SOIL MOBILITY AND PERSISTENCE OF SULFONYLUREA HERBICIDES AS INFLUENCED BY INORGANIC CATIONS AND WATER-SOLUBLE POLYMERS

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STATEMENT OF THE PROBLEM

Normal agricultural production practices have been shown to significantly alter the concentration of inorganic cations in the surface soil. Those practices also have a major influence on the movement of water through the soil--and thus on the movement of solutes and ions in the water. These ions are directly involved with most of the chemical processes that take place in agricultural soils. Specifically, the ionic status of the soil directly influences the retention and movement of pesticide molecules or ions in the soil. Reduced tillage systems are beginning to become widely used in southwestern U.S. wheat production, and such systems almost invariably call for improved weed control utilizing herbicides and for modified fertilization practices. Reduced tillage procedures also directly influence the penetration of water into and through the soil.

Several herbicides of the sulfonylurea chemical family are now being introduced for weed control in reduced tillage grains and row crops. They are useful herbicides at very low rates--only a few ounces per acre being needed for effective weed control. However, based on their soil persistence characteristics, water solubility, and ionic characteristics, there is a distinct possibility of their movement through the soil after application. The sulfonylurea herbicides chlorsulfuron, triasulfuron, and metsulfuron particularly are expected to become widely used in small grains such as wheat in this part of the U.S.; chlorsulfuron is already used. Chlorimuron may become useful in soybeans. Penetration and distribution of such herbicides depends on soil water movement and such factors as soil pH, clay content, organic matter content, and the presence of various ions (Abernathy et al., 1971; Blair et al., 1988).

There is limited evidence that selected water-soluble acrylic co-polymers may have some potential for reducing the soil mobility of sulfonylurea herbicides (Mahnken, 1988). Such polymers have been used to develop controlled release pesticide formulations in the past. Application of the polymer in the spray, if successful in reducing herbicide mobility, would have considerable potential for reducing herbicide soil movement and would thus lessen concerns about potential groundwater contamination.

Several different mathematical models are currently used to attempt to predict the movement of pesticides through the soil under various conditions. However, none of the widely used models consider the ionic status of the soil other than the pH level (Nofziger et al., 1986; Wagenet et al.,1986).

OBJECTIVES

1. Determine the influence of varying levels of calcium (Ca), potassium (K), magnesium (Mg), and soil pH changes on the phytotoxicity and soil movement of several new sulfonylurea herbicides.

2. Evaluate the potential for anionic acrylic co-polymers to reduce the movement of the herbicides through soil columns.

3. Utilizing the data obtained, assess the ability of currently used mathematical models to successfully predict the movement of the herbicides through the soil to groundwater under the varying soil ionic conditions.

METHODOLOGY

Bioassay development: A rapid and sensitive soil bioassay technique was developed to attempt to detect the presence of the phytotoxic moiety of the sulfonylurea herbicides in soil at minute concentrations. The soils used in these studies are described in the following table.

Table 1. Characteristics of soils used in the bioassay studies.

Type	Texture	Sand	Silt	Clay	OM[a]	pH	CEC[b]
			%				
Teller - a	Loam	45	36	19	1.5	4.8	5.0
" - b						6.5	8.0
Pond Creek -a	Silt loam	32	52	15	1.1	5.1	5.6
" " -b						7.3	9.2
Taloka - a	Silt loam	33	53	15	1.9	4.8	7.2
" - b						7.5	20.2

[a] organic matter content
[b] cation exchange capacity

The procedure developed and utilized in these studies was to use air dried and sieved (2 mm) soil treated in the laboratory with the requisite amount of herbicide in water to produce the desired herbicide concentration in the soil on a w/w basis. The treated soil was mixed in a stainless steel inverting "V" twin-shell blender for two minutes. Treated and untreated soil was placed in disposable 100 by 15 mm petri dishes. Prior to placing the soil in the dish, a 2.5 cm wide double-thick strip of paper toweling was placed along the interior bottom of the dish, long enough that a 4 cm "tongue" protruded over the side. The top was then placed over the surface of the soil in the petri dish and gently tamped down. The soil was then moistened by placing the dish on a platform in a pan of water in such a manner that the dish was not in the water but the "tongue" of paper toweling was. The water then moved into the soil in the petri dish by capillary action. The paper "tongue" was then cut off.

A line was then made across the soil in the petri dish about one-third of the distance from one edge. Five corn or sorghum seeds, which had been pregerminated for 24 hours in a 27 C germination chamber, were placed on the moist soil in the petri dish, with the tip of the radicle at the previously drawn line pointing "down" along the soil surface. After placing the top on the petri dish, a strip of transparent tape was placed across the dish in such a manner as to seal it closed. The edge of the tape was put precisely along the line previously made in the soil to provide a reference point for later measuring. The sealed petri dishes were placed in a 30 C growth chamber in the dark in an inverted position at a 45 degree angle so that the plant roots would grow along the face of the petri dish.

After 24 hours of incubation, the plates were removed from the chamber and the root lengths measured along the face of the plate. The bioassay root length data was subjected to analysis of variance and the differences separated by LSD tests. The readings were analyzed as four subsamples per replication. All experiments consisted of 4 or 5 replications. Experiments were duplicated and the results combined for analysis (Sunderland et al., 1991).

Soil pH variation: Soil samples of Teller loam and Pond Creek silt loam soils were collected from adjacent areas in large field blocks that had been treated differently with agricultural limestone over a period of several years and thus had different pH levels (designated -a and -b in Table 1). Varying pH levels for the Taloka silt loam (pH 4.8 in the field) were achieved by applying $CaCO_3$ and allowing the soil to equilibrate for four weeks to achieve a pH of 7.5 (Prater et al., 1991). Soil samples at the various pH levels were treated with a sulfonylurea herbicide, and a corn or sorghum root petri dish bioassay was conducted (as described above) to evaluate phytotoxicity.

Soil mobility studies: Samples of three soils used for agricultural crop production in Oklahoma were packed into duplicate 5 x 30 cm plastic pipe soil leaching columns (Weber et al., 1982). Both pH and other soil ionic modifications were performed prior to column filling. The soil surface in the columns was then treated with a sulfonylurea herbicide, alone or in combination with an acrylic co-polymer. The columns were then leached with one or two pore volumes of distilled water, applied slowly. After 24 hours of equilibration, the columns were sectioned into 3 cm layers, and each layer was bioassayed as described above for the presence of herbicide. In all instances non-herbicide treated columns were run simultaneously as untreated checks.

Soil ion variation: Mobility of some sulfonylurea herbicides utilizing soil samples with the pH variations listed above were compared in the soil columns. In addition, samples of the Teller-b soil were treated with either KCl or $MgCl_2$ in order to increase the specific cation content by a factor of from two to four. Mobility of the herbicide in the low and high cation soils was evaluated by the column and bioassay methods described previously.

FINDINGS

Bioassay development: Using the petri dish method described with the sulfonylurea herbicide chlorimuron (2-[[[[(4-chloro-6-methoxy-2-pyrimidinyl)-amino]carbonyl]amino]sulfonyl]benzoic acid), there was a significant reduction in the growth of the sorghum roots at the 2 ppbw level of treatment in both soils. In addition, there was a steady decrease in root lengths at rates up to 25 ppbw--the maximum concentration evaluated. Corn and sicklepod were evaluated with the same procedure and were found to work equally well. The Coefficients of Variation (CV's) for these studies were generally in the range of 12 to 25%. Chlorsulfuron (2-chloro-N-[[(4-methoxy-6-methyl-1,3,5-triazin-2-yl)amino]carbonyl]benzenesulfonamide) was also found to work well with this bioassay procedure. Using corn as the assay species, 1 ppbw was detected in both the Teller and the Taloka soils. Again, CV's were usually from 12 to 20.

Using only corn as the assay species, the bioassay procedure was also evaluated utilizing triasulfuron (2,2-(2-chloroethoxy)-N-[[(4-methoxy-6-methyl-amino]carbonyl]benzenesulfonamide), metsulfuron (2-[[[[(4-methoxy-6-methyl-1,3,5-triazin-2-yl)amino]carbonyl]amino]sulfonyl] benzoic acid), and sulfometuron (2-[[[[(4,6-dimethyl-pyrimidinyl)amino]carbonyl]amino]- sulfonyl]benzoic acid). There was a slight difference between soils in bioassay species' sensitivity to the herbicide, but 1 to 4 ppbw could be detected in all instances.

Several sulfonylurea herbicides could be detected in the soil at concentrations as low as 1 ppbw utilizing the described bioassay procedure. Lower concentrations were not attempted except with sulfometuron, but indications were that they might be detectable. The bioassay species were more sensitive to sulfometuron than the other sulfonylurea herbicides, rates as low as 0.25 ppb being detectable. Using this procedure, we were also able to establish effective standard curves to determine the concentration of the herbicides in soil in other studies.

Varietal differences were found to exist as to herbicide sensitivity in the bioassay procedure. For most studies, corn was found to be the most available and reliable assay species to use. We also tried to bioassay water samples by this procedure, using 6 ml of water containing a desired concentration of herbicide to wet 6 filter papers instead of soil in the dishes. Although these were less convenient to work with, we were able to detect concentrations of herbicide in the low ppb range in the water.

Soil pH variation: The influence of soil pH levels on herbicide phytotoxicity was evaluated with the three soils and the five sulfonylurea herbicides. A distinct soil pH influence was noted. For example, in all three soils, chlorsulfuron was found to be phytotoxic at the 1 ppb concentration at the high pH levels but was only phytotoxic at the 4 ppb concentration under the more acid conditions (Table 2). Thus, the herbicide could be expected to provide greater toxicity to sensitive species under the more basic soil conditions. A similar response was noted with chlorimuron (Table 3). Triasulfuron was slightly less phytotoxic to the bioassay species, but a similar response was noted at a slightly higher concentration level. The response of metsulfuron was found to vary more greatly with the soil type, and the pH response was the opposite of the previous statements in the Taloka soil. Sulfometuron phytotoxicity was found not to vary with the soil pH.

Table 2. Effect of soil pH on the phytotoxicity of chlorsulfuron

Herb.	Teller Loam		Pond Creek SiL		Taloka SiL	
Conc.	Low pH	High pH	Low pH	High pH	Low pH	High pH
(ppb)	- - - - root growth as % of check - - - - - - - - -					
0	100.0	100.0	100.0	100.0	100.0	100.0
1	95.5	90.4*	97.2	88.1*	95.5	89.1*
2	91.4	85.6	93.8	84.3	92.8	86.1
4	85.7*	75.0	85.2*	74.2	86.1*	80.0
6	84.6	72.2	80.8	71.4	82.4	76.9
8	81.3	68.2	-	-	-	-
10	-	-	76.9	67.5	76.2	70.0
LSD$_{.05}$	10.3	9.5	11.4	11.2	11.1	10.3

Table 3. Effect of soil pH on the phytotoxicity of chlorimuron

Herb.	Teller Loam		Pond Creek SiL		Taloka SiL	
Conc.	Low pH	High pH	Low pH	High pH	Low pH	High pH
(ppb)	---- root growth as % of check ---------					
0	100.0	100.0	100.0	100.0	100.0	100.0
1	94.1	89.9*	92.7	84.7*	94.8	88.5*
2	90.1*	81.7	90.9	82.0	92.7	84.7
4	82.1	75.2	82.1*	73.6	84.2*	81.0
6	74.9	67.3	78.3	68.7	78.4	75.8
8	71.1	65.4	-	-	-	-
10	-	-	64.2	61.3	70.2	67.8
LSD$_{05}$	10.3	9.5	11.4	11.2	11.1	10.3

Soil mobility studies--pH: Initial results indicate that chlorimuron, chlorsulfuron, and triasulfuron were sometimes more mobile in soils at the higher pH than at the lower. Chlorimuron was slightly more mobile than chlorsulfuron and triasulfuron in the Pond Creek soil at the higher pH and also in the Teller loam. Chlorsulfuron and triasulfuron remained fairly immobile in the Teller loam soil with no significant movement from the surface of the soil, while chlorimuron was only slightly mobile.

Soil mobility studies--polymers: The polymers utilized were not found to significantly influence the phytotoxicity of the herbicides. In the column studies neither the Acrysol nor the Carboset consistently influenced the movement of chlorimuron, chlorsulfuron, or triasulfuron through the soil. In some instances the polymers did appear to inhibit the movement of triasulfuron through the soil in that higher concentrations of herbicide were detected at the lower depths in columns that did not receive the polymer. This generally occurred when 2 pore volumes of water were used in the leaching process.

Soil mobility studies--ionic status: The soil layers tended to show slightly higher concentrations of both triasulfuron and chlorsulfuron in the deeper depths of the soil columns when lower levels of K ions were present. For example, there was more chlorsulfuron in the deeper layers when the soil contained 243 lb/A of K than when there was 761 lb/A. The differences in concentration were relatively minor and were more likely to be apparent at the 0.5 oz/A rate of the herbicide. This difference was less consistent when Mg was the ion of concern.

Mathematical modeling comparisons: Since variations in herbicide mobility in the soil due to ionic status were not consistently obtained no attempt was made to evaluate the ability of models to predict the herbicide movement.

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