white crystalline solid.
Melting point	174-178°C
Decomposition temperature	192°C
Vapor pressure	4.6×10^{6} mm Hg at 25°C
Photodecomposition	stable to artificial sunlight as a dry film on glass plate. In one month, it undergoes 30% decomposition on dry plant tissue and 15% on dry soil.
Hydrolysis	Decomposition occurs by hydrolysis with an average half-life of 4 to 8 weeks in distilled water.

Solvent	Temperature (°C)	Solubility (g/100 ml)
Acetone	22	5.7
Hexane	22	<0.001
Methanol	22	1.4
Methylene chloride	22	10.2
Water (distilled)	25	100 to 125 ppm

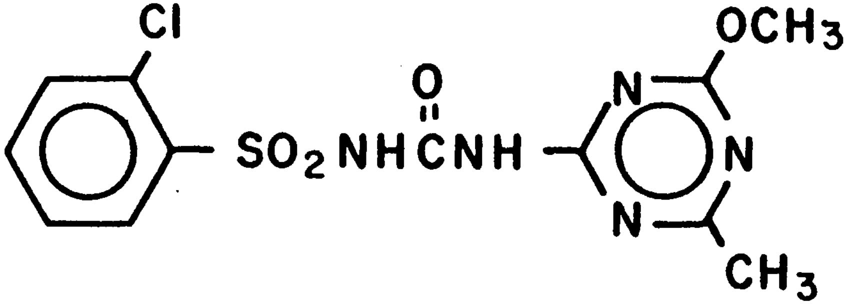

Fig. 1. Chemical structure of chlorsulfuron.

Chlorsulfuron as a postemergence herbicide

Introductory papers by Finnerty et al. (12) and Miller and Nalewaja (26) gave reviews of field research with chlorsulfuron for the North Central Plains and North Dakota regions, respectively. Both papers reported excellent crop tolerance and good broadleaf weed control by chlorsulfuron at rates ranging from 15 to 60 g/ha.

Levitt et al. (20) summarized initial worldwide developmental efforts whereas Palm et al. (31) gave an extensive global review on chlorsulfuron efficacy. In the spring cereal belt of Canada and North Central United States, 20 to 30 g/ha of chlorsulfuron alone as a postemergence treatment was found adequate to control the typical spectrum of broadleaf weeds which commonly includes the genera _Galium_, _Galeopsis_, _Chenopodium_, _Polygonum_, _Stellaria_, _Kochia_, _Amaranthus_, _Spergula_, _Matricaria_ and members of the Cruciferae family. In the winter cereal belt in North America and Australia, similar rates also controlled _Helianthus_, _Erodium_, _Lithospermum_, _Lamium_, _Oxalis_ and _Emex_ species. Under European conditions chlorsulfuron has demonstrated excellent control of many broadleaf weeds in wheat and barley.

Chlorsulfuron, apart from its unusually high activity at low rates, exhibits many unique herbicidal properties. As reported by Palm et al. (31) chlorsulfuron has a remarkably flat curve in response to rates. In field research, experimental rates have been reduced from 70 to 280 g/ha to 5 to 60 g/ha with very little loss of activity on many broadleaf weeds. Miller and Nalewaja (26) also reported that wild mustard (_Sinapis arvensis_ L.), redroot pigweed (_Amaranthus retroflexus_ L.) and wild buckwheat

(*Polygonum convolvulus* L.) control with chlorsulfuron was similar at 35 and 70 g/ha.

Chlorsulfuron has also demonstrated control of "hormone tolerant" weed species such as catchweed bedstraw (*Galium aparine* L.), common chickweed (*Stellaria media* L.) mayweed (*Anthemis cotula* L.), prickly lettuce (*Lactuca serriola* L.) field pennycress (*Thlaspi arvense* L.), henbit (*Lamium amplexicaule* L.), and Bermuda buttercup (*Oxalis pes-caprae* L.) (28, 38, 39).

Chlorsulfuron is also unique in its capacity in providing selective season-long control of generally herbicide tolerant species like Canada thistle (*Cirsium arvense* L.) (1, 2, 7, 17, 21). Alley and Whitson (2) reported that chlorsulfuron at 34 g/ha reduced Canada thistle shoot regrowth by 94% two years following treatments. Rates higher than 34 g/ha resulted in 100% shoot reduction. Messersmith and Lym (21) obtained Canada thistle control for 12 to 15 months from chlorsulfuron applied at 275 to 560 g/ha. Chlorsulfuron also controls Canada thistle at several growth stages. Chlorsulfuron treatments (34 to 275 g/ha) at the rosette, prebud and flower stages provided greater than 90% control in the following fall (17). Donald (7) evaluated the effect of 67 g/ha of chlorsulfuron on Canada thistle root regrowth in greenhouse trials. He found that cuttings taken from controls formed more secondary shoots than did chlorsulfuron-treated plants 2 weeks following treatments. Foliar treatments or a combination of foliar and soil treatment inhibited root accumulation and secondary shoot growth equally 1 month following treatment relative to harvested controls.

Chlorsulfuron as a postemergense treatment provides flexibility both in rates and timing of application. Schaat et al. (38) evaluated fall and spring applications of chlorsulfuron in winter wheat. The herbicide provided good (85%) to excellent (100%) control of many broadleaf weeds at both times of application. Russell (36) also reported that either fall or spring applications of chlorsulfuron were effective against corn chamomile (*Anthemis arvensis* L.).

Several researchers have evaluated combinations of chlorsulfuron with other broadleaf and grass selective herbicides. Schaat et al. (37, 40, 41) reported 85% control of catchweed bedstraw from chlorsulfuron + bromoxynil (3,5-dibromo-4-hydroxybenzonitrile) (17 + 280 g/ha or 5.8 + 280 g/ha). Howard and Whitesides (18) evaluated the interaction between chlorsulfuron and bromoxynil, dicamba (3,6-dichloro-2-methoxybenzoic acid) and MCPA (4-chloro-2-methylphenoxy)acetic acid) on mayweed in the field and greenhouse. They found antagonism between chlorsulfuron and dicamba at three different rates. Antagonism between chlorsulfuron and wild oat herbicides have been reported by O'Sullivan and Kirkland (30). Mixtures of chlorsulfuron with difenzoquat (1,2-dimethyl-3,5-diphenyl-1H -pyrazolium) caused a 0 to 19% reduction and mixtures with flamprop (N-benzoyl-N-(3-chloro-4-fluorophenyl)-DL-alanine) a two to three fold reduction in the control of wild oats. In field experiments chlorsulfuron mixed with diclofop [(±)2-[4-(2,4-dichlorophenoxy)phenoxy]propanoic acid] caused a 4 to 35% reduction in control of wild oat.

Tolerance of wheat, barley and rye is excellent to postemergence applied chlorsulfuron. There was no differential yield response to postemergence chlorsulfuron treatments among spring wheat cultivars, nor with four barley, three oat and three durum wheat cultivars in Minnesota (13). Whiteside and Nagle (46) evaluated the tolerance of three winter wheat varieties to chlorsulfuron (18 g/ha) against the "standard" wheat herbicides 2,4-D [(2,4-dichlorophenoxy)acetic acid] amine (0.84 kg/ha), MCPA amine (0.84 kg/ha) and bromoxynil (0.43 kg/ha). There were no visible symptoms and no yield differences among treatments in any variety.

The tolerance of winter wheat (variety Daws) to chlorsulfuron and other broadleaf weed herbicides was evaluated at intervals from tillering through the soft-dough stages of growth. In almost every case, application of the other herbicides after the node stage resulted in a reduction of yield. Wheat treated with chlorsulfuron, however, was not greatly affected at any growth stage (47). As pointed out by Brewster and Appleby (4) the high tolerance of wheat to chlorsulfuron is unique among herbicides used in this crop. A treatment of 560 g/ha chlorsulfuron, which did not suppress wheat yield, is 21-fold higher than the maximum labeled rate. No other wheat herbicide currently in use has shown this kind of safety margin.

Chlorsulfuron for residual weed control

Chlorsulfuron can also be applied as preplant soil incorporated or preemergence in wheat. Behrens and Elakkad (3) evaluated preemergence applications of chlorsulfuron at 150 and 280 g/ha for broadleaf weed and foxtail (Setaria spp.) control. The herbicide controlled over 85% of the broadleaf weeds at 150 g/ha and 95% at 280 g/ha. Common ragweed (Ambrosia artemisiifolia L.) and eastern black nightshade (Solanum ptycanthum

Dun.) were not controlled. Foxtail control was greater than 80% with both rates. No damage was observed on the spring wheat or oats.

Nalewaja and Miller (27) evaluated preplant and preemergence applications of chlorsulfuron for foxtail control. Over 98% of foxtail control was observed with 70 g/ha for chlorsulfuron alone or in combination with trifluralin [2,2-dinitro-N,N-dipropyl-4-(trifluoromethyl)benzenamine] at 840 g/ha with either one or two incorporations. Similar control was observed with preemergence applications of chlorsulfuron at 70 g/ha.

O'Sullivan (29) evaluated preplant incorporated (PPI), preemergence incorporated (PEI), and soil surface application (PE) of chlorsulfuron for broadleaf weed control. The PPI treatments were more effective for control of tartary buckwheat (Fagopyron tataricum (L.) Gaertn.) than the PEI or PE methods of application. Chlorsulfuron also provided weed control 8 months after application 20 g/ha in the greenhouse and 12 months after application at 40 g/ha in the field.

Chlorsulfuron has also been evaluated for use in fallow systems (22, 23, 24, 25). Miller (22) evaluated preemergence application of 70 and 140 g/ha in spring 1979 and preemergence applications of 140 and 280 g/ha in 1978 in small grain stubble at three locations in North Dakota. These treatments controlled yellow foxtail (Setaria lutescens (Weigel) Hubb.), green foxtail (Setaria viridis(L.) Beauv.), wild mustard and kochia (Kochia scoparia (L.) Schrad.).

Stahlman (44) applied 140 g/ha of chlorsulfuron to wheat stubble to evaluate weed control during the fallow period in a wheat-fallow-wheat rotation. During 1980, the herbicide controlled Russian thistle (Salsola kali L.), kochia and pigweed (Amaranthus spp.). Miller (23) also made fall and spring applications of chlorsulfuron at 60 and 120 g/ha and obtained greater than 90% vegetation control.

The above cited works and others have demonstrated that chlorsulfuron controls weeds in many situations when applied to the soil and has adequate persistence in fallow cropping systems. However, as crop rotation is a common practice in many diversified farming areas, chlorsulfuron residues in soil are of concern. Because of its high activity at very low rates, residues of chlorsulfuron might injure any susceptible crop planted in these areas.

Brewster and Appleby (4) reported that chlorsulfuron at 35 g/ha reduced foliage weight of sugarbeet (Beta vulgaris L.) seeded 26 months after application. Phytotoxic levels of the herbicide were detected 10 to 20 cm deep 168 days after application to silt loam soil. In Idaho, Thill et al. (45) showed that several crops, except spring wheat were injured one year following a 10 g/ha application. Evans and Gunnel (11) in Utah reported that barley stands were reduced 20 to 80% when seeded one year after postemergence application of chlorsulfuron at 140 g/ha. Norris et al. (28) in California found several crops to be sensitive to chlorsulfuron residue.

Peterson and Arnold (32) planted flax (Linum usitatissimum L.), sunflower (Helianthus annuus L.), corn (Zea mays L.), soybean (Glycine max (L.) Merr.) and sorghum (Sorghum bicolor (L.) Moench.) in the spring of 1982 on plots at two sites which had been treated postemergence with chlorsulfuron at 17 and 68 g/ha in the spring of 1981. Assessed in June 1982, crop phytotoxicity at one site on most crops at both rates of chlorsulfuron was severe (over 50% reduction in plant dry weight). At the other site, crop phytotoxicity was low, with no plant dry weight reduction. The major differences between the sites were soil pH and organic matter.

Dyer and Fay (9) applied chlorsulfuron at 35, 70, and 140 g/ha in October 1981 and spring wheat, barley, sunflower, safflower (*Carthamus tinctorius* L.), corn, and sugarbeet were planted in the spring of 1982. The dry weights of all the crops except spring wheat and barley were significantly reduced by chlorsulfuron residue from all rates. Dyer and Fay (10) also examined the effect of chlorsulfuron (35, 70, and 140 g/ha) soil residue on 11 crops, 36 months after herbicide application. Dry weights of sugarbeet, safflower, sunflower, corn, lentil (*Lens culinaris* Medic.), and flax were reduced by all rates of application of chlorsulfuron. Dyer and Fay (10) pointed out that degradation of chlorsulfuron is a limiting factor to the planting of rotational crops in the highly alkaline soils of Montana. It appears that chlorsulfuron is persistent in high pH soils.

Chlorsulfuron reportedly has a half-life in the soil of 1 to 2 months (31). Degradation is by hydrolysis to inactive compounds. The rate of breakdown is influenced by soil temperature, with no degradation occurring at temperatures below 5°C. Hydrolysis is also more rapid at low pH.

Basis of selectivity and mode of action of chlorsulfuron

Sweetser et al. (42) studied several factors that contribute to the tolerance of plants to chlorsulfuron. They found that selectivity in cereal crops such as wheat and barley and tolerant grass weeds such as wild oats (<u>Avena fatua</u> L.) was due to the plant's ability to metabolize chlorsulfuron rapidly to a herbicidally inactive product. The chlorsulfuron metabolite was characterized as the O-glycoside of chlorsulfuron, where the phenyl ring had undergone hydroxylation followed by conjugation with a carbohydrate moiety. In contrast sensitive broad plants showed little or no metabolism of the herbicide.

In addition to grasses, some broadleaf plants including flax and black nightshade (<u>Solanum</u> <u>nigrum</u> L.) show tolerance to chlorsulfuron. Hageman and Behrens (15) have reported that Eastern black nightshade is especially tolerant to chlorsulfuron and that metabolism may be the factor responsible. They found that factors such as spray retention, penetration and translocation did not explain the large difference in tolerance between nightshade and velvetleaf (<u>Abutilon theophrasti</u> Medic.).

Hutchison et al. (19) also studied the metabolism of chlorsulfuron in flax and black nightshade. They reported metabolism to be the basis of selectivity to chlorsulfuron for tolerant broadleaf plants as in grasses. However, in the case of grasses, metabolism occurred on the phenyl ring (42) whereas in broadleaved species it occurred on the heterocyclic portion. They showed that broadleave species also tolerate chlorsulfuron by detoxifying the parent compound. Thus both broadleaf and grass species appear to use similar detoxifying mechanisms, but the reactions take place on different portions of the molecule.

Chlorsulfuron is absorbed by both roots and foliage of plants and is readily translocated. Death of treated plants is generally slow and is accompanied by chlorosis, necrosis, terminal bud death, vein discoloration and complete inhibition of plant growth. Mode of action studies by Ray (33) have indicated that chlorsulfuron is an inhibitor of plant growth and cell division. Continuous growth measurements of chlorsulfuron-sensitive seedlings demonstrated that the herbicide inhibited growth within 2 h of application and after 8h reduced growth by 80%. This reduction in growth was closely associated with an inhibition of plant cell division. No significant effects were observed on auxin-, cytokinin- or gibberellin-induced cell expansion, photosynthesis, respiration, RNA synthesis or protein synthesis under conditions where plant cell division was strongly inhibited.

Hatzios and Howe (16) indicated that the herbicidal action of chlorsulfuron could be related to its effects on lipid synthesis. They also reported that photosynthesis, RNA and protein synthesis were affected only by the higher concentration of chlorsulfuron. In isolated bean (Phaseolus vulgaris L.) leaf cells, Devilliers et al. (8) found inhibition of photosynthesis, respiration and the synthesis of protein, RNA and lipid at 0.5 mM chlorsulfuron. This concentration, however, is too high to draw any conclusion on herbicidal mode of action.

Hageman and Behrens (14) reported that chlorsulfuron stimulated ethylene and cellulase production in the abscission zone of leaves. Accelerated leaf abscission of velvetleaf following chlorsulfuron application appears to result from a chlorsulfuron-induced increase in endogenous ethylene production and cellulase activity. Suttle and Schreiner (43) also indicated an increased endogenous ethylene production in chlorsulfuron-treated soybean seedlings. This increased ethylene production was accompanied by an increase in anthocyanin and an eight-fold increase in phenylalanine ammonia lyase. However, the increase in anthocyanin content was not related to an increase in ethylene production as application of silver nitrate (an inhibitor of ethylene action) to the herbicide treated seedlings did not prevent the anthocyanin accumulation.

Ray (34) found no inhibitory effects of chlorsulfuron on isolated plant nuclei and the enzymes DNA polymerase and thymidine kinase. Nucleoside precursors of DNA were not effective in lessening chlorsulfuron inhibition of thymidine incorporation into DNA of corn root tips. From this study he concluded that chlorsulfuron does not inhibit cell division by direct inhibition of DNA synthesis. In a later study, Ray (35) found the enzyme acetolactate synthase (ALS) to be the site of action of chlorsulfuron. This enzyme which catalyzes the first step in the biosynthesis of valine and isoleucine was extremely sensitive to the herbicide, having I_{50} values ranging from 18 to 36 nM. Addition of valine and isoleucine to excised pea root cultures incubated in the presence of chlorsulfuron completely alleviated herbicide-induced growth inhibition.

Chalef and Ray (5) studied the mode of inheritance of chlorsulfuron resistance using herbicide resistant mutants (S4) from tobacco cell cultures. They found that resistance was inherited as a single dominant or semi-dominant mutation in all cases. Studies of plants homozygous for mutation showed the mutant plants to be completely resistant to treatment with a concentration of chlorsulfuron 100 times higher than that which produces symptoms of phytotoxicity on normal plants.

Biochemical characterization of these mutant (S4) plants has further confirmed the site of action of chlorsulfuron and the mechanism by which resistance is effected. Chalef and Ray (6) demonstrated that mutants resistant to chlorsulfuron possess an altered form of ALS that is insensitive to chlorsulfuron and that the resistant form of ALS cosegregates with the resistant phenotype in genetic crosses.

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II. ABSORPTION AND TRANSLOCATION OF ROOT APPLIED CHLORSULFURON IN WHEAT AND BARLEY

Abstract. To determine the basis for chlorsulfuron (2-chloro- N-[[(4 -methoxy-6-methyl-1,3,5,-triazin-2-yl)amino]carbonyl]benzene sulfonamide) selectivity between wheat (Triticum vulgare L. 'Taylor') and barley (Hordeum vulgare L. 'Henry'), the dose response of chlorsulfuron and the movement of ^{14}C-labeled chlorsulfuron were studied. Chlorsulfuron at 10, 20, and 40 ppb was applied to hydroponically cultured plants at the 2½ leaf stage under conditions simulating root application. Barley cultured in 20 and 40 ppb chlorsulfuron solution had a greater reduction in fresh weight than did wheat. Wheat absorbed more ^{14}C-label than barley after 48 and 72 h exposures. In both species the majority of the activity taken up remained in the roots. But wheat roots retained significantly more ^{14}C-label herbicide than the barley roots. The results indicate that although wheat roots took up more chlorsulfuron than barley roots, barley was less tolerant to chlorsulfuron and chlorsulfuron was more mobile in barley. This study showed that differences in uptake or translocation cannot explain the differential response of the two species to root-applied chlorsulfuron.

INTRODUCTION

Chlorsulfuron selectively controls many annual broadleaf weeds in cereals at rates of 10 to 40 g/ha. Mode of action studies by Ray (7) have shown that chlorsulfuron is an inhibitor of plant growth and cell division in susceptible plants. Selectivity in cereal crops such as wheat and barley and tolerant grass weeds such as wild oats (Avena fatua L.) was due to the plant's ability to metabolize chlorsulfuron to a herbicidally inactive product. In contrast sensitive broadleaf plants showed little or no metabolism of the herbicide (8).

Chlorsulfuron can be applied pre- and post-emergence on wheat and only postemergence on barley. Barley lacks the tolerance of preemergence-applied or soil-residual chlorsulfuron (5). Evans and Gunnel (2) reported that barley stands were reduced 20 to 80% when seeded 1 year after application of chlorsulfuron at 35 to 140 g/ha. Barley plants in areas treated with chlorsulfuron 1 year prior exhibited injury in the form of chlorosis, and stunting; also, by harvest time, barley heads failed to form in all plots treated with chlorsulfuron at 105 and 140 g/ha. Hageman and Behrens (3) evaluated the tolerance of several barley, oat (Avena sativa L.) and wheat cultivars to pre- and post-emergence chlorsulfuron under greenhouse and field conditions. In the greenhouse 'Morex', 'Conquest', and 'Bonanza' barley cultivars were less susceptible than six other barley cultivars to preemergence chlorsulfuron at 1.0 kg/ha. But barley cultivars were similar in response to postemergence chlorsulfuron.

This study was initiated to examine the physiological basis for this difference in the tolerance of wheat and barley to root-applied chlorsulfuron by comparing absorption and translocation of ^{14}C-chlorsulfuron by these species.

MATERIALS AND METHODS

General procedure. Wheat and barley were germinated in vermiculite in the greenhouse and at 2½-leaf stage were transferred to 100 ml of half-strength and ph 6.5 Hoagland and Arnon nutrient solution (4) in foil-wrapped, 250 ml jars. The plants were grown in a greenhouse with 14-h photoperiod supplemented with artifical light and with day/night temprature of 29/22 C.

Response studies. Wheat and barley seedlings were grown for 48 h as described above and three seedlings were transferred to foil-wrapped jars containing nutrient solution and chlorsulfuron. The concentrations of chlorsulfuron in the jars were 0, 10, 20, and 40 ppb. There were four replications in each experiment and treatments were arranged in a randomized complete block design with a 2 (species) × 4 (concentration) factorial arrangement. Nutrient solutions containing the respective amounts of chlorsulfuron were changed every 3 days. Two weeks after treatment plants were harvested and sectioned to roots and shoots, and fresh weights were measured. The percent fresh weight reduction of each treatment from that of the control was calculated. Percent reduction data were transformed to arscin values and subjected to analysis of variance with mean separation using Duncan's multiple range test. Experiments were repeated and data with lower coefficient of variation were presented.

Absorption and translocation studies. The planting procedures described above were followed. Two seedlings (one for autoradiography and another for absorption and translocation) were treated by adding 0.12 μCi of ^{14}C-chlorsulfuron (specific activity 6.01 μCi/mg) to 100 ml of nutrient solution. Plants were harvested 8, 24, 48, and 72 h after treatment and roots were washed three times with acetone. The plant parts were dried at 50°C for 48 h, weighed, and combusted in a sample oxidizer. The $^{14}CO_2$ was trapped in 20 ml of a CO_2 absorber (Carbosorb II, Packard Instrument Company, Downers Grove, IL) and scintillation fluid (Scintiverse E Fisher Scientific Fair Lawn NJ 07410). The radioactivity was quantified using liquid scintillation spectrometry, with corrections for quenching. Distribution of ^{14}C in the various plant sections was expressed as a percentage of ^{14}C recovered from the whole plant. A completely randomized block design with four replications was used and each experiment was repeated once. Percent data were transformed to arcsin values and subjected to analysis of variance with mean separation using Duncan's multiple range test at the 5% level.

Translocation was also determined qualitatively by autoradiography. Pressed plants were exposed to X-ray film for 2 weeks and the distribution of ^{14}C was visualized on the developed films.

RESULTS AND DISCUSSION

Response studies. The relative tolerance of wheat and barley to root applied chlorsulfuron was established by measuring the fresh weights of hydroponically cultured plants. The tolerance of wheat and barley to root-applied chlorsulfuron varied greatly (Table 1). At the lowest rate of chlorsulfuron (10 ppb) the two species had similar fresh weight reductions. However, the two higher rates of chlorsulfuron caused a significantly higher fresh weight reduction in barley compared to wheat. The results indicated barley to be more sensitive than wheat to root-applied chlorsulfuron. Palm et al. (5) have also reported that wheat had adequate tolerance while barley was sensitive to preemergence applied chlorsulfuron. Shoots and roots of wheat and barley also responded differently to chlorsulfuron (Table 2). At the lowest chlorsulfuron concentration, fresh weights of barley roots were significantly lower than the corresponding shoot weights. Wheat shoots and roots did not show such differential sensitivity to any chlorsulfuron treatment. Laboratory studies by Ray (7) have demonstrated that chlorsulfuron is an inhibitor of plant growth and cell division. Roots which are in continuous contact with the herbicide would be expected to be more affected than the shoot. In addition, the relative root and shoot sensitivity could be due to a limited translocation of chlorsulfuron from roots to shoots resulting in higher concentration of the herbicide in roots.

Absorption and translocation. The amount of chlorsulfuron absorbed by wheat and barley was similar at 8 and different after 24, 48, and 72 h

Table 1. Fresh weight reduction from untreated wheat and barley 3 weeks after root application of chlorsulfuron[a].

Species	Chlorsulfuron concentration	% reduction[b]
	(ppb)	
Wheat	10	23.2 a
Barley		24.0 a
Wheat	20	35.2 b
Barley		49.8 c
Wheat	40	51.2 c
Barley		59.5 d

[a] Weights of 3 untreated wheat plants = 841 mg. Weights of 3 untreated barley plants = 839 mg.

[b] Means with similar letters are not siginficantly different at 5% level using Duncan's multiple range test.

Table 2. Fresh weight reduction from untreated wheat and barley plant parts 3 weeks after root application of chlorsulfuron[a].

Chlorsulfuron concentration	Plant part	Species	
		Wheat[b]	Barley[c]
		(% reduction)	(% reduction)
10	Shoot	23 a	23 a
	Root	24 a	35 b
20	Shoot	34 b	42 b
	Root	40 bc	53 bc
40	Shoot	51 cd	56 cd
	Root	53 d	64 d

[a] Means within a column followed with similar letters are not significantly different at 5% level using Duncan's multiple range test.

[b] Weights of 3 untreated wheat shoots = 742 mg. Weights of 3 untreated wheat roots = 99 mg.

[c] Weights of 3 untreated barley shoots = 734 mg. Weights of 3 untreated barley roots = 105 mg.

after treatment (Table 3). ^{14}C-chlorsulfuron uptake by wheat was significantly higher than by barley at 24, 48, and 72 h. The movement and accumulation increased with time for both species (autoradiogram not shown). Wheat which was tolerant to root-applied chlorsulfuron, absorbed more ^{14}C-chlorsulfuron than did the sensitive barley. Therefore, differential root uptake of ^{14}C-chlorsulfuron does not explain the differences in chlorsulfuron selectivity between these two species.

The distribution of ^{14}C indicated limited translocation of the herbicide to the shoot (Table 4). In both species most of the absorbed ^{14}C-chlorsulfuron remained in the roots. Less than 10% of the absorbed herbicide was translocated out of the roots of both species at 48 and 72 h. Similar results were obtained by Petersen and Swisher (6) in experiments with Canada thistle (<u>Cirsium</u> <u>arvense</u> L.). They reported that radioactivity translocated from the treated root system represented 10% of the amount applied; 8% was in the parent shoot and 2% was in the shoots derived from root buds. Ray (7) stated that chlorsulfuron was readily absorbed by both the foliage and roots of plants and moved systemically. Donald (1) concluded that chlorsulfuron was translocated slowly in Canada thistle, because regrowth from root buds was not reduced by the herbicide until 1 to 2 weeks after foliar treatment. Sweetser et al. (8) reported translocation ranging from 2.5 to 18.4% of applied ^{14}C-chlorsulfuron from the treated leaves of a number of sensitive and tolerant plants. The proportion of ^{14}C translocated from roots to shoots was different for the two species for the same time interval (Table 4). Higher percentage of the absorbed ^{14}C was detected in shoots of barley than in wheat for the same exposure time.

Table 3. Total amount of ^{14}C-chlorsulfuron recovered in wheat and barley harvested 8, 24, 48 and 72 h after root application.

Harvesting time	Species	^{14}C recovered[a]
		Dpm/mg tissue dry weight
8	Wheat	218 fg
	Barley	176 g
24	Wheat	326 e
	Barley	235 f
48	Wheat	578 c
	Barley	404 d
72	Wheat	805 a
	Barley	714 b

[a] Means followed with similar letters are not significantly different at 5% level using Duncan's multiple range test.

Table 4. Distribution of ^{14}C in wheat and barley plants harvested 8, 24, 48 and 72 h after root application of chlorsulfuron.

	^{14}C present in plant parts at various times after treatment			
Plant part	8 h	24 h	48 h	72 h
		(%)		
		Wheat		
Root	86	89	93	94
Shoot	15	11	6	5
		Barley		
Root	63	78	90	91
Shoot	37	23	10	9

[a] Differences in the percentage of ^{14}C detected in comparable parts of the two species after the same exposure interval, were significant using student's t-test at the 0.05% level.

The results indicate that chlorsulfuron was more mobile in barley than in wheat. Again differences in translocation did not appear to be an important factor in the selectivity of root applied chlorsulfuron to to wheat and barley.

These studies indicate that although wheat roots take up more chlorsulfuron than barley roots, barley is less tolerant of chlorsulfuron and chlorsulfuron is more mobile in barley. Both wheat and barley have adequate tolerance to postemergence-applied chlorsulfuron. Studies by Sweetser et al. (8) demonstrated that both species rapidly metabolize foliar-applied chlorsulfuron to a polar, inactive product. But this study and others indicate that wheat is tolerant to root-applied chlorsulfuron while barley is sensitive. This difference in barley sensitivity to foliar- and root- applied chlorsulfuron could be due to a difference in the metabolism of the herbicide in shoot vs root. The detoxification of the herbicide might be faster in the shoot of barley than in roots.

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III. INTERACTION OF CHLORSULFURON AND DICLOFOP ON ITALIAN RYEGRASS

Abstract. The influence of chlorsulfuron (2-chloro-N-[[(4-methoxy-6-methyl-1,3,5-triazin-yl)amino]carbonyl]benzene sulfonamide) at 10, 20, and 40 g/ha on Italian ryegrass (Lolium multiflorum Lam.) control with diclofop (±)[-2-[4-(2,4-dichlorophenoxy]phenoxy] propanoic acid] at 0.25, 0.5, and 0.75 kg/ha was tested in the greenhouse. Chlorsulfuron when tank mixed with diclofop caused a 4 to 28% reduction in the control of ryegrass. Significant chlorsulfuron antagonism on ryegrass control with diclofop was observed at all tested combinations of the two herbicides. Increasing the rates of both chlorsulfuron and diclofop in the tank mixture tended to reduce this antagonism. Chlorsulfuron at 40 g/ha did not reduce ryegrass control when applied as a sequential treatment 16 or 24 h before or after diclofop at 0.75 kg/ha. Diclofop did not affect the degree of control of common chickweed (Stellaria media (L) Vill.) with chlorsulfuron.

INTRODUCTION

Ryegrass is an important weed pest in wheat (Triticum aestivum L.) and other small grain crops causing severe yield reductions, field abandonment and expense of cleaning seeds. Liebl and Worsham (4) reported that 20 ryegrass plants/m^2 resulted in wheat seed yield and head number reductions of 9.3 and 10.5%, respectively.

Chlorsulfuron controls many broadleaf weeds with excellent selectivity to small grains. It would be advantageous if chlorsulfuron could be mixed in the spray tank with diclofop for control of ryegrass and thus permit control of a broad spectrum of weeds in one spray operation. However, when two or more herbicides are applied in combination, responses cannot be predictable from the performance of either herbicide alone.

Many researchers have reported that the phytotoxicity of diclofop to annual grasses was decreased when tank mixed with herbicides such as MCPA [(4-chloro-2-methylphenoxy)acetic acid], 2,4-D [(2,4-dichlorophenoxy) acetic acid)] and dicamba (3,6-dichloro-2-methoxy benzoic acid) for broad spectrum weed control (1, 6, 11). O'Sullivan and Kirkland (9) also reported that chlorsulfuron mixed with diclofop caused a 4 to 45% reduction in control of wild oat (Avena fatua L.) but an earlier report by Hall et al. (3) indicated that chlorsulfuron did not reduce the phytotoxicity of diclofop to oat (Avena sativa L.).

The antagonism of weed control caused by an interaction between two herbicides can be affected by the time interval between applications and the sequence of the applications. Miller and Nalewaja (5) reported that flamprop (N-benzoyl-N-(3-chloro-4-fluorophenyl)-DL-alanine) applied 2 days after, or as a tank mix with 2,4-D, gave less wild oat control than did flamprop applied alone or 4 days after or 2 days before 2,4-D. MCPA at 0.6 kg/ha did not reduce wild oat control when applied as a sequential treatment 2 days before or 1 day after diclofop at 1.1 kg/ha (8).

The objectives of this research were to evaluate the interaction between chlorsulfuron and diclofop with respect to Italian ryegrass control and to determine the effect of split sequential treatments on the interaction between these two herbicides.

MATERIALS AND METHODS

General procedures. Ryegrass plants were grown in a greenhouse with 14-h photoperiod and day/night temperatures of 29°C/22°C. Ryegrass (10 seeds/cup) was sown 2.5 cm deep in a 2:2:1 (v/v/v) mixture of potting medium consisting of Weblite (Weblite Corp., Blue Ridge, VA), vermiculite, and peat contained in 473-ml plastic cups. A controlled-release N-P-K fertilizer (14-14-14) was added to the medium to supplement nutrient levels. Plants were thinned to five plants/pot 1 week after emergence. Chlorsulfuron, a mixture of chlorsulfuron plus diclofop or diclofop alone was sprayed with a link-belt sprayer at 25 psi in 225 L/ha spray volume on ryegrass at the 2½-leaf stage. All cups were watered from the top as required. All experiments were repeated and average data are presented

Effect of chlorsulfuron on ryegrass control with diclofop. Chlorsulfuron at 0, 20, and 40 g/ha alone or in combination with diclofop at 0.25, 0.5, and 0.75 kg/ha was applied to ryegrass as described above. Three weeks after spraying ryegrass shoots were harvested and weighed. The data were analyzed for variance as a four by four factorial experiment in a randomized complete block design (10). The standard errors of the observed mean responses were calculated. Statistically significant interactions for each treatment combination between the two herbicides were identified by the use of F tests for a two by two comparison of that treatment with the control and the separate rates of chlorsulfuron and diclofop as has been described by Nash (7). In addition, the expected responses for each treatment were calculated by the multiplicative survival model (2). For example, in Table 1, the expected response of ryegrass seedlings to the combined treatment of chlorsulfuron at 10 g/ha and diclofop at 0.25 kg/ha was calculated as follows:

$$\frac{(1.05)\ (3.67)}{(7.47)} = 0.52\text{g}.$$

All the observed values exceed their respective expected value, hence antagonism is indicated for all chlorsulfuron and diclofop combinations.

Effect of diclofop on common chickweed control with chlorsulfuron. Common chickweed was grown in a greenhouse as described for ryegrass and was treated at a 5-cm height with chlorsulfuron, chlorsulfuron plus diclofop, or diclofop alone. Twenty-one days after spraying chickweed shoots were harvested and weighed. The data were analyzed as in the previous experiment.

Effect of various times of split applications of chlorsulfuron and diclofop on ryegrass. Chlorsulfuron at 40 g/ha was applied at various times after diclofop, and diclofop at 0.75 kg/ha was applied at various times after chlorsulfuron on ryegrass. Chlorsulfuron plus diclofop tank mixture, chlorsulfuron alone, diclofop alone, and the initial herbicide of the split application treatments were applied to ryegrass with the subsequent applications applied at various times later. The subsequent applications were immedietely (IM) and 1, 2, 4, 8, 16, and 24 h after the initial application. The plant foliage was allowed to dry for 1 to 2 min between the initial and IM applications. The experimental design was a randomized complete block with a split plot arrangement of treatments replicated four times. The main plots were the sequence of chlorsulfuron and diclofop split applications, and the subplots were the timing intervals between split applications. The data from the tank-mixture treatment were not included in the statistical analysis because the treatment was not repeated at different time intervals.

RESULTS AND DISCUSSION

Effect of chlorsulfuron on ryegrass control with diclofop. Chlorsulfuron alone caused a significant reduction in ryegrass fresh weight compared to the untreated control (Table 1). Diclofop at all rates did not reducee the phytotoxicity of chlorsulfuron to ryegrass. One week after foliar application of the herbicides, the plants treated with either diclofop alone or in combination with chlorsulfuron showed a broad chlorotic band in the midsection of the leaves. However, chlorosis in the leaves treated with diclofop alone was more pronounced than those treated in combination with chlorsulfuron. With time this difference progressively increased and, 2 weeks after application, chlorosis in the leaves treated with diclofop alone was severe and the chlorotic band had spread out from the midsections; whereas, the chlorotic band in the leaves treated with the combination of chlorsulfuron and diclofop appeared to be restricted.

Ryegrass control with diclofop was reduced by tank mixtures with chlorsulfuron compared to diclofop alone (Table 1). This chlorsulfuron antagonism of ryegrass control with diclofop was significant at all combinations of the two herbicides. However, control of ryegrass was markedly improved with mixtures containing the high rates of both chlorsulfuron and diclofop over mixtures with low rates. This indicates that it may be possible to reduce certain amounts of the antagonism of control of ryegrass under field conditions by increasing the rates of both herbicides in the mixture. However, further work in the field is necessary to confirm weed control effectiveness and crop tolerance for such mixtures.

Table 1. Shoot fresh weights of ryegrass treated with the combination of chlorsulfuron and diclofop.

		Shoot fresh weight			
		Diclofop (kg/ha)			
Chlorsulfuron	Type of response	0	0.25	0.5	0.75
(g/ha)		(g)			
0	Observed[a]	7.47 ± 0.24	1.05 ± 0.50	0.28 ± 0.05	0.23 ± 0.06
10	Observed	3.67 ± 0.29	2.08 ± 0.18	2.42 ± 0.64	0.75 ± 0.12
	Expected[b]		(0.52)	(0.14)	(0.11)
20	Observed	2.65 ± 0.53	1.98 ± 0.18	1.75 ± 0.29	0.73 ± 0.13
	Expected		(0.37)	(0.09)	(0.08)
40	Observed	1.08 ± 0.18	1.1 ± 0.33	1.13 ± 0.22	0.56 ± 0.06
	Expected		(0.15)	(0.04)	(0.03)

[a] Mean weight values are from four replications ± standard error of each mean. All interactions are significant at the 1% level of probability as determined by F values for each combination treatment calculated for 2-by-2 comparisons of the observed response of that treatment with the observed responses for the control and the separate levels of chlorsulfuron and diclofop.

[b] Expected values in parentheses calculated according to multiplicative survival model (see Materials and Methods).

Similar reduced antagonism of chlorsulfuron to wild oat control with higher rates of diclofop was noted by O'Sullivan and Kirkland (9).

Effect of diclofop on chickweed control with chlorsulfuron. Control of chickweed with chlorsulfuron was not influenced by the addition of diclofop to the tank mixture (Table 2). Both rates of chlorsulfuron reduced the fresh weight of this weed compared to the untreated control. Diclofop applied at 0.5 or 0.75 kg/ha did not control chickweed. Olson and Nalewaja (8) also reported that control of common lambsquarters (*Chenopodium album* L.), redroot pigweed (*Amaranthus retroflexus* L.), and wild mustard (*Sinapis arvensis* L.) with MCPA was not influenced by the addition of diclofop to the tank mixture.

Effect of various times of split application of chlorsulfuron and diclofop on ryegrass. Chlorsulfuron antagonism of ryegrass control by diclofop was greater with tank mixture than with a split application before or after diclofop (Table 3). A tank mixture of chlorsulfuron at 40 g/ha with diclofop at 0.75 g/ha reduced ryegrass control 28% as compared to 7% for the split application 24 h before or after diclofop. Thus, chlorsulfuron antagonism of ryegrass control with diclofop was reduced 21% by applying chlorsulfuron as a separate application rather than as a tank mixture with diclofop. Similar reduction of MCPA antagonism with increased time interval for wild oat control with diclofop has been reported by Olson and Nalewaja (8). Antagonism of ryegrass control was the same whether chlorsulfuron was applied before or after diclofop at all time intervals.

Table 2. Shoot fresh weights of chickweed treated with the combination of chlorsulfuron and diclofop.

	Shoot fresh weight		
	Diclofop (kg/ha)		
Chlorsulfuron	0	0.5	0.75
(g/ha)	(g)		
0	9.4 ± 0.3[a]	8.1 ± 0.1	8.3 ± 0.4
10	1.8 ± 0.8	1.0 ± 0.3	1.0 ± 0.5
20	1.1 ± 0.6	0.5 ± 0.1	0.7 ± 0.2

[a] Mean weight values ± standard error of each mean. Interactions between chlorsulfuron and diclofop were not significant at the 5% level of probability.

Table 3. Percent ryegrass control, based on shoot fresh weight reduction, as influenced by diclofop at 0.75 kg/ha and chlorsulfuron at 40 g/ha with various time intervals between split applications.

Time after initial herbicide application	Ryegrass control Chlorsulfuron after diclofop applied 0 h	 Chlorsulfuron 0 h before diclofop
(h)	(%)	
0[a]	85	50
IM[b]	63	65
1	62	60
2	68	71
4	67	67
8	71	72
16	73	69
24	76	80
Tank mixture[c]	57	
LSD (0.05) = 6 for time intervals		

[a] The initial diclofop or chlorsulfuron treatments were applied alone without a subsequent treatment.

[b] The sequential treatment was applied immediately after the initial 0 h application.

[c] The tank mixture data were not included in the statistical analysis.

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IV. SAFENING CORN, SUGARBEET AND SOYBEAN AGAINST CHLORSULFURON AND METSULFURON INJURY.

Abstract. Greenhouse experiments showed that the tolerance of corn (Zea mays L.) to chlorsulfuron (2-chloro-N-[[(4-methoxy-6 -methyl-1,3,5, -triazin-2-yl)amino]carbonyl]benzenesulfonamide) and metsulfuron (2-[[[[(4-methoxy-6-methyl-1,3,5,-triazin-2yl)amino] amino] carbonyl]amino]sulfonyl]benzoic acid] greatly increased by seed dressing with the herbicide safener NA (1,8-naphthalic anhydride) and to a lesser degree by M-32988 (2-dichloroacetylimino-3-methyl-1,3-thiazol-4-ine). NA provided up to an eight-fold protection of corn against chlorsulfuron and metsulfuron at 10 g/ha. M-32988 dressed corn yielded significantly lower than NA treated corn at all equivalent rates of chlorsulfuron and metsulfuron. No improvement in protection of corn against both herbicides was obtained by increasing the rate of NA from 0.5% to 1% by seed weight. Seed dressing with M-32988 failed to protect soybean (Glycine max (L.) Merr.) and sugarbeet (Beta vulgaris L.) against chlorsulfuron or metsulfuron.

INTRODUCTION

Chlorsulfuron and metsulfuron are forerunners of a new chemical family of very active herbicides, the sulphonylureas. Chlorsulfuron has a broad spectrum of herbicidal activity and has shown excellent crop selectivity in small grains such as (*Triticum aestivum* L.), barley (*Hordeum vulgare* L.), oats (*Avena sativa* L.) and rye (*Secale cereale* L.) as reported by Levitt et al. (7) and Palm et al. (9). Metsulfuron has also been extensively evaluated in wheat and barley for control of broadleaf weeds. It has provided total control of Mediterranean saltwort (*Salsola vermiculata* L.) and 90% control of common lambsquarters (*Chenopodium album* L.) in spring barley (6). Morishita et al. (8) also obtained good to excellent control of henbit (*Lamium amplexicaule* L.), mayweed (*Anthemis cotula* L.), and shephedspurse (*Capsella bursa-pastoris* (L.) Medic.) with metsulfuron at 9 g/ha applied postemergence to wheat. Similarly Peabody (12) and Schaat et al. (13) reported best overall control of annual broadleaf weeds with early postemergence metsulfuron in spring wheat and barley.

Although wheat and barley show excellent tolerance to chlorsulfuron and metsulfuron, major crops such as corn, soybean, and sugarbeet remain very sensitive to these sulfonylureas. This sensitivity apart from precluding the use of sulfonylureas in susceptible crops, creates problems of residue carryover in rotational cropping.

One way of enhancing the tolerance of sensitive crops to sulfonylureas is by the use of herbicide safeners. Herbicide safeners are chemical agents that selectively protect crop plants from herbicide injury without protecting weeds. Hoffman (5) was the first to report the safening of corn by NA against injury from the herbicide EPTC (S-ethyl dipropyl carbamothioate). NA as a seed dressing is a very versatile herbicide safener exhibiting limited botanical or chemical specificity. It offers complete protection to corn (*Zea mays* L.), sorghum (*Sorghum bicolor* (L.) Moench), oats, and wheat against a number of herbicides such as the thiocarbamates and chloroacetanilides (3, 10).

NA was not found to be an effective protectant of broadleaf crops against herbicide injury. However, seed treatment with NA resulted in partial protection against EPTC injury to field beans (*Phaseolus vulgaris* L.) and trifluralin (2,6-dinitro-N,N-dipropyl-4-(trifluoromethyl) benzenamine) injury to tomato (*Lycopersicon esculentum* Mill.) (2). Parker et al. (11) and Hatzios (4) have also reported that NA is an effective protectant of corn against injury from chlorsulfuron. M-32988 is a new safener whose activities and properties are yet to be reported.

The objectives of this study were to examine the possible safening of corn, soybean and sugarbeet from metsulfuron and to evaluate the potential of a new safener, M-32988, for chlorsulfuron and metsulfuron.

MATERIALS AND METHODS

The experiments were conducted in a glasshouse in 475-ml pots for corn and soybean, and 200-ml pots for sugarbeet. The pots were filled with a 2:2:1 blended potting medium (Weblight, Vermiculite and Sphagnum peat) containing a controlled-release fertilizer (14-14-14) and an agricultural 4-9-3 fertilizer All experiments were replicated four times.

NA (technical ca 98%) and M-32988 were applied as seed dressing by shaking the weighed amounts of safener and seed in polyethylene bags. Seeds of corn variety 'Pioneer 3320' and soybean variety 'Essex' were sown 2 cm deep while sugarbeet variety 'US H23' was sown 1 cm deep.

Herbicides were applied preemergence of corn by a laboratory sprayer comprising a single Teejet band spray nozzle delivering 327 l/ha. Herbicide rates are expressed on an active ingredient basis. Watering was applied from overhead to the soil surface as required. Assessment was by measurement of fresh weight of shoots and plant heights four weeks after sowing. Results were subjected to analysis of variance.

RESULTS AND DISCUSSION

M-32988 failed to protect soybean from chlorsulfuron (Table 1) and metsulfuron (Table 2) injury. M-32988 alone at 3% reduced the fresh weight of soybean when compared to untreated plants. M-32988 also did not protect sugarbeet and treated plants were dead by harvest time. In an earlier study (11), NA also failed to protect soybean and sugarbeet from chlorsulfuron damage.

As shown in Figure 1, NA provided up to eight-fold protection of corn against metsulfuron at 10 g/ha. NA at 1% by seed weight provided more safening than at 0.5% by seed weight; but NA alone at 1% slightly inhibited the growth of corn. Although the protection factor afforded by NA against metsulfuron at 40 g/ha was 30-fold, the fresh weight of corn was only 50% of the untreated control. This indicates that NA is less effective in overcoming the phytotoxicity of metsulfuron at high rates.

The protection with M-32988 was less than four-fold at all rates of metsulfuron. M-32988-dressed corn yielded significantly lower than NA-treated corn at all equivalent rates for metsulfuron. As indicated by Parker et al. (11), protection factors less than four-fold are probably inadequate where there is not already selectivity in favor of the crop. In this case corn was found highly sensitive to metsulfuron, indicating the poor potential of M-32988 as a corn safener against metsulfuron injury.

The data in Figure 2 show comparable effects of the safeners to those observed on shoot fresh weight (Figure 1). Metsulfuron at both rates significantly reduced the height of nondressed corn.

Table 1. Shoot yield of soybean seed-dressed with various rates of M-32988 safener and sprayed preemergence with chlorsulfuron.

Rate of chlorsulfuron	No safener	Rate of M-32988		
		0.5%	1%	3%
(g/ha)			(g)	
0	16.8	15.5	15.3	9.3
5	4.5	4.3	4.3	4.0
10	2.4	2.9	2.5	2.5
S.E.		1		

Table 2. Shoot yield of soybean seed-dressed with various rates of M-32988 safener and sprayed preemergence with metsulfuron.

Rate of metsulfuron	No safner	Rate of M-32988		
		0.5%	1%	3%
(g/ha)			(g)	
0	13.2	11.6	12.9	9.4
5	2.8	2.5	2.7	2.4
10	2.1	1.8	1.8	2.4
S.E.		0.89		

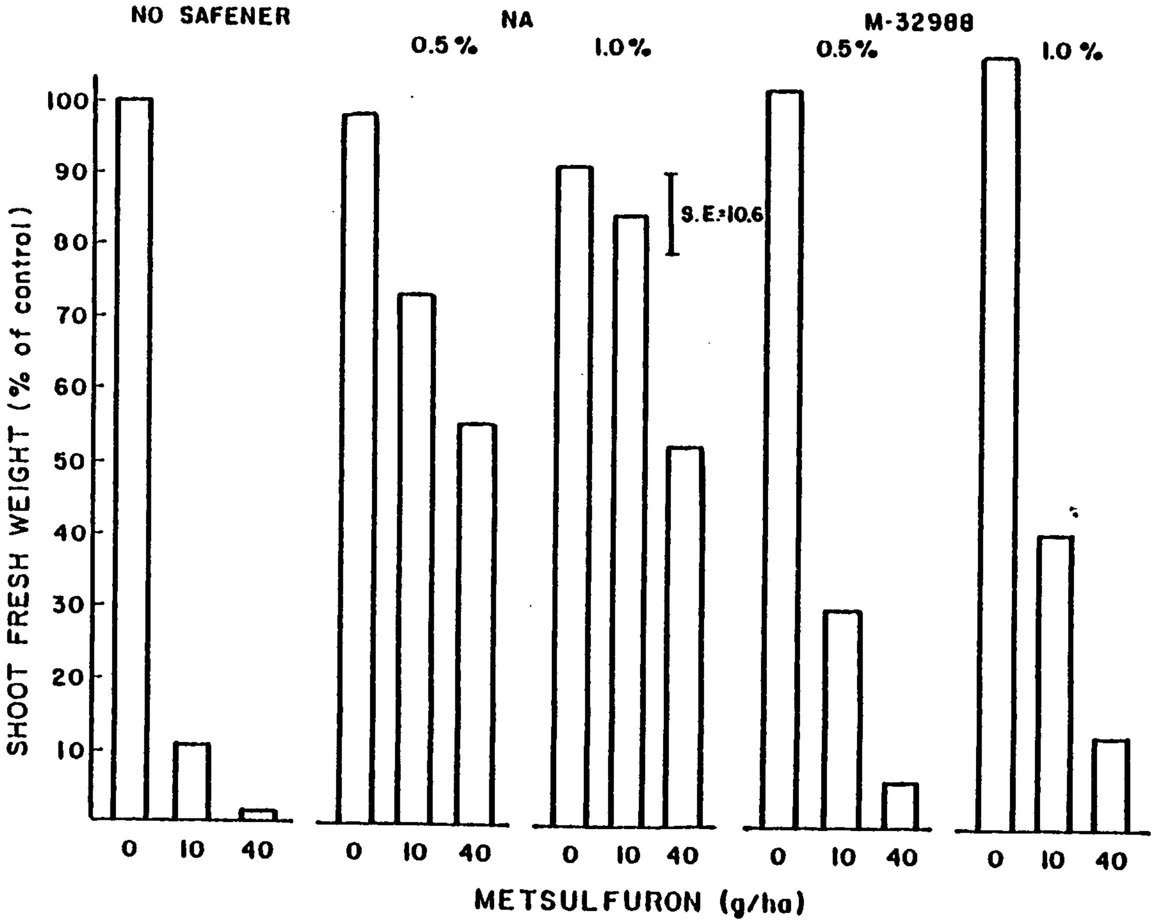

Figure 1. Fresh weights of corn with and without NA and M-32988 following preemergence treatment with metsulfuron.

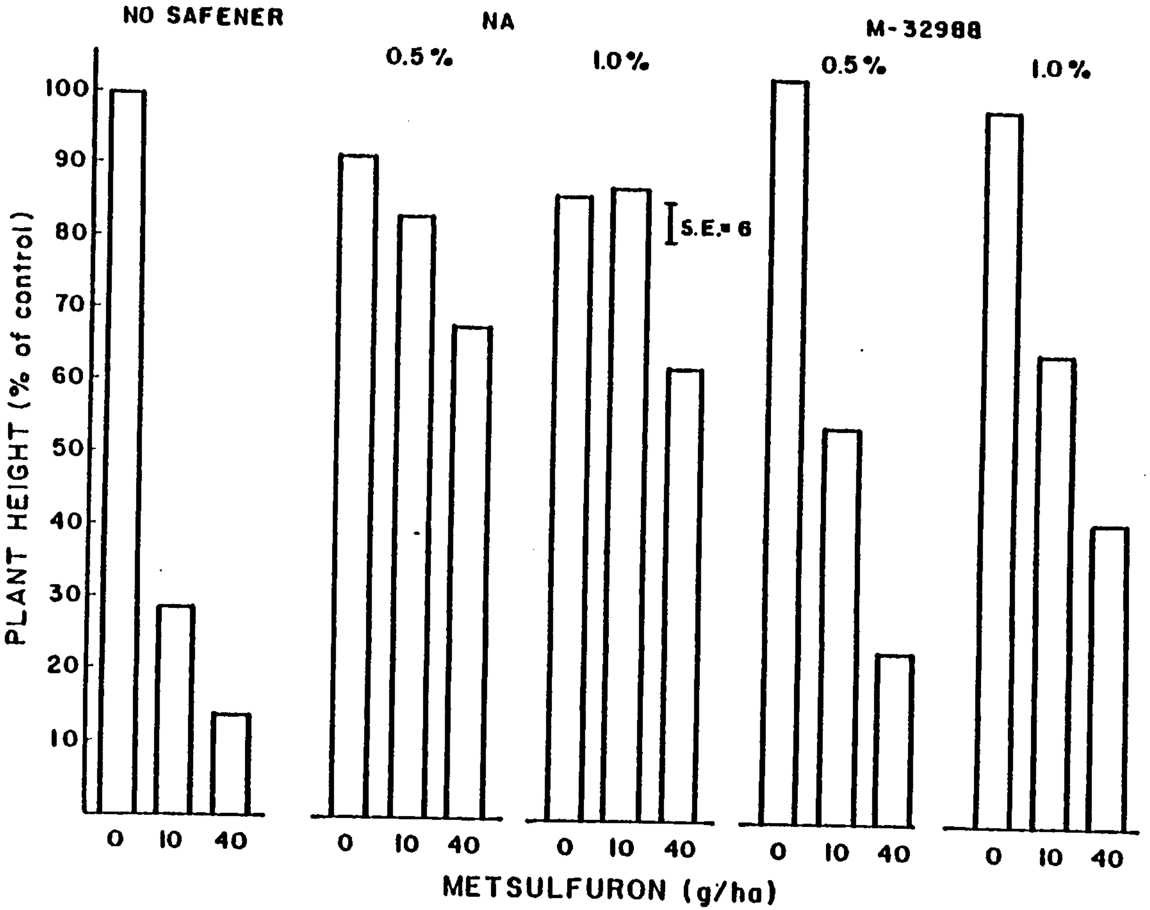

Figure 2. Plant heights of corn with and without NA and M-32988 following preemergence treatment with metsulfuron.

Nonsafened plants were greatly stunted with severly pruned root systems as observed at harvest. At 1%, NA alone also significantly stunted the corn.

Figure 3 confirms the eight-fold protection of corn by NA reported earlier (11). Toxicity due to chlorsulfuron alone was severe and at 40 g/ha was damaging even with NA. No improvement in protection was obtained by increasing the rate of NA dressing from 0.5 to 1% by seed weight. Seed dressing by M-32988 again failed to protect corn adequately from chlorsulfuron damage. The effect of both safeners on plant height (Figure 4) was greater than on shoot weight seen in Figure 3. All plant height measurements for dressed corn were above 50% of the control. Visual observations at harvest indicated that the major effects of these herbicides on corn appear to be due to their root inhibition rather than reduction of shoot growth.

The results of this study confirm the versatility of NA as a safener for both metsulfuron and chlorsulfuron. The protection of corn by NA from metsulfuron and chlorsulfuron might allow growers to combat some difficult weeds in corn which could be susceptible to these herbicides. In addition, the safening effect of NA could permit the planting of corn in fields which had been treated with chlorsulfuron or metsulfuron without any danger from possible toxic soil residues. Such danger could arise when immediate replanting is necessary because of failure of tolerant crops or under environmental condition which favor long persistence of sulfonylureas.

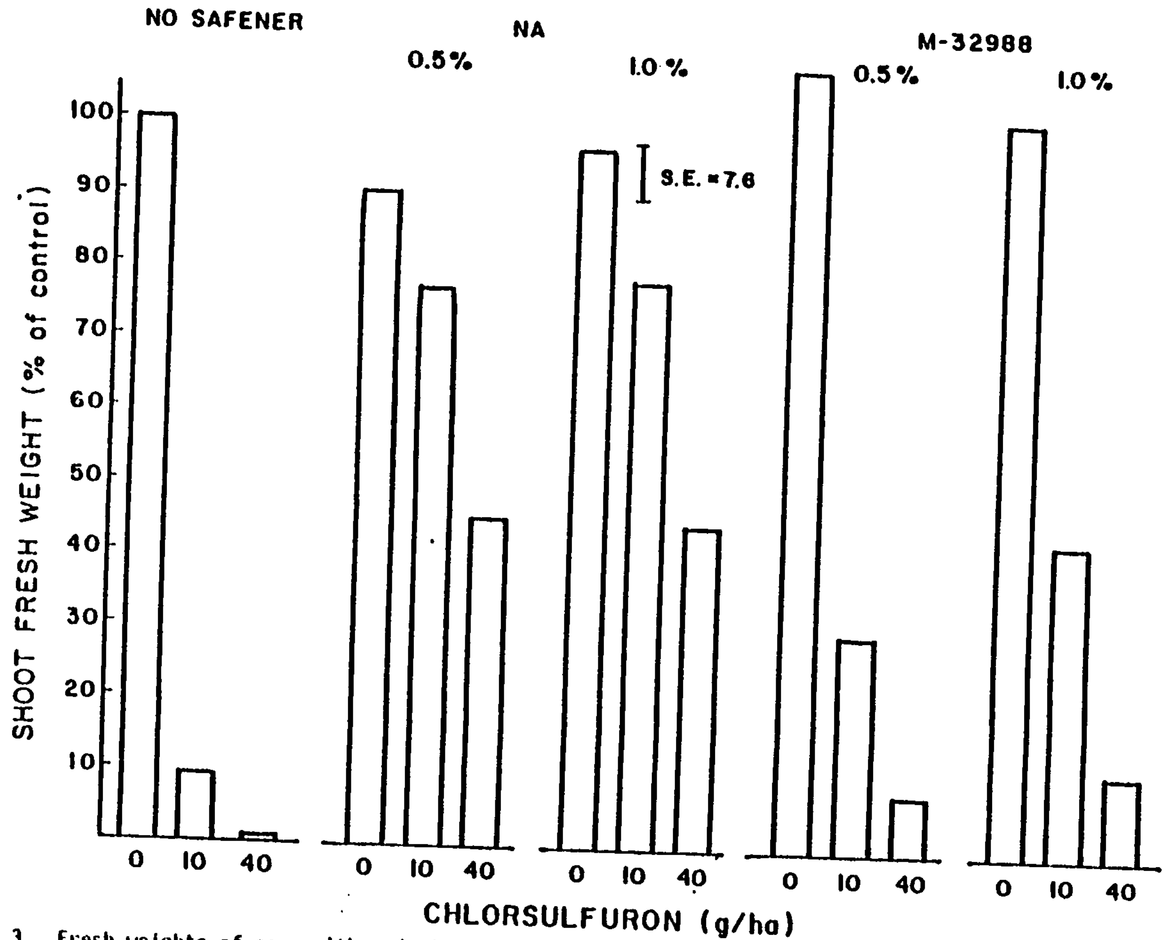

Figure 3. Fresh weights of corn with and without NA and M-32988 following preemergence treatment with chlorsulfuron.

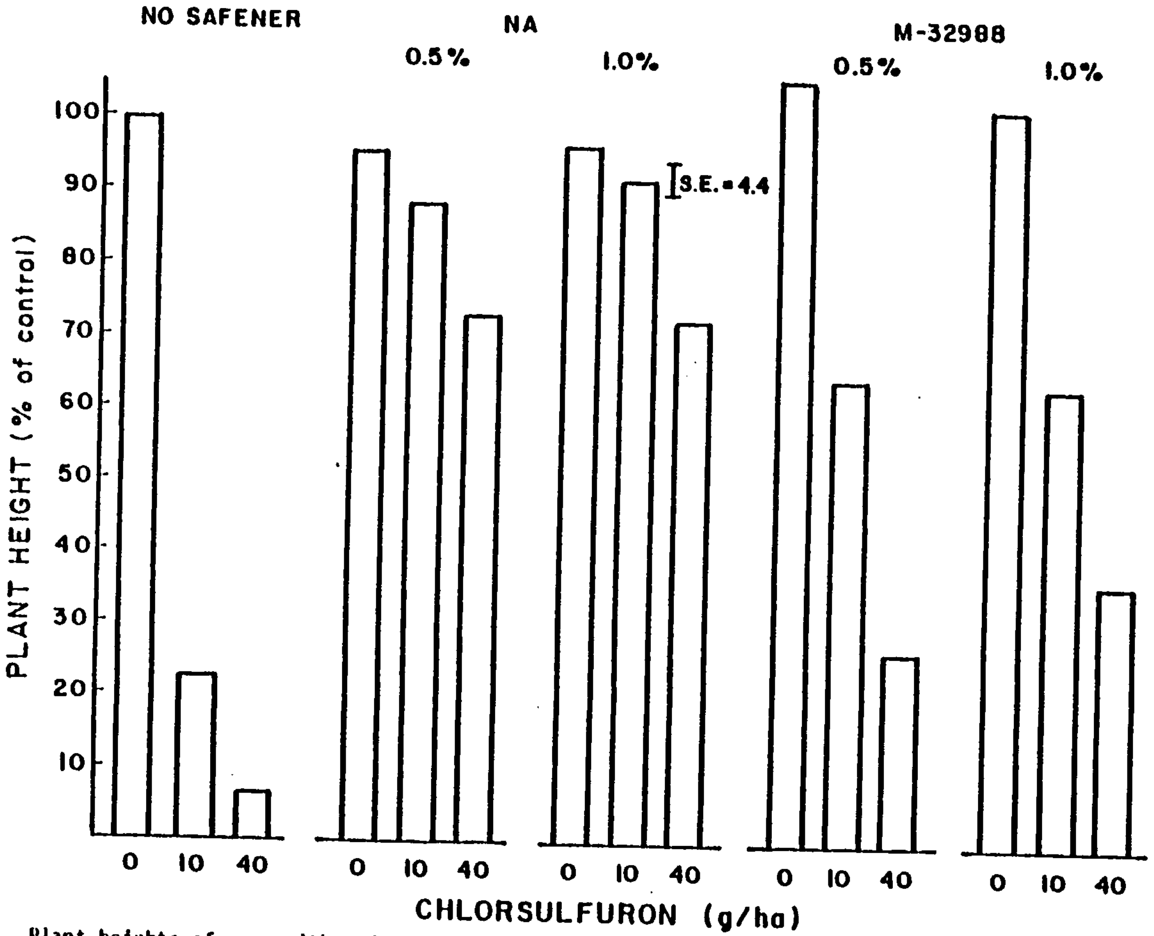

Figure 4. Plant heights of corn with and without NA and M-32988 following preemergence treatment with chlorsulfuron.

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V. EFFECT OF APPLICATION TIME ON SOIL RESIDUE AND EFFICACY OF SULFONYLUREAS

Abstract. Chlorsulfuron (2-chloro-N-[[(4-methoxy-6-methyl-1,3,5-triazin-yl)amino]carbonyl]benzenesulfonamide} and metsulfuron (2-[[[[(4-methoxy-6-methyl-1,3,5-triazin-2-yl)amino]carbonyl]amino]amino]sulfonyl]benzoic acid) applied at rates of 10 and 40 g/ha to barley (Hordeum vulgare L.) at the tillering stage provided excellent control of common chickweed (Stellaria media L.), henbit (Lamium amplexicaule L.), and mayweed chamomile (Anthemis cotula L.) but poor control of common speedwell (Veronica officinalis L.). At equivalent dosages, metsulfuron was more active than chlorsulfuron. Corn (Zea mays L.) (' Pioneer 3320') adequately tolerated soil residues present 10 months following postemergence application of chlorsulfuron and metsulfuron at 10 to 120 g/ha. However, at the same site and rates, residues from both herbicides injured corn when sampled 2 months after application. Phytotoxic levels of both herbicides were also detected at the 10 to 20-cm depth 2 months after application.

INTRODUCTION

Chlorsulfuron and metsulfuron belong to the novel class of highly active herbicidal compounds called sulfonylureas. Chlorsulfuron has a broad spectrum of herbicidal activity and has shown excellent crop selectivity in small grains such as wheat (*Triticum aestivum* L.), barley, and rye (*Secale cereale* L.) (2, 7).

Wheat has been reported to tolerate up to 21-fold the recommended rate of chlorsulfuron (1). A major factor for selectivity of chlorsulfuron in these crops is the ability of the small grains to metabolize the herbicide to a polar, inactive product while sensitive broadleaf species show little or no metabolism of the herbicde (10). Mode of action studies by Ray (8) have indicated that chlorsulfuron is an inhibitor of plant growth and cell division. Miller and Nalewaja (3) reported good control of broadleaf and some grass weeds under North Dakota conditions. Similarly, studies in western Canada have shown good control of a variety of broadleaf weeds by chlorsulfuron with excellent cereal tolerance (6).

Several herbicides are currently registered for broadleaf weed control in cereals. However, none of these herbicides controls all major cereal broadleaf weeds adequately.

The objectives of this study were to investigate the effect by bioassay in the greenhouse of soil residues of chlorsulfuron and metsulfuron on corn and to compare fall versus spring applications of these herbicides for weed control.

MATERIALS AND METHODS

Field experiments Three field studies were conducted from 1982 through 1984 at the same location at Blacksburg, Virginia (Table 1). The soil type was silt loam with 2.5% organic matter content and pH 6.5. Experiments were randomized complete block designs with replications ranging from three to five. Herbicide treatments were applied using a CO_2-pressurized, hand-carried sprayer with a three-nozzle boom containing flat fan nozzles. Surfactant WK, a spray adjuvant containing trimethylnonylpolyethoxyethanol (E. I. duPont de Nemours and Co. Inc., Wilmington, DE 19898), at 0.1% by volume, was included in all chlorsulfuron and metsulfuron sprays. Barley variety 'Maury' was planted in all experiments.

Chlorsulfuron was applied as a 75% dry formulation while a 70% wettable powder of metsulfuron was used in all experiments. Other herbicides evaluated include: the octanoic acid ester formulation of bromoxynil (3,5-dibromo-4-hydroxybenzonitrile), the dimethyl amine salt of dicamba (3,6-dichloro-2-methoxybenzoic acid), both amine and ester formulations of 2,4-D [(2,4-dichlorophenoxy)acetic acid)] and the dimethyl amine salt of MCPA (4-chloro-2-methylphenoxy)acetic acid).

Residue and mobility studies on chlorsulfuron and metsulfuron. A corn root bioassay was used to estimate chlorsulfuron and metsulfuron residues in soil collected from Experiments 1 and 3. The bioassay method was based upon the reduction in the root length of corn grown in soil containing known chlorsulfuron and metsulfuron concentrations from 0 to 15 ppbw on

Table 1. Timing of cultural operations for the field experiments.

Exp. no.	Planting date	Time of spraying		Scoring date	Date of harvest
		Date	Growth stage		
1	9-17-82	10-27-82	2-leaf		
		4-1-83	tillering	5-30-83	6-8-83
2	9-17-82	4-1-83	tillering	5-30-83	6-15-83
3	9-17-83	4-27-84	tillering	5-18-84	6-23-84

a dry soil basis.

Soil cores were taken from all chlorsulfuron and metsulfuron treated plots 10 months after treatment in Experiment 1 and 2 months after treatment in Experiment 3. Four cores were taken in each plot using a 5-cm diameter soil probe from soil depths of 0 to 5, 5 to 10, and 10 to 20 cm. Soil was collected from control plots at each depth and was treated with 0, 0.25, 0.5, 1, 2, 4, 8, 10, or 15 ppbw (dry soil basis) of chlorsulfuron or metsulfuron to establish a standard curve of herbicide concentration versus root length (percent of control).

For Experiment 1, 10 corn seeds were planted in 85 g of soil per 55-mm diameter petri dish. The soil was moistened with 10 ml of water, covered, and the petri dishes were placed in the bottom of pans lined with moistened paper towels. The pans were placed in a growth chamber at 27°C for 68 h after which the roots were measured. The same procedures were used for soil samples from the field containing unknown chlorsulfuron and metsulfuron concentrations. Soil samples from Experiment 3, were placed in 148-ml waxed cups and three uniformly germinated corn seeds were planted in each cup and grown in a greenhouse maintained at 22 to 27°C. Water was added to the cups as needed to provide good plant growth. Ten days after corn emergence, seedlings were pulled and root lengths measured. Residue levels were quantified from dosage-response curves.

Greenhouse residue experiments in both years (1983 and 1984) were repeated using four replications per bioassay in a randomized complete block design. The data were subjected to analysis of variance and LSDs (0.05) were determined.

RESULTS AND DISCUSSION

Field experiments. Three months after treatment, metsulfuron at 120 g/ha caused crop damage while chlorsulfuron at 120 g/ha and metsulfuron at 70 g/ha caused slight but noticeable damage to barley (Table 2). A similar trend but increased crop damage was observed seven months after application. Common chickweed, mayweed chamomile and henbit were susceptible to chlorsulfuron and metsulfuron while common speedwell showed moderate tolerance. Grain yield from plots treated with chlorsulfuron at 10 g/ha was significantly higher than from plots treated with chlorsulfuron or metsulfuron at 120 g/ha. Yields of barley treated with the highest rate of metsulfuron were not significantly different from the untreated plots because of the severe crop phytotoxicity.

Both chlorsulfuron and metsulfuron at 10 g/ha were superior to 2,4-D as indicated by grain yield. Experiments 1 and 2 were conducted at the same site under the same conditions except for the time of application. As shown in Tables 2 and 3, all rates of chlorsulfuron and metsulfuron applied at the tillered stage of barley provided less weed control than the corresponding rates applied at the two-leaf stage in the fall (Table 1). The results obtained from Experiments 2 (Table 3) and 3 (Table 4) are similar, with the weed control being slightly better in the former. This difference, despite similarity in site and weed flora, could be attributed to the later application in Experiment 3. However, the overall barley yield was lower in Experiment 2 than in Expriment 3 which was the result of heavy grain loss during harvest in Experiment 2.

Table 2. Response of barley and weed species to several herbicides[a] (Experiment 1).[†]

			Visual ratings (0-10)[‡]									
			2-12-83		5-30-83							
							Weed control					
Herbicide	Rate (g/ha)	Growth stage at application	Crop injury	Weed control	Crop injury	Overall	Common chick-weed	Mayweed camomile	Henbit	Common speed-well	Plant height (cm)	Yield (kg/ha)
Chlorsulfuron	10	two-leaf	0.5 d	8.6 cd	0.3 e	9.6	9.8 a	9.7 a	10.0 a	7.6 b-d	88 a	1946 a
	40	two-leaf	0.6 d	9.0 c	1.1 d	9.5	9.9 a	9.8 a	10.0 a	8.4 a-c	83 ab	1626 a-c
	70	two-leaf	1.7 c	9.2 b	2.4 c	9.7	10.0 a	10.0 a	10.0 a	9.5 a	80 a-c	1530 a-c
	120	two-leaf	2.5 b	9.5 a	3.0 bc	9.8	10.0 a	10.0 a	10.0 a	9.0 ab	75 bc	1494 bc
Metsulfuron	10	two-leaf	1.0 c	8.7 cd	0.8 d	9.2	9.4 a	9.6 a	9.4 a	6.8 cd	82 ab	1570 ab
	40	two-leaf	1.3 c	9.0 c	3.0 bc	9.1	10.0 a	10.0 a	10.0 a	7.6 b-d	80 a-c	1848 ab
	70	two-leaf	2.4 b	9.2 a	4.3 b	9.5	10.0 a	10.0 a	9.6 a	8.2 a-d	75 bc	1590 a-c
	120	two-leaf	4.3 a	9.7 a	6.0 a	9.9	10.0 a	10.0 a	10.0 a	9.5 a	71 c	1218 cd
Bromoxynil	560	two-leaf	0 e	7.1 d	0 e	6.9	8.0 b	8.0 b	8.2 b	6.6 d	83 ab	1821 ab
2,4-D	560	tillered	---	---	0 e	2.4	4.6 c	4.6 c	7.0 c	2.0 f	81 ab	1294 cd
2,4-D+dicamba	140+140	tillered	---	---	0 e	3.4	4.4 c	4.4 c	5.8 d	4.2 e	82 ab	1550 a-c
Untreated	---	---	0 e	0 e	0 e	0	0 d	0 d	0 e	0 g	85 a	1062 d

[†] Means within a column followed by the same letter are not significantly different at the 5% level according to Duncan's multiple range test.

[‡] 0-10 ratings: 0 = no crop injury or no weed control and 10 = complete crop or weed destruction.

Table 3. Weed response, crop injury, plant height and yield of barley treated with several herbicides at fully tillered stage of barley (Experiment 2).[†]

		Visual ratings (0-10)[‡]							
			Weed control						
Herbicide	Rate (g/ha)	Crop injury	Overall	Common chickweed	Hayweed camomile	Common speedwell	Plant height (cm)	Yield (kg/ha)
Chlorsulfuron	10	0 d	2.3 d	2.3 d	5.3 b	3 b-d	78 ab	1024 bc
	40	1.3 c	4.3 c	4.0 c	8.3 a	5.5 a	74 a-c	1205 b
	70	2.3 bc	6.5 b	6.7 b	9.0 a	5.0 ab	70 a-c	1274 b
	120	2.7 b	8.2 a	8.0 ab	9.3 a	6.7 a	69 c	1699 a
Metsulfuron	10	2.7 b	8.2 a	8.7 a	9.3 a	4.7 ab	68 c	1152 b
	40	2.7 b	8.2 a	9.3 a	9.3 a	4.3 a-c	72 a-c	1635 a
	70	2.7 b	8.5 a	9.3 a	10.0 a	5.7 a	67 c	1796 a
	120	4.3 a	8.8 a	9.7 a	9.7 a	5.7 a	65 c	1744 a
Bromoxynil	560	0 d	1.0 ef	0.7 de	1.3 de	1.3 de	78 ab	690 d
2,4-D	560	0 d	2.0 de	1.0 de	3.3 bc	2 d	85 a	828 cd
2,4-D+dicamba	140+140	0 d	1.7 de	1.0 de	2.0 cd	2 d	74 a-c	1068 bc
Untreated	---	0 d	0 f	0 e	0 e	0 e	83 ab	234 e

[†] Means within a column followed by the same letter are not significantly different at the 5% probability level according to Duncan's multiple range test.

[‡] 0-10 ratings: 0 = no crop injury or no weed control and 10 = complete crop or weed destruction.

Table 4. Weed response, crop injury and yield of barley treated with several herbicides at the fully tillered stage of barley (Experiment 3).[+]

Herbicide	Rate (g/ha)	Visual ratings (0-10)[‡] Crop injury	 Weed control	Barley yield (kg/ha)
Chlorsulfuron	10	0.8 d-f	5.3 d-f	2614 bc
	40	1.3 c-e	5.8 d	2663 a-c
	70	1.5 c-e	7.0 bc	2722 ab
	120	3.0 a-c	6.8 bc	2356 bc
Metsulfuron	10	2.0 b-d	4.8 fg	2421 a-c
	40	1.8 c-e	7.3 bc	2555 a-c
	70	2.5 b-d	7.5 bc	2609 a-c
	120	3.8 a	8.5 a	2292 c
Bromoxynil	560	1.0 d-f	8.5 gh	2513 a-c
2,4-D	560	0 h	0.8 j	2335 bc
2,4-D+dicamba	140+140	0.3 e-g	3.3 hi	2792 a
Untreated	---	0 h	0 j	1899 d

[+] Means within a column followed by the same letter are not significantly different at the 5% probability level according to Duncan's multiple range test.

[‡] 0-10 ratings: 0 = no crop injury or no weed control and 10 = complete crop or weed destruction.

The results from the field experiments indicate that both chlorsulfuron and metsulfuron at low rates of application have excellent potential as postemergence herbicides for control of a wide variety of broadleaf weeds, with good barley tolerance. Both herbicides have shown excellent activity at low rates against "hard-to-kill" weeds like common chickweed. In earlier studies, postemergence- applied chlorsulfuron at rates ranging from 15 to 70 g/ha provided excellent broad spectrum weed control in small grains (4, 5, 6, 9,). However, growth stage of weeds at the time of application was critical to the herbicidal activity especially at lower rates. Sensitive species except common chickweed generally became more tolerant with age. These results further confirm the higher efficacy of fall- over spring-applied chlorsulfuron reported earlier (7).

Residue and mobility studies on chlorsulfuron and metsulfuron. Corn adequately tolerated herbicide residues which were present in the soil taken from Experiment 1, 10 months following postemergence application of chlorsulfuron and metsulfuron. The results (not presented) showed no significant differences in growth of corn in soils sampled from plots treated with 10 to 120 g/ha of chlorsulfuron or metsulfuron. Chlorsulfuron and metsulfuron soil residues from the highest rate of applications were detected in amounts about 0.1 to 0.3 μg/kg of dry soil in the 0 to 5 and 5 to 10-cm depth soil segments. The residue level in 10 to 20-cm depth soil segments for both herbicides was less than 0.1 μg/kg. In this case again, the data did not show significant differences among soil depth means. However, corn grown in treated soil collected 2 months after application was injured (Table 5), indicating the presence of chlorsulfuron and metsulfuron residues. The mobility of both herbicides in soil was also reflected by the injury levels in soils taken from the 10- to 20-cm depths.

Chlorsulfuron has a reported half-life in the soil of 1 to 2 months and degradation is by hydrolysis to inactive compounds (7). Walker and Brown (11) also found rapid decline of chlorsulfuron in sandy loam soil, with time for 50% loss being between 40 and 50 days. Overall, higher concentrations of chlorsulfuron than metsulfuron were detected from all three soil depths. However, similar degrees of injury were obtained, indicating the higher activity of metsulfuron than chlorsulfuron as evidenced in the field experiments.

The high activity of these herbicides, even at low residue levels, could be beneficial in controlling annual weeds in summer fallow situations. On the other hand, it could create problems in double cropping systems where sensitive crops like soybeans follow small grains. As shown in this study, both chlorsulfuron and metsulfuron leach into the 10 to 20-cm depth. As pointed out by Brewster and Appleby (1), even moldboard plowing probably will not eliminate injury to subsequent crops.

Table 5. Corn root length and estimated residue levels of chlorsulfuron and metsulfuron from treated soil collected from three depths 60 days after application.

	Chlorsulfuron		Metsulfuron	
Rate (g/ha)	Root length (% of untreated)	Concentration (µg/kg soil)	Root length (% of untreated)	Concentration (µg/kg soil)
0-5 cm depth				
0	100	0	100	0
10	53	4.6	65	0.5
40	43	5.9	53	0.8
70	43	7.1	59	0.7
120	33	9.9	39	6.0
LSD (0.05)		1.5		1.6
5-10 cm depth				
0	100	0	100	0
10	68	1.3	78	0.3
40	47	3.2	53	0.3
70	39	5.8	51	0.3
120	33	4.3	46	0.4
LSD (0.05)		1.9		0.1
10-20 cm depth				
0	100	0	100	0
10	53	1.3	75	0.2
40	48	2.6	55	0.2
70	48	2.2	58	0.3
120	40	4.3	49	0.4
LSD (0.05)		2.4		0.1

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VI. ADSORPTION,DESORPTION AND MOBILITY OF CHLORSULFURON IN SOILS

Abstract. 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 increased with pH and decreased with organic carbon. Results indicated that chlorsulfuron could be mobile in non-acidic soils that are low in organic matter.

INTRODUCTION

Chlorsulfuron has shown good selectivity in small grains and is highly active at low rates (10 to 40 g/ha) against a wide range of broadleaf weeds (10, 14). 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, and, thus persistence. Organic pesticides adsorb on both organic and inorganic surfaces depending upon the chemical properties of the adsorbents and adsorbates involved (17). Basic pesticides were strongly adsorbed by soil organic matter (20) and clay minerals (18). Acidic pesticides tend to be adsorbed in moderate amounts in organic matter and in relatively low amounts on clay minerals (3).

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 herbicides in the soil profile is dependent upon soil factors such as pH (2, 12, 15), clay, and organic matter (15). 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. Four soils in agricultural use in Virginia, representing a range of organic matter, clay content and soil pH levels were selected for this study. Soil samples from the top 15 cm of the Ap horizon were collected, air dried and sieved through a 2-mm screen. Soils used were Acredale (Typic Ochraqualfs; fine silty, mixed, thermic), Cullen loam (Typic Hapludults, clayey, mixed, thermic), Roanoke loam (Typic Ochraquults, clayey, mixed, thermic), and Kenansville loamy sand (Arenic Hapludults, loamy, siliceous, thermic). Organic matter was determined by NaOH extraction of humic acid and was converted to organic carbon using a conversion factor of 1.724. The composition and physical characteristics of these soils are presented in Table 1.

Adsorption and desorption. The soil adsorption-desorption techniques used for chlorsulfuron were similar to those employed by other workers (1, 13). 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 µCi/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 to 27°C for 24 h, a period which preliminary studies showed was sufficient to attain equilibrium. Afterwards samples were centrifuged at 1200 rpm for 20 min.

Table 1. Chemical and Physical Characteristics of the Four Soils Studied.

Soil	Particle size distribution, % Sand	Particle size distribution, % Silt	Particle size distribution, % Clay	pH	OC %	CEC, meq/100 g	Bulk density g/cc
Acredale	26.4	50.8	22.8	4.6	2.45	23.9	0.93
Cullen loam	41.4	27.1	31.5	5.6	0.42	13.9	1.12
Roanoke loam	55.2	35.1	9.7	6.4	0.61	10.6	1.25
Kenansville loamy sand	83.7	12.5	3.8	6.9	0.28	3.2	1.48

A 0.5-ml aliquot was removed from each tube, placed in 10 ml of scintillation placed and counted with liquid scintillation counter. The scintillation fluid consisted of 120 g of naphthalene, 4 g of 2,5-diphyloxazole (PPO) and 50 mg of 1,4-bis-2-(5-phenyloxazoyl) benzene (POPOP) made to 1:1 volume with p-dioxone. 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 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; 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:

$$x = kc^{\frac{1}{n}}$$

where x = adsorbed amount (μg/g),

k, n = constants

c = equilibrium concentration (μg/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 (5) was followed. A 3-ul droplet of ^{14}C-chlorsulfuron (0.06 µCi) was spotted 2 cm from the bottom of 15-cm x 20-cm glass plates. The lower 5 mm of each plate was immersed in 0.01 N $CaCl_2$ 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 for 4 weeks. Four replications were made for each soil with R_f values being calculated for each treatment.

Soil column leaching study. Soil columns, 35-cm long, of polyvinyl chloride (PVC) pipe (inside diameter, 9.7 cm) were prepared in the same manner as described by Weber and Whitacre (19). 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 two 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 (2188 g/column), Cullen loam (2628 g/column), Roanoke 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 a week, until it topped the columns. Then each column was allowed to drain free for a period of 24 h. Chlorsulfuron, equivalent to 40 g/ha, was added to the top of each column. Water with 0.01 N $CaCl_2$ was applied dropwise from burets supported over each column, 1.2 cm/day applied for 2 weeks. After the 2-weeks 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 soil followed by Roanoke loam, Cullen loam and Kenansville loamy sand soils (Table 2). 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 a pKa of 3.8. This moderate affinity to organic matter and the relatively low adsorption to clay is similar to results reported for other acidic pesticides (3). 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 by Mersie and Foy (11), 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 (7), and by Grover (4) for phenylurea herbicides.

The desorption data can also be described by the Freundlich equation as shown by Van Genucheten et al. (16).

Table 2. Freundlich Constants of Chlorsulfuron in the Four Soils.

Soil	K	$^1/n$
Acredale	2.4	0.87
Cullen loam	1.1	0.75
Roanoke loam	2.0	0.71
Kenansville loamy sand	1.0	0.78

The Freundlich parameters for each initial herbicide concentration and soil type are given in Table 3. 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 and Roanoke were consistently higher than that of Kenansville and Cullen 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 the Kenansville loamy sand soil, chlorsulfuron migrated with the water front while in the heavier textured soils (Cullen and Roanoke) chlorsulfuron exhibited less movement from the origin. The R_f values from the soil thin-layer chromatography (Table 4) showed that chlorsulfuron moved 2.6 times greater distance in Kenansville loamy sand than in Acredale soil. Regression analysis of R_f values and pH, organic carbon and clay content 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

Table 3. Freundlich Equation Parameters for Desorption of Chlorsulfuron.

		Initial chlorsulfuron concentration, μg/ml			
Soil type	Values	1	4	8	12
Acredale	K	0.31	0.81	1.57	1.93
	1/n	0.38	0.47	0.41	0.41
Cullen loam	K	0.23	0.61	0.71	1.09
	1/n	0.31	0.35	0.40	0.40
Roanoke 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

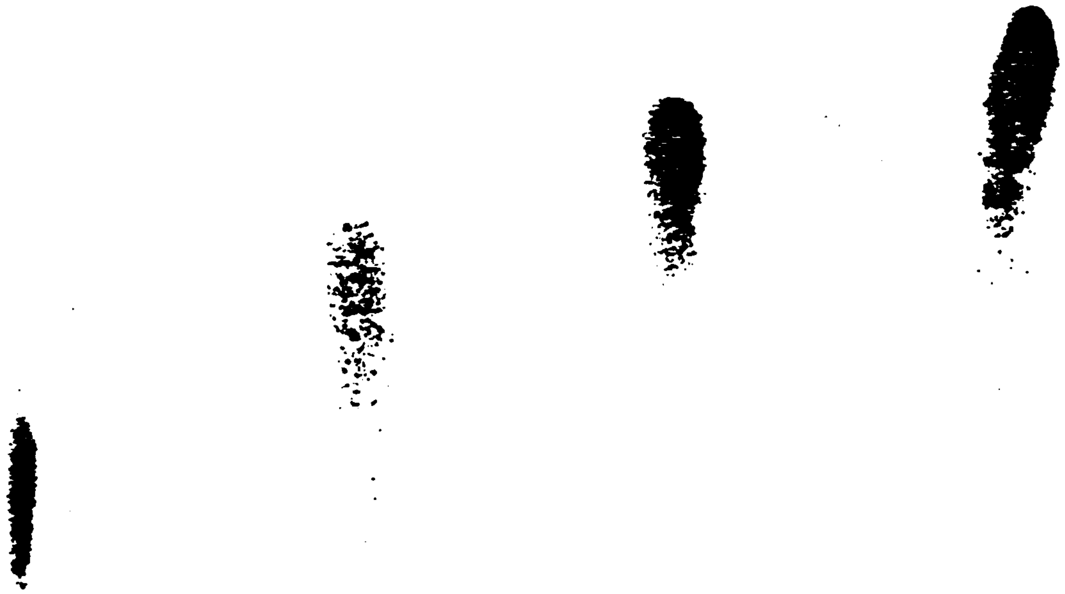

Figure 1. Autoradiogram showing the movement of chlorsulfuron on four soil thin-layer chromatograms: (A) Acredale; (B) Cullen loam; (C) Roanoke loam; and (D) Kenansville loamy sand.

Table 4. Movement of ^{14}C-chlorsulfuron in Four Soils.

Soil	R_f value[a]
Acredale	0.36 a
Cullen loam	0.74 b
Roanoke 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.

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 soil, chlorsulfuron remained in the upper 5-cm segment. The growth of mustard in the top 5 cm of Acredale (Fig. 3) was not retarded as compared in the other soil types. This indicates that not only the herbicide was less mobile in Acredale, but was also unavailable to mustard. 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 4. The least movement of chlorsulfuron observed in the Acredale soil would be anticipated from the adsorptions value. But adsorption values did not substantiate the lower mobility in the less adsorptive Cullen loam soil compared to that of the Roanoke 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 (9). Since diffusion occurs slowly over several months (8), 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 loam soil was very slow, and it has been pointed out by Kohnke (6) 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 loam soil, the rate of uptake of chlorsulfuron by mustard roots might have been reduced as a result of low concentration. Furthermore, chlorsulfuron is

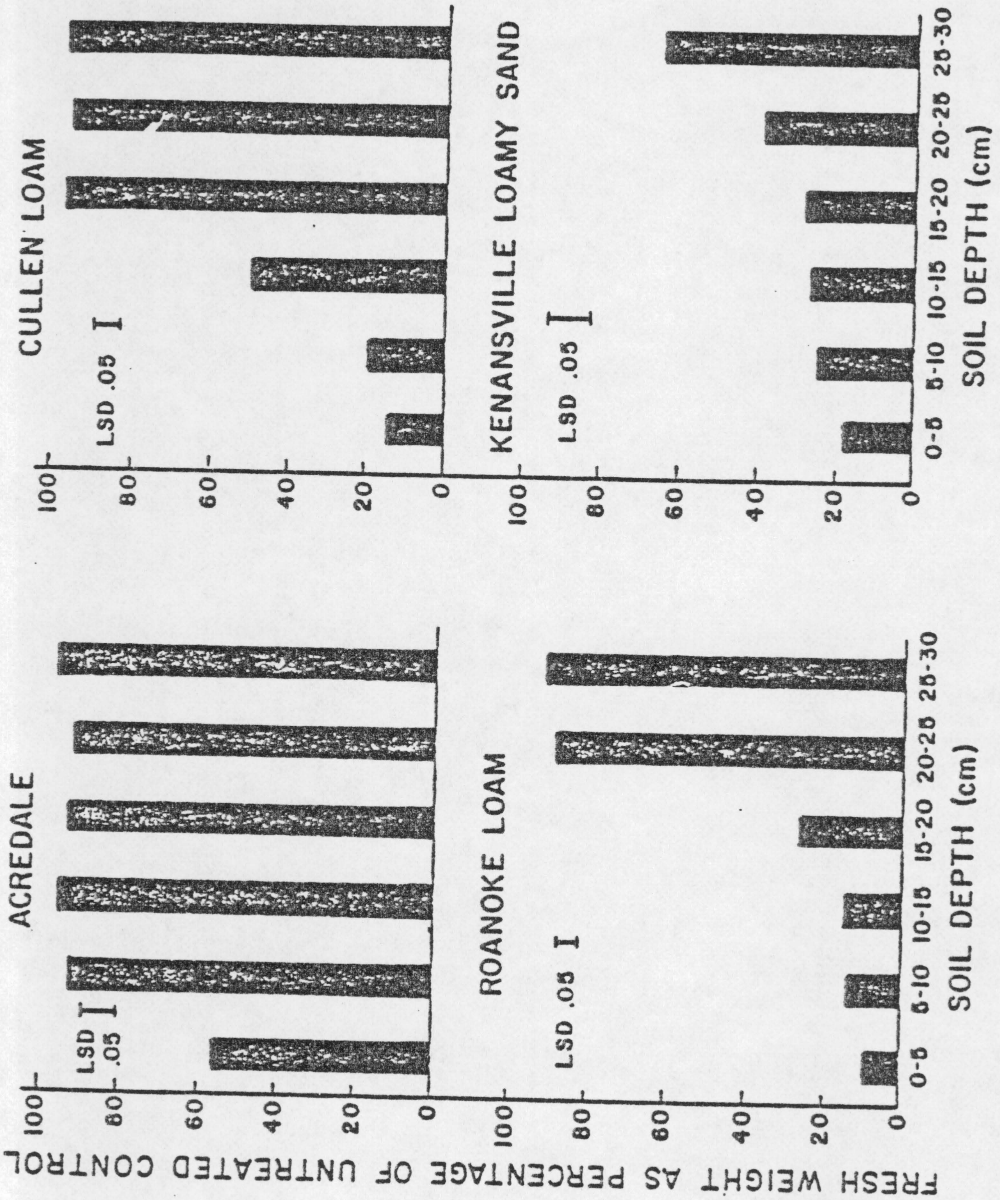

Figure 2. Mustard bioassay of chlorsulfuron in soil column sections.

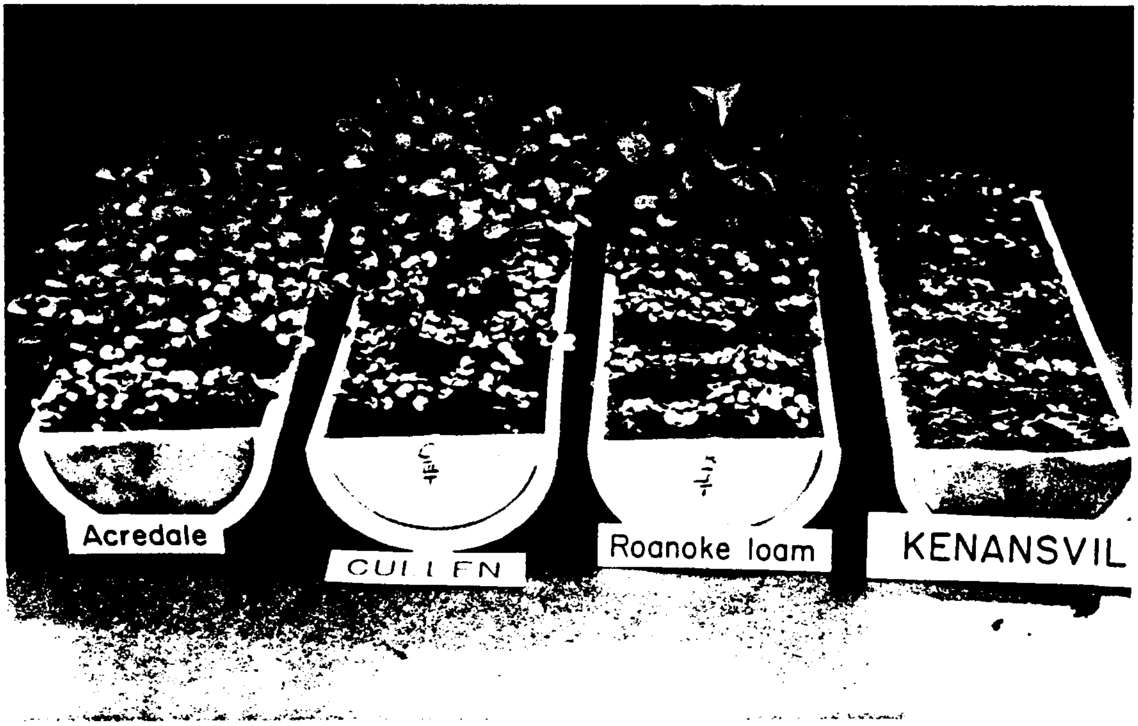

Figure 3. Mustard bioassay showing the distribution of chlorsulfuron in split soil leaching columns of the four soil types. From left to right; Acredale, Cullen loam, Roanoke loam and Kenansville loamy sand. Front is the top of the column while the far end is the bottom.

more soluble in alkaline (27,900 ppm at pH 7) than in acidic solutions (300 ppm at pH 5). Both Acredale and Cullen 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 from 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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VII. PHYTOTOXICITY AND ADSORPTION OF CHLORSULFURON AS AFFECTED BY SOIL PROPERTIES

Abstract The phytotoxicity of chlorsulfuron (2-chloro-N-[[4-methoxy-6-methyl-1,3,5-triazin-2-yl)amino]carbonyl]benzenesulfonamide) compared in six soils and the relationship of activity to soil physical and chemical properties evaluated. The influence of soil pH (4.2 to 7.8) on phytotoxicity and adsorption of chlorsulfuron incorporated into high-organic matter soil was also studied. For the phytotoxicity studies, corn (Zea mays L. 'Pioneer 3320') was used as the bioassay plant. Organic matter was the soil variable most highly correlated with chlorsulfuron phytotoxicity. There was an inverse relationship between phytotoxicity and organic matter. No significant relationship between clay content and chlorsulfuron toxicity was observed. The adsorption of chlorsulfuron decreased with increasing soil pH while desorption was greater at alkaline pH. Phytotoxicity of chlorsulfuron increased with increasing soil pH and reached a maximum at pH 6.9.

INTRODUCTION

Chlorsulfuron has shown good selectivity in cereal crops and is highly active at low rates (10 to 40 g/ha) against a wide range of broadleaf weeds (15). Because soil is a complex system, herbicide behavior may be influenced by many edaphic factors. Investigators have studied the effects of organic matter (17, 20), pH (2, 7, 12), and clay (2, 8) on herbicide activity. Correlation studies (9, 10, 16) have clearly indicated that the organic fraction of the soil is the factor most highly related to the activity of many herbicides. Palm et al. (15) have also noted high activity of chlorsulfuron on gravelly sand soils with less than 1% organic matter.

Soil pH may directly or indirectly influence the activity and detoxification of herbicides by affecting the ionic or molecular character of the chemical, the ionic character of soil colloids, the cation exchange capacity, and the capacity of microbial populations to attack a herbicide (6). Adsorption of the s-triazines by soil colloids is dependent on pH, and many studies (3, 14, 18) have shown the s-triazines to be less phytotoxic under acidic conditions. Because soil pH is subject to considerable change, either by liming or applying sulfur or other acidifying materials, the effect of soil pH on the adsorption and phytotoxicity of herbicides is important in agronomic practice.

The objectives of this study were to identify soil properties influencing the phytotoxicity of chlorsulfuron and to determine the effect of pH on adsorption and toxicity of chlorsulfuron.

MATERIALS AND METHODS

Influence of soil properties on the phytotoxicity of chlorsulfuron. Six agricultural soils in Virginia, representing a wide range of organic matter, textures, and soil pH level, were selected for this study. Soils used were: Acredale (Typic Ochraqualfs, fine silty, mixed, thermic), Emporia sandy loam (Typic Hapludults, fine loamy, siliceous, thermic), Kenansville loamy sand (Arenic Hapludults, loamy, siliceous, thermic), Roanoke loam (Typic Ochraquults, clayey, mixed, thermic), Cecil fine sandy loam (Typic Hapludults, clayey, kaolinitic, thermic), Cullen loam (Typic Hapludults, clayey, mixed, thermic). Soil samples from the top 15 cm of the Ap horizon were collected, air dried, and sieved through a 2 mm-mesh screen.

The soil particle sizes were characterized before sieving by standard soil analyses (4, 5). The bulk density was determined by weighing a known volume of dry soil. The percent organic matter (OM) was determined by the Walkley-Black colorimetric procedure (5) and by NaOH extraction of humic acid. In the latter method, the organic matter was expressed on both soil volume and weight bases. Soil pH was determined for 1/1 (w/v) soil/water suspensions using a combination calomel-glass electrode. Exchangeable bases (Ca^2 and Mg^2) were determined by 1 N NH_4OAc, pH 7, extraction with quantification by atomic absorption spectrophtometry. Exchangeable Al^3 extracted with 1 N KCl and determined by titration with 0.1 N NaOH using phenol-phthalein as an indicator. The sum of exchangeable cations and exchangeable acidity was termed cation exchange capacity (CEC). Base saturation was expressed as the percent of the CEC occupied by Ca, Mg, and K.

The experiment was conducted twice during the summer of 1984 in a greenhouse without supplemental light, maintained between 20 and 27 °C. For each soil there were seven chlorsulfuron concentrations (0, 0.5, 1.0, 2.0, 8, 32, and 128 µg/kg of air dried soil) and each concentration was replicated six times. Portions of air-dried soil (500 g) were weighed and combined with chlorsulfuron by alternately adding one-third of the soil and one-third of an aqueous suspension of the 75% dry flowable formulation of chlorsulfuron. After the incorporation of chlorsulfuron, the soils were potted in 148-ml waxed cups with no drainage. Five corn seeds were planted per cup and after germination plants were thinned to three seedlings per cup. The cups were watered daily as required to maintain adequate soil moisture for growth of corn. Ten days after emergence, the lengths of 3 corn roots were measured from each cup. The herbicide GR_{50} value (concentration of herbicide required to reduce the growth of roots by 50%) for each soil was derived through quadratic regression analyses. A quadratic regression equation was determined which related root growth to herbicide concentration. The regression equation was $Y = b_0 + b_1X + b_2X^2$ where Y was predicted root growth as percent of control, b_0, b_1 and b_2 were partial regression coefficients, and X was herbicide concentration.

The relationship between the GR_{50} values for each soil was evaluated through correlation studies.

The effect of pH on adsorption - desorption of chlorsulfuron. A high organic matter soil, Hyde (silt loam, mixed, thermic, Typic Umbraquults), was collected from the top 15 cm of the Ap horizon and screened through a 2 mm-mesh sieve after being air-dried. Soil properties were organic matter content 12%, pH 4.2, clay content 20.9% and CEC 32.9 meq/100 g. Two weeks before the start of the experiment, portions of the soil were titrated to pH 5.6, 7.0, and 7.8 by adding the required volumes of a $Ca(OH)_2$ solution. Five hundred-gram portions of pH-adjusted soil (air dry basis) were incubated for 2 weeks in polyethylene bags at 27°C to allow equilibrum between the added base and the functional groups of the organic matter.

Adsorption at each pH was determined by placing 1 g of soil (air dry basis) and 10 ml of ^{14}C-phenyl-labeled chlorsulfuron (specific activity 6.03 µCi/mg) in weighed 50-ml, sealed, stainless-steel centrifuge tubes. Commercially formulated chlorsulfuron and ^{14}C-chlorsulfuron (0.06 µCi/10 ml) were combined to obtain an initial herbicide solution concentration of 8 ppm. Each treatment was replicated three times. The samples were shaken for 24 h at 24°C to approach equilibrium. Samples were then centrifuged at 704 g for 20 min. A 0.5-ml sample of the supernatant was removed from each tube, placed in 10 ml of scintillation fluid, and assayed for ^{14}C by scintillation spectrometry. The amounts of radioactivity in these solutions were compared to 0.5-ml samples of the concentration standards. Differences between amounts of ^{14}C present in the standard solutions and in the supernatants of the samples were considered to be the amounts of chlorsulfuron adsorbed.

To assess desorption, supernatant solutions from the weighed tubes were decanted and the tubes were reweighed. Sufficient 0.01 N $CaCl_2$ solution was added to each tube to achieve a 1:10 ratio between soil and solution. The tubes and contents were shaken again for 24 h and centrifuged as described above; a 0.5-ml sample was then removed and assayed.

Influence of pH on the phytotoxicity of chlorsulfuron. Hyde soil was titrated to five pH levels (5.2, 5.6, 5.9, 6.9, 7.8) as described for the adsorption-desorption experiment. Chlorsulfuron to give concentrations of 1, 2, 8, 40, and 80 µg/kg air-dried soil was incorporated into the soil for each pH level. Soil was then potted in 148-ml cups with no drainage. Corn was planted and grown in the greenhouse as described in the first experiment. Ten days after emergence, corn roots were measured and GR_{50} values were determined by curve fitting. Each treatment was replicated four times and the experiment was repeated once.

RESULTS AND DISCUSSION

Influence of soil properties on the phytotoxicity of chlorsulfuron. The six soils varied greatly in their physical and chemical properties (Table 1). Contents of organic matter varied from 1.5 to 7.2% for the Walkley-Black colorimetric determination, while the other two methods used indicated a similar amount of organic matter for the different soils. Clay of the Ap horizon is mainly of mixed mineralogy and the amounts ranged from 3.8 to 31.5%. The soils also varied in their pH values from acidic (4.6) to nearly neutral (6.9). Exchangeable calcium, magnesium and aluminum varied greatly among the soils and ranged from 1.1 to 4.2, 0.33 to 2.2, and 0.05 to 5.51 meq/100 g, respectively. The cation exchange capacity (CEC) which ranged from 3.15 to 23.4 meq/100 g increased with an increase in OM, but no such trend was observed with clay content.

The GR_{50} values for chlorsulfuron in the six soils are shown in Table 1. The herbicide was most toxic in the Emporia soil and least toxic in the Acredale soil. The phytotoxicity of chlorsulfuron in the other four soils was intermediate between these extremes. A lower dosage was required in Cullen soil than in Acredale to reduce root growth by 50%, although the clay content was greater in the former. A similar trend was observed between the Emporia and Roanoke soils. In both cases, Acredale and Roanoke soils had higher organic matter content than Cullen and Emporia soils, respectively. The relationships among the soil properties was examined by comparing simple correlation coefficients (Table 2). Variation in organic matter content correlated with pH and CEC. There was no direct relationship between clay and organic matter content in the

Table 1. Physical and chemical properties of the Ap horizons of the six soils and their GR_{50} values for chlorsulfuron.

Soil property	Acredale	Emporia	Kenansville	Roanoke	Cecil	Cullen
Organic matter (%)						
Acid-dichromate[a]	7.2	1.9	1.5	3.2	2.3	3.0
HA volume[b]	2.28	0.45	0.42	0.76	0.36	0.47
HA weight[c]	2.45	0.33	0.28	0.61	0.29	0.42
Sand (%)	26.4	67.4	83.7	55.2	55.1	41.4
Silt (%)	50.8	22.3	12.5	35.1	24.0	27.1
Clay (%)	22.8	10.3	3.8	9.7	20.8	31.5
Volume weight (g/cc)	0.93	1.36	1.48	1.25	1.26	1.12
Exch. Ca (meq/100 g)	1.10	1.78	1.90	4.20	1.25	3.00
Exch. Mg (meq/100 g)	0.81	0.80	0.33	2.20	0.44	0.90
Exch. K (meq/100 g)	0.30	0.20	0.13	0.11	0.17	0.50
Exch. Al (meq/100 g)	5.51	0.05	0.05	0.05	0.55	0.15
Exch. acidity (meq/ 100 g)	21.19	1.58	0.79	4.16	6.73	9.50
CEC (meq/100 g)	23.40	4.36	3.15	10.67	8.59	13.90
Base saturation (%)	9.44	63.76	74.92	61.01	21.65	31.65
pH	4.6	6.8	6.9	6.4	5.2	5.6
GR_{50} (ppb)[d]	60.3 a	1.2 c	7.9 bc	12.6 b	18.8 b	16.1 b

[a] Walkley-Black colorimetric determination.

[b] NaOH extracted humic acid expressed on soil volume basis.

[c] NaOH extracted humic acid expressed on soil weight basis.

[d] Means with the same letters are not significantly different at the 5% level using Duncan's multiple range test.

Table 2. Simple correlation coefficients (*r*) among soil properties.

Soil property	O.M.[b]	O.M.[c]	Clay	pH	Exchangeable Ca	Exchangeable Mg	Exchangeable Al	CEC	Base saturation
					(*r*)				
Organic matter[a]	0.97	0.98	0.45	-0.77	-0.22	0.17	0.95	0.96	-0.71
Organic matter[b]		0.99	0.26	-0.65	-0.30	0.11	0.97	0.86	-0.58
Organic matter[c]			0.30	-0.68	-0.33	0.07	0.98	0.88	-0.62
Clay				-0.78	-0.10	-0.10	0.34	0.67	-0.83
pH					0.39	0.14	-0.75	-0.85	0.99
Exch. Ca						0.85	-0.50	-0.10	0.40
Exch. Mg							-0.11	0.19	0.18
Exch. Al								0.85	-0.69
CEC									-0.81

[a] Walkley-Black colorimetric determination.

[b] NaOH extracted humic acid expressed on soil volume basis.

[c] NaOH extracted humic acid expressed on soil weight basis.

six soils. The lack of correlation in this study helped to isolate the separate influences of these soil properties on the phytotoxicity of chlorsulfuron. Soil pH was negatively correlated with CEC, indicating the presence of pH-dependent charges.

The inverse relationship between chlorsulfuron phytotoxicity and the soil organic matter content is clearly shown by the correlation coefficient (r) values given in Table 3. Such influence of organic matter on the phytotoxicity of other herbicides has been shown previously (9, 10). The degree of correlation between GR_{50} values and the Walkley-Black colorimetric procedure is lower than that of the NaOH extraction method.

There was no significant correlation between percent clay and chlorsulfuron phytotoxicity, suggesting a low affinity of chlorsulfuron to clay (Table 3). The r values showed an increased trend of chlorsulfuron phytotoxicity with an increase in soil pH, exchangeable Ca and base saturation. Exchangeable Al and CEC were related to the activity of chlorsulfuron, in descending order. Because of the high correlations between these soil properties and organic matter in the six soils, it was not possible to isolate their separate relationships, if any, with the GR_{50} values.

Adsorption-desorption. Chlorsulfuron was adsorbed by the Hyde soil in the largest amount at pH 4.2 and adsorption decreased with an increase in pH (Table 4). This decrease in adsorption with increase in pH was significant at the 5% level. Chlorsulfuron is a weak organic acid with pKa value of 3.8 (21). Although the suspension pH was 4.2, the pH at the colloid surface was probably much lower due to surface acidity (2).

Table 3. Simple correlation coefficients ($\underline{r}$) between GR_{50} values of chlorsulfuron and selected soil properties.

Soil property	Correlation[a]
	($\underline{r}$)
Organic matter[b]	0.86*
Organic matter[c]	0.92**
Organic matter[d]	0.93**
Clay	0.29
pH	-0.62
Exch. Ca	-0.59
Exch. Mg	-0.28
Exch. Al	0.96**
CEC	0.75*
Base saturation	-0.58

[a] Significant at the 5% level (*); significant at the 1% level (**).

[b] Walkley-Black colorimetric determination.

[c] NaOH extracted humic acid expressed on soil volume basis.

[d] NaOH extracted humic acid expressed on soil weight basis.

Table 4. Adsorption-desorption of chlorsulfuron from Hyde soil at different pH values.

pH	Adsorption		Desorption	
	(μg/g)	(%)	(μg/g)	(%)
4.2	14.4 a	18	2.0 a	14.2
5.6	8.9 b	11	1.1 b	10.0
7.0	3.3 c	4	1.0 b	31.2
7.8	0.5 d	0.6	0.2 c	44

[a] Means within columns with the same letter are not significantly different at the 5% level using Duncan's multiple range test.

Maximum adsorption of many organic compounds reportedly occurs at pH ≈ pKa (20) and this could explain the strong adsorption of chlorsulfuron at pH 4.2. At pH values below 3.8, a majority of the chlorsulfuron molecules would be in their molecular form. Because organic matter has a net negative charge (17), chlorsulfuron molecules could be adsorbed by weak physical forces or, as Weber (19) suggested for dicamba (3,6-dichloro-2-methoxybenzoic acid), through hydrogen bonding of molecular species.

Adsorption is said to decrease as solubility in the solvent increases. Solubility of chlorsulfuron in water is pH-dependent with a higher solubility at pH 7 than in acidic solutions, and this could further account for the low adsorption under alkaline conditions. Such an effect has been reported by several workers (2, 11), and Ashton (1) showed that the mobility of triazine herbicides increased in the order of their solubilities.

The desorption of chlorsulfuron from the Hyde soil at pH 4.2 was quite low (Table 4). An average desorption of only 14.2% was found from the acidic Hyde soil while 31.2% was desorbed from soil with pH 7.0. Adsorption of chlorsulfuron on this soil appears reversible and desorption increased with an increase in pH. This study suggests that chlorsulfuron would be adsorbed in lesser amounts by calcareous soils, which are near neutrality in soil reaction, than by acidic soils.

Influence of pH on chlorsulfuron phytotoxicity. Chlorsulfuron became more toxic to corn as the soil pH increased (Table 5). Although the pH optimum for phytotoxicity was 6.9, similar herbicidal activity was noted at pH

Table 5. GR_{50} values of chlorsulfuron determined by corn root bioassay in Hyde soil of different pH values.

pH	GR_{50}[a]	Lower and upper confidence limits (95%)
	(μg/kg)	(μg/kg)
4.2	51.6 a	47.1-56.1
5.2	27.5 b	23.3-32.0
5.6	18.8 c	14.3-23.0
5.9	7.2 d	2.7-11.7
6.9	3.3 d	1.2-7.8
7.8	7.0 d	2.5-11.5

[a] Means with the same letter are not significantly different at the 5% level using Duncan's multiple range test.

5.9 and 7.8. A dramatic decrease in phytotoxicity occurred between pH 5.9 and 4.2. It appears that negatively charged functional groups in the soil dominated. As pH was increased above 5.6, the negative charge on soil colloids would repel the anionic form of chlorsulfuron. This would increase the concentration of chlorsulfuron available for uptake by corn roots. Similar behavior in phytotoxicity has been reported for the acidic herbicides 2,4-D [(2,4-dichlorophenoxy)acetic acid], dicamba, and chloramben (3-amino-2,5-dichlorobenzoic acid) (7), and for a basic herbicide metribuzin [4-amino-6-(1,1-dimethyl-3-(methylthio)-1,2,4-triazin-5(4H)-one] (18). Lavy (13) also found that plant uptake of ^{14}C-atrazine [6-chloro-N-ethyl-N-(1-methylethyl)-1,3,5-triazine -2,4 -diamine] decreased as soil acidity increased.

Although the adsorption of chlorsulfuron at low pH was stronger than at high pH (Table 4), it was not as dramatic as the corresponding decrease in phytotoxicity with decrease in pH (Table 5). This suggests the involvement of other factors in reducing the phytotoxicity of chlorsulfuron under acidic conditions. Zahnow (21) noted a fast rate of chlorsulfuron decomposition at low pH. Corbin and Upchurch (6) reported similar soil pH effects on the detoxication of 2,4-D and dicamba with optimum degradation at pH 5.3 and greatest persistence at 7.5. Since several days are required for corn to germinate and roots to penetrate the soil and thereby contact the incorporated herbicide, it is apparent that the faster chemical or microbial detoxication of chlorsulfuron under acidic conditions could have influenced the phytotoxicity observed in this experiment. Low adsorption coupled with the high desorption and increased phytotoxicity near neutral pH indicate that liming would increase chlorsulfuron activity and, hence, its phytotoxic potential.

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SUMMARY AND CONCLUSION

This research addressed the selectivity and soil behavior of chlorsulfuron. It provided information on the differential response of wheat and barley to root-applied chlorsulfuron, indicated the presence of antagonism between chlorsulfuron and diclofop, demonstrated the safening of corn by naphthalic anhydride against sulfonylurea injury, and showed the influence of soil properties on the availability and movement of chlorsulfuron.

The research on selectivity eliminated uptake and translocation as possible factors for the differential tolerance of wheat and barley to root-applied chlorsulfuron. However, the reason for the differential tolerance is not known. The attempt to determine the relative metabolism of chlorsulfuron in wheat and barley roots was not successful due to low recovery of the herbicide from both species. This type of investigation is still warranted as it could explain the differential tolerance between the two species.

The investigation on the mixture between chlorsulfuron and diclofop demonstrated antagonistic interaction between the two herbicides. It further showed that increasing the rates of the herbicides in the tank mix and separating their application by 16 and 24 h would overcome this antagonism. The bases of this antagonism were not investigated in this research. Future studies on the influence of chlorsulfuron on the uptake, hydrolysis to free acid, and movement of diclofop to meristematic areas might explain the antagonistic interaction between the two herbicides. The action of chlorsulfuron on corn was antagonized by the herbicide safener napthalic anhydride and to a lesser extent by M-32988. The lack of protection of soybean and sugarbeet against chlorsulfuron injury indicates that safeners are effective when there is already some tolerance to the herbicide. However, the eight-fold protection of corn by naphthalic anhydride against chlorsulfuron would permit the planting of corn in fields which had been treated with chlorsulfuron without any danger from possible toxic soil residue. The findings of this research indicate that such carryover could occur in limed soils because chlorsulfuron is readily available at neutral and alkaline pH levels as evidenced by the data in Chapter VII.

The results of field experiments, soil thin-layer chromatography, and hand packed column studies indicated that chlorsulfuron is readily mobile in coarse textured, low organic and high pH soils. The soil type in the field study was silty loam with pH 6.7 with similar physical properties to that of Kenansville loamy sand with pH 6.9 used in the hand packed columns. In both cases chlorsulfuron was detected to a depth of 20 cm. This high mobility is possible because of the low organic matter content and high pH as the adsorption of chlorsulfuron is low at pH 6.9 as shown in the results of Chapter VII.

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