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Sulfentrazone behavior in surface soil : dissipation, degradation, adsorption and mobility

George Anthony Ohmes

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To the Graduate Council:

I am submitting herewith a dissertation written by George Anthony Ohmes entitled "Sulfentrazone behavior in surface soil : dissipation, degradation, adsorption and mobility." I have examined the final electronic copy of this dissertation for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Doctor of Philosophy, with a major in Plant, Soil and Environmental Sciences.

Thomas C. Mueller, Major Professor

We have read this dissertation and recommend its acceptance:

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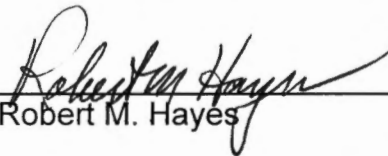
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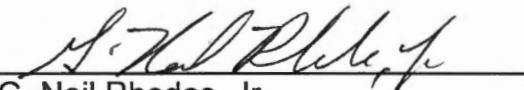
To the Graduate Council:

I am submitting herewith a dissertation written by George Anthony Ohmes, Jr. entitled "Sulfentrazone Behavior in Surface Soil: Dissipation, Degradation, Adsorption and Mobility." I have examined the final copy of this dissertation for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Doctor of Philosophy, with a major in Plant and Soil Sciences.

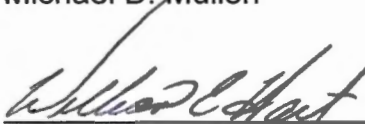

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We have read this dissertation
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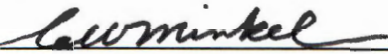

Robert M. Hayes


G. Neil Rhodes, Jr.


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William E. Hart

Accepted for the Council:


Associate Vice Chancellor and
Dean of The Graduate School

**SULFENTRAZONE BEHAVIOR IN SURFACE SOIL:
DISSIPATION, DEGRADATION, ADSORPTION AND MOBILITY**

A Dissertation

Presented for the

Doctor of Philosophy

Degree

The University of Tennessee, Knoxville

George Anthony Ohmes, Jr.

May 1999

AG-VET-MED.

Thesis

99

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DEDICATION

I dedicate this dissertation to my wife Rebecca Ohmes, whose patience, love and encouragement made this endeavor possible and to my son, Clayton Ohmes, who made it bearable.

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The author would like to express his appreciation to the following:

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Dr. Andy Kendig and Dr. Mike DeFelice, the Missouri boys who started it all.

ABSTRACT

A rapid method for the determination of sulfentrazone in soils is described. The method consists of extraction of soil samples with methanol, filtration, liquid chromatographic separation of methanol-soluble components by using a C₁₈ column, and ultraviolet detection with absorbance at 220 nm. Recoveries from fortified soils were >85% for sulfentrazone from the surface soils. Average percent relative standard deviations over the soils examined was 7.7%. The limit of detection for sulfentrazone was 40 ng/g soil.

Sulfentrazone dissipation and degradation was examined in field and laboratory experiments. Field studies were conducted in 1995, 1996 and 1997 at Knoxville, TN on soils of the Sequatchie loam series. Sulfentrazone half-life varied with rainfall under field conditions. In 1995, the half-life of sulfentrazone was 113 d. In 1996, the half-life was 25 d. In 1997 (location one), the half-life of sulfentrazone was 24 d. In 1997 (location two), the half-life of sulfentrazone was 85 d. Injury to cotton from sulfentrazone was observed the year following application when half-lives were \geq 85 d.

Sulfentrazone degradation, under controlled conditions, in autoclaved soil and nonautoclaved soil taken from 0 to 10 cm and 30 to 40 cm depths had half-lives of 198, 93, and 102 d, respectively. In general, sulfentrazone dissipation was influenced by both microbial and chemical degradation mechanisms.

Sulfentrazone adsorption and mobility was evaluated in seven soils with varying soil properties under laboratory conditions. Adsorption was evaluated

using a modified slurry technique. Mobility was evaluated using packed soil columns under saturated flow conditions. The order of adsorption to soil was Drummer silt loam > Sequatchie loam > Dothan loamy sand > Bosket sandy loam > Malden loamy sand > Commerce silty clay loam > Harkey clay loam. Greater adsorption of sulfentrazone occurred in soils with greater organic matter content and lower pH. The Malden loamy sand was the only soil that did not follow this trend possibly due to high sand and low organic matter content. Sulfentrazone movement under saturated flow conditions in 27 cm soil-packed columns varied with each soil. In general, movement was greater in soils with low adsorption. Sulfentrazone movement was limited to the upper 9 cm in the Sequatchie loam and Drummer silt loam. Movement increased down the column with increasing pH. Sulfentrazone movement was greater in coarse textured soils regardless of pH.

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PART I

Introduction

Herbicide Characteristics

Sulfentrazone, [*N*-{2,4-dichloro-5-{4-(difluoromethyl)-4,5-dihydro-3-methyl-5-oxo-1*H*-1,2,4-triazol-1-yl}phenyl}methanesulfonamide], was discovered by FMC corporation in 1985 (Hancock 1995). Sulfentrazone is in the *N*-phenyl heterocycle subclass of protoporphyrinogen oxidase (PROTOX) inhibitors and a member of the triazolinone chemistry (Anderson et al. 1994; Leung et al. 1991). Sulfentrazone uptake is by plant root and foliage, however, like diphenyl ethers, translocation from foliar applications is minimal due to rapid plant cell membrane disruption (Duke et al. 1990; Duke et al. 1991). Tolerance of sulfentrazone is primarily through differential metabolism (Dayan et al. 1996, 1997). Sulfentrazone is a weak acid with a pKa of 6.56 (FMC Corp. 1989). Sulfentrazone has a water solubility of 110 $\mu\text{g/g}$ at pH of 6.0, 780 $\mu\text{g/g}$ at pH of 7.0, and 1600 $\mu\text{g/g}$ at pH of 7.5 and a vapor pressure of 1×10^{-9} mm Hg at 25 C (FMC Corp. 1989). This suggests that sulfentrazone is fairly soluble and has low volatility.

Biological Activity

Sulfentrazone is labeled for weed control in soybeans (*Glycine max* L.) as a package mix with chlorimuron, ethyl 2-[[[(4-chloro-6-methoxy-2-pyrimidinyl)amino]carbonyl]amino]sulfonyl]benzoate, and in tobacco (*Nicotiana tabacum* L.) as a single entity product. Sulfentrazone controls a broad spectrum of broadleaf and grass weed species when applied preplant incorporated or preemergence (Ohmes et al. 1998; Oliver et al. 1995; Vidrine et al. 1996). Ivyleaf morningglory

(*Ipomoea hederacea* L.), entireleaf morningglory (*Ipomoea hederacea* var. *intergriuscula* Gray), pitted morningglory (*Ipomoea lacunosa* L.) and common cocklebur (*Xanthium strumarium* L.) are common weeds in Mid-South soybean fields. Sulfentrazone has proven to be effective at controlling entireleaf morningglory at rates as low as 0.14 kg/ha, where common cocklebur, pitted morningglory (*Ipomoea lacunosa* L.), and yellow nutsedge (*Cyperus esculentus* L.) are less sensitive and required rates up to 0.42 kg/ha (Hancock 1992; Vidrine et al. 1996). Sicklepod (*Senna obtusifolia* L.) is not controlled by sulfentrazone (Dayan et al. 1996).

Reduction of early season soybean competition can have a positive influence on soybean yield (Radosevich et al. 1997). Preemergence weed control is one way of providing this reduction. There were no known cases of weed resistance to PROTOX inhibitors in 1996 (Duke et al. 1996), therefore the addition of sulfentrazone could be important in resistance management.

There are genotype differences for response to sulfentrazone (Schmidt et al. 1998), resulting in injury to sensitive soybean varieties, in particular 'Hutcheson' cultivar and related genetic backgrounds (Dayan et al. 1997; Swantek et al. 1998). Conditions that are conducive to injury include soils with low organic matter and high soil moisture (Wehtje et al. 1995).

Dissipation Under Field Conditions

The benefits of a soil applied herbicide like sulfentrazone is that it remains in the soil long enough to provide season-long weed control. The dissipation rate

of an herbicide in soil affects weed control and influences the environmental fate of that herbicide (Cheng 1990). Persistence is not solely dependent on the herbicide but is affected by transport and transformation processes which can vary between soils, location, and seasons (Hurle and Walker 1980). Herbicide dissipation is influenced by several factors which include environmental condition, soil properties, transformation processes, and transport processes. Environmental conditions, which include rainfall and temperature, impacted the fate of a soil applied herbicide because moisture and temperature are known to aid in transformation processes and rainfall may influence the potential for movement (Basham and Lavy 1987; Braverman et al. 1986; Gan et al. 1995; Grey et al. 1997). Soil properties which include soil texture, pH, and organic matter content influence the potential availability of a herbicide to the plant or movement through the soil profile (Baughman et al. 1996; Beckie and McKercher 1989; Grey et al. 1997; Loux and Reese 1992; Vencill and Banks 1994). Transformation processes include microbial, photochemical and chemical degradation (Guth 1980; Basham and Lavy 1987; Braverman et al. 1986; Gan et al. 1995; Yen et al. 1994). Dissipation may also be influenced by application method (Renner et al. 1988), tillage (Brown et al. 1994; Mills and Witt 1991), previous herbicide use (Harvey 1987; Wagner et al. 1996) and herbicide formulation (Hurle and Walker 1980; Peterson et al. 1988). However, dissipation is usually independent of application rate (Hurle and Walker 1980; Keys and Friesen 1968; Mueller et al. 1990). One study indicated that sulfentrazone efficacy was related to organic matter, pH and moisture (Wehtje et al. 1995). It

was found that decreased weed control was effected predominantly by increased organic matter (Wehtje et al. 1995). Sulfentrazone availability in soil solution increases as soil texture becomes coarser and pH increases (Grey et al. 1997).

Persistence and potential carryover of soil applied herbicides can be affected by soil type, environmental conditions and rotational crop selected (Rogers et al. 1986).

Microbial Degradation

Microbial degradation is an important part of dissipation of many compounds (Basham and Lavy 1987; Krueger et al. 1991; Mueller et al. 1991; Mueller et al. 1992), however, separating abiotic and biotic factors can be difficult (Joshi et al. 1985; Wallnofer and Engelhardt 1989).

There are several factors that influence rate of microbial degradation of herbicides, including soil pH, moisture, temperature, and depth (Basham and Lavy 1987; Hurlle and Walker 1980; Mueller et al. 1991 and 1992; Torstensson 1980). Microbial degradation maybe reduced at lower soil moisture and lower temperatures (Basham and Lavy 1987). For example, imazaquin phytotoxicity was rapidly lost when soil conditions were warm and moist (Basham and Lavy 1987). Microbial degradation of fluometuron is slower at increasing soil depths (Mueller et al. 1992). Previous herbicide use can enhance degradation due to an increase in microbial populations, which results in rapid degradation of that same herbicide or related products in subsequent years (Harvey 1987; Mueller et al. 1991; Wagner et al. 1996). The organic matter content of the soil is related to increased adsorption (Mueller et al. 1992; Peter and Weber 1985), which can

also decrease amount of degradation due to less available herbicide. For example, alachlor and metolachlor adsorption was positively correlated with soil organic matter (Peter and Weber 1985).

Microbial transformations are predominantly caused by enzymes under aerobic conditions, and since most herbicides possess a structure normally not occurring in nature, these enzymes which catalyze reactions may be induced and cause an initial lag period (Wallnofer and Engelhardt 1989). Anaerobic metabolism of herbicides can occur in the environment, although it usually occurs at a slower rate (Gennari et al. 1994; Krueger et al. 1991). Researchers have classified enzymatic reactions involved in pesticide decomposition and transformation as: 1) direct degradation through intracellular metabolism in which the pesticide serves as a source of energy for growth (catabolism), 2) incidental transformation in which microorganisms cannot derive energy for growth (co-metabolism), 3) transformation by extracellular enzymes, and 4) conjugation of pesticide molecules with other synthetic or natural substances resulting in complex new products (Torstensson 1980; Wallnofer and Engelhardt 1989). However, there are cases where non-enzymatic reactions contribute to transformation of an herbicide, either through pH changes or production of substances that react with herbicides in photochemical and chemical reactions (Torstensson 1980). The chemical structure of the herbicide is important on how the microorganisms will transform the herbicide molecule (Wallnofer and Engelhardt 1989). Microorganisms may attack non-aromatic compounds or side chains of aromatic compounds by oxidation and/or hydrolysis (Wallnofer and

Engelhardt 1989). Hydrolysis is one of the predominant herbicide transformations by microorganisms, where water and enzyme catalysts reduce large complex molecules (Wallnofer and Engelhardt 1989). For most herbicides, microbial degradation is most rapid near the surface under warm and moist soil conditions (Basham and Lavy 1987).

Adsorption and Mobility

Organic compounds can be adsorbed to the soil colloid surface and absorbed into soil organic matter. Since both of these processes usually occur to some degree, the term sorption is used to refer to this phenomenon. Organic compounds that are absorbed are considered unavailable. Therefore, adsorption is one of the main factors controlling soil solution concentration (Walker 1980). Adsorption is a surface process that is affected by organic matter, clay content and pH (Loux and Reese 1992; Mueller et al. 1992). Due to these variations, herbicide rates sometimes vary according to soil type and are generally lower for soils with low clay or low organic matter compared to high clay or organic soils (Walker 1980). Both physical and chemical forces are involved in adsorption of herbicides. Physical adsorption is the result of van der Waals forces (Grey et al. 1997). Chemical adsorption include high-energy interactions, such as ionic bonds, and/or low-energy relations, such as hydrogen bonds (Calvert 1980;). Adsorption depends on three factors: molecular properties of herbicide, the make up of the soil and the experimental conditions under which the adsorption is studied (Calvert 1980).

Electronic configuration, molecular volume, and water solubility are primary

aspects of a herbicide's molecular makeup (Calvert 1980). These aspects dictate how well that particular herbicide adsorbs, which ultimately affects the fate of that product. The electronic configuration of an herbicide determines if the herbicide carries a permanent charge, can be ionized or neutral (Calvert 1980). The possibility of an herbicide to be charged or neutral explains the varying persistence under different soil conditions, such as pH (Loux and Reese 1992; Schneiders et al. 1993; Talbert and Fletchall 1965). However, it is difficult to predict adsorptive behavior in herbicides that dissociate to form an ion (Bailey et al. 1968).

Sulfentrazone is a weak acid with a pKa of 6.56 (FMC Corp. 1989). Acidic herbicides exist as either anions or neutral molecules depending on soil solution pH (Grey et al. 1997). Water solubility of an herbicide indicates the potential for movement through the soil profile.

Soil characteristics also affect adsorption of herbicides (Calvert 1980; Carringer et al. 1975; Mueller and Banks 1991; Mueller et al. 1992; Peter and Weber 1985). The type and amount of clay can affect adsorption due to increased surface area (Calvert 1980; Carringer et al. 1975; Mueller and Banks 1991; Peter and Weber 1985). For example, adsorption of alachlor and metolachlor increased with increasing surface area, clay content and organic matter content (Peter and Weber 1985). Increasing soil organic matter content tends to correlate with increased adsorption (Mueller and Banks 1991). Soil pH can influence adsorption of soil applied herbicides. For example, sulfentrazone and imazaquin adsorption decreases with increasing pH (Grey et al. 1997; Loux

and Reese 1992), while chlorimuron adsorption increases with increasing pH (Wiese et al. 1988). When herbicide molecules are cationic, clay and organic matter are most significant with respect to adsorption (Grey et al. 1997). Anion adsorption is largely dependent on the presence of a pH dependent charge of soil components present, such as hydroxides and oxyhydroxides of aluminum or iron (Sparks 1995). Therefore, anion adsorption can be pH dependent. The adsorption of both anion and cations can occur in agricultural soils (Grey et al. 1997).

Adsorption can also be affected by characteristics of the experimental procedures used to obtain adsorption data. These characteristics include temperature (Talbert and Fletchall 1965), ionic composition and pH of the solution (Calvert 1980; Loux and Reese 1992), and soil:water ratios (Calvert 1980).

Herbicide mobility is both an agronomic and environmental concern. Agronomically, soil applied herbicides that readily move in the soil can result in decreased weed control. Environmentally, herbicides that readily move in the soil may be a potential groundwater contaminant, due to vertical movement through the soil profile. Mobility has been studied using soil columns (Fleming et al. 1992; Mueller and Banks 1991; Peter and Weber 1985) and in field studies (William et al. 1997) because they offer a good representation of a field and have been used to evaluate potential leaching through a soil profile.

Sulfentrazone in soil solution should exist as either the neutral form at $\text{pH} < 6$, or as an anion at $\text{pH} > 7$ and both when pH is between 6 and 7. Grey et al.

(1997) determined that pH had the greatest effect on adsorption, with adsorption decreasing in response to increasing pH. The greatest decrease occurring at pH above the pKa of sulfentrazone (Grey et al. 1997). Mobility generally reflected adsorption (Grey et al. 1997).

Knowledge on the behavior of sulfentrazone in soil will give insight on its performance under varying environments. The following sections describe development of a method to detect sulfentrazone using high performance liquid chromatography. Then how the method was used to evaluate sulfentrazone dissipation and carryover potential under field conditions, degradation mechanisms, absorption, and mobility in soils with varying properties.

PART II

Liquid Chromatographic Determination of Sulfentrazone in Soil¹

¹To be submitted for publication in Journal of Association of Official Analytical Chemists. Authors: G. Anthony Ohmes and Thomas C. Mueller. Graduate Research Assistant and Associate Professor, The University of Tennessee, Dept. of Plant and Soil Sciences, PO Box 1071, Knoxville, TN 37901.

Introduction

Sulfentrazone [*N*-{2,4-dichloro-5-{4-(difluoromethyl)-4,5-dihydro-3-methyl-5-oxo-1*H*-1,2,4-triazol-1-yl}phenyl}methanesulfonamide] is a soil-applied herbicide for use in soybeans and tobacco (Figure 1)². Sulfentrazone is in the N-phenyl heterocycle subclass of protoporphyrinogen oxidase (PROTOX) inhibitors and a member of the triazolinone chemistry (Anderson et al. 1994). The application rate ranges from 275 to 425 g ai/ha. Sulfentrazone has a water solubility of 110 $\mu\text{g/g}$ at pH 6.0, 780 $\mu\text{g/g}$ at pH 7.0, and 1600 $\mu\text{g/g}$ at pH 7.5 and a vapor pressure of 1×10^{-9} mm Hg at 25 C (FMC Corp. 1989).

A method of detection for sulfentrazone currently does not exist in the literature. Analytical methodology was developed for the determination of sulfentrazone at ppb levels in soil, using an external standard liquid chromatographic (LC) method with ultra-violet (UV) detection. This methodology could be used to support studies on the bioavailability and environmental fate of sulfentrazone.

Materials and Methods

Apparatus and Reagents

a) *LC system*.- Waters liquid chromatograph, including Model 680 control unit, Model 717 autoinjector, Model 510 solvent delivery system, Model 486 tunable UV detector (Milford, MA). Additionally, a Hewlett-Packard (San Fernando, CA) chemstation software analysis was used.

²Figures and Tables are located in Appendices A and B.

b) Analytical column.- 25 cm x 4.6 mm id, 5 μ m, LC-C₁₈ 18% carbon-load, end-capped (Whatman, Clifton, NJ).

c) Solvents.- HPLC grade (Fisher Scientific, Fair Lawn, NJ and Burdick and Jackson, Muskegon, MI).

d) Mobile phase.- Initially, isocratic acetonitrile-acidified (0.1% H₃PO₄) water (50 + 50, v/v) (0-12 min) followed by a solvent flush of acetonitrile-acidified water (90 + 10, v/v) (8 min).

e) Analytical standards.- Sulfentrazone (FMC Corporation, Princeton, NJ). Standard was 92.8% pure and used without purification.

Soil Selection

Soils were collected from the 0 to 10 cm depth from seven locations. Soils used were from Sequatchie loam (fine-loamy, siliceous, thermic Humic Hapudult), Drummer silt loam (fine-silty, mixed, mesic Typic Haplaquolls), Malden loamy sand (coarse-sandy, mixed, thermic Typic Udipsammments), Bosket fine sandy loam (fine-loamy, mixed, thermic Mollic Hapludalfs), Commerce silty clay loam (fine-silty, mixed, nonacid, thermic Aeric Fluvaquents), Harkey clay loam (coarse-silty, mixed, calcareous, thermic Typic Torrifuvent), and Dothan loamy sand (coarse-sandy, mixed, Plinthic Kandiudults) series. Soil selected represented a variation in texture, pH, cation exchange, organic matter content (Table 1) and had no previous sulfentrazone exposure. These soil properties influence the efficiency of extraction as well as the environmental fate of the herbicide. Determination of soil characteristics was made using standard

procedures (Chapman 1965; Gee and Bauder 1986; McLean 1982; Nelson and Sommers 1982). All soils were passed through a 10-mesh (2 mm) sieve prior to analysis.

UV Detection

UV detectors measure the absorbance of an organic compound at a specific wavelength (Snyder and Kirkland 1979). Maximum absorbance for sulfentrazone was 220 nm. Several acetonitrile-water and methanol-water combinations were evaluated for herbicide retention time and capacity factor (k') (Table 2). Capacity factor was determined by the formula $k' = (\text{retention time} - \text{dwell time})/\text{dwell time}$ (Snyder and Kirkland 1979), where retention time is the time in minutes for sulfentrazone peak to elute and dwell time is the time in minutes for a nonretained component (solvent peak) to pass through the system. Acidifying the water with 0.1% v/v of phosphoric acid (H_3PO_4) in the mobile phase improved resolution of sulfentrazone and peak shape. The mobile phase selected was acetonitrile-water (50+50, v/v). Because of interference from soil extracts, a solvent flush (90% acetonitrile) was added after sulfentrazone elution. The total run time per sample was 30 min. The accuracy of the analysis was examined by injection of a series of standards containing sulfentrazone in methanol at 0.005 to 1 $\mu\text{g}/\text{mL}$. Injection volume was 50 μL . This range corresponded to herbicide soil concentration of 0.01 to 2 $\mu\text{g}/\text{g}$.

Extraction

Analytical sulfentrazone (in methanol) was added to duplicate 250 mL

polyethylene bottles with screw-top caps (Nalgene, Rochester, NY) containing 40 g of air-dried soil to achieve soil concentrations of 950 ng/g (ppbw). After allowing the methanol to dry the bottles were capped and hand shaken, then allowed to statically equilibrate for 24 hr. Additional controls included sulfentrazone added to bottles containing no soil and each soil containing no sulfentrazone. The seven soils were examined for extraction efficiency in a single experiment using duplicate samples. Methanol (80 mL) was added to each bottle before they were placed on a shaker (Eberbach, Ann Arbor, MI) operated at 180 rpm at 25 C for 16 hr. The extract was then filtered through 2 Whatman No. 1 filter papers (Whatman, Clifton, NJ) directly into 4 mL autosampler vials.

Results and Discussion

Injection of 50 μ L of sulfentrazone standards produced a peak with a retention time of 3.7 to 14.9 min, depending on mobile-phase composition (Table 2). At equal relative concentrations, methanol-containing mobile phases had greater capacity factors than those containing acetonitrile (Table 2). The acetonitrile-water (50+50) mobile phase provided adequate separation and good peak symmetry without an excessively long analysis time.

The sulfentrazone standard curve (0 to 1000 ng/ml) was linear with an $r^2=0.98$ ($n=7$, data not shown). Liquid chromatograms of soil extracts had no major peaks eluding in the retention window of sulfentrazone. Sulfentrazone recoveries from all soils ranged from 88 to 103% (Table 3). The precision of the method was good, as indicated by an average relative standard deviation (RSD)

of 7.7% for all recoveries (Table 3).

With a signal-to-noise ratio of 3:1, a conservative limit of detection for this methodology is 20 ng/ml for sulfentrazone. The simple extraction method would allow the rapid determination of sulfentrazone in large numbers of samples at levels suitable for many agronomic purposes. The method probably lacks the necessary sensitivity to perform environmental analysis of trace concentrations of sulfentrazone.

PART III

Sulfentrazone Dissipation in Surface Soil³

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Introduction

The dissipation rate of an herbicide in soil affects weed control and influences the environmental fate of that herbicide (Wehtje et al. 1995; Cheng 1990). The environmental fate is governed by the retention, transformation, and transport processes (Cheng 1990). Persistence and potential carryover of soil applied herbicides can be affected by soil texture, environmental conditions and rotational crop selected (Rogers et al. 1986). One study indicated that sulfentrazone efficacy was related to organic matter, pH and moisture, with weed control decreasing predominantly with increasing organic matter (Wehtje et al. 1995). Sulfentrazone availability in the soil solution increases as soil texture becomes coarser and pH increases (Grey et al. 1997). The primary method of soil dissipation is considered microbial degradation and the reported half life is 110 to 280 d depending on soil and environmental conditions (FMC Corp. 1989).

Sulfentrazone inhibits protoporphyrinogen oxidase (PROTOX) and is a member of the triazolinone chemistry (Anderson et al. 1994; Leung et al. 1991). Sulfentrazone has a water solubility of 110 $\mu\text{g/g}$ at pH 6.0, 780 $\mu\text{g/g}$ at pH 7.0, and 1600 $\mu\text{g/g}$ at pH 7.5 and a vapor pressure of 1×10^{-9} mm Hg at 25 C (FMC Corp. 1989). This suggests that sulfentrazone is fairly water soluble and has low volatility. Conditions that are conducive to injury include soils with low organic matter and high soil moisture (Wehtje et al. 1995). Sulfentrazone is labeled for weed control in soybeans (*Glycine max* L.) as a package mix with chlorimuron and in tobacco (*Nicotiana tabacum* L.) as a single entity product. Sulfentrazone

controls many dicot and monocot weed species when applied preplant incorporated or preemergence (Ohmes et al. 1998; Oliver et al. 1995; Vidrine et al. 1996).

Detailed research on the dissipation and degradation of this product is currently unavailable. This research will help achieve a better understanding of the characteristics of sulfentrazone that influence its environmental fate.

The objectives of this research were to characterize sulfentrazone dissipation in surface soil under field conditions, evaluate potential injury to cotton, and determine degradation mechanisms under laboratory conditions.

Material and Methods

Field dissipation. Field experiments were conducted in 1995 and 1996 at one location, and in 1997 at two locations in Knoxville, TN. The 1997 study was initiated at two separate field locations to obtain more information on sulfentrazone dissipation. The soil was of the Sequatchie loam series (fine-loamy, siliceous, thermic Humic Hapudult) with a pH of 6.1, organic matter of 1.27%, cation exchange capacity of 5.48 cmol/kg, and sand/silt/clay percentages of 43/44/13, respectively. Determination of soil characteristics was made using standard procedures (Chapman 1965; Gee and Bauder 1986; McLean 1982; Nelson and Sommers 1982). Plots were four rows wide with row spacing of 76 cm by 8 m long. Soybeans were planted, followed immediately by herbicide application the third week of May in 1995 and 1996. In 1997 at location one, sulfentrazone was applied the second week of May. Study initiation for location

two in 1997 was June 30. It should be mentioned that when this study was initiated in 1995 current labeled rates for sulfentrazone had not been determined. Therefore the most probable rate to be selected at that time for the label and a double rate were used. Treatments were sulfentrazone applied at 0, 420 and 840 g/ha. The double sulfentrazone rate (840 g/ha) was evaluated using liquid chromatography to insure good chromatography and because dissipation is usually independent of application rate (Hurle and Walker 1980). The 420 g/ha rate was included for the cotton field bioassay.

Treatments were applied preemergence (PRE) in a randomized block design. Each treatment was replicated four times. Herbicide applications were made with a CO₂-pressurized backpack sprayer in 170 L water/ha. To allow for weed free soybean (*Glycine max* L.) plots with no chemical interference, glyphosate tolerant soybeans were planted and treated with glyphosate each year. Cotton (*Gossypium hirsutum* L.) was planted approximately 12 months after sulfentrazone application in the plots following the dissipation experiments to assess potential carryover injury. Injury was assessed in the form of height reduction. Fields were tilled prior to initiating the dissipation experiments and recropping experiments were planted under no-till conditions. Planting depth for both crops was approximately 2.5 cm. Location one was tilled the fall of 1997, therefore plot integrity was compromised and the cotton recropping study was not implemented at that location. Weed control in cotton was maintained chemically with glyphosate on glyphosate tolerant cotton in 1996 and 1997 and

pyrithiobac followed by MSMA in 1998, all applied at standard label rates.

This dissipation project implemented the quality control procedures outlined in a previous review by Blumhorst and Mueller (1997). Soil was collected from each plot, using a plugger-type sampler (8 cm diameter). Two samples were taken to a depth of 8 cm from each plot and composited. In 1995, cores were collected 0-, 28-, 42-, 56-, and 77-days after treatment (DAT). In 1996, cores were collected 0-, 7-, 14-, 26-, 35-, 50-, and 95-DAT. In 1997, cores were collected 0-, 14-, 24-, 34-, 64-, 98-, 120-, and 150-DAT at location one. Cores were collected 0-, 12-, 20-, 38-, 54-, 76-, 105-, 133-, 172-, and 227-DAT at location two. Sampling did not follow strict sampling intervals due to environmental conditions, in particular rain. As more information was obtained about sulfentrazone dissipation, the sampling period progressively went further into the season. Soil samples were frozen at -10 C after collection, later thawed and air-dried, ground to pass through a 2-mm sieve, and stored frozen at -10 C until chemical analysis.

Rainfall data from time of sulfentrazone application to cotton planting is provided for the three years in Table 4. Environmental conditions impact the performance and dissipation of an herbicide. Rainfall is one environmental condition that generally has the largest impact on dissipation (Brown et al. 1996; Vencill and Banks 1994). In all three years sulfentrazone received an adequate and timely activating rainfall, with the longest period between application and activation being approximately five days. In all three years cotton was planted in the sulfentrazone treatments as a biological indicator of sulfentrazone

persistence. Cotton is sensitive to sulfentrazone as preliminary data indicated (data not shown).

Microbial degradation. Surface and subsurface soil was collected from the field study location prior to sulfentrazone application. Research has indicated that degradation of soil applied herbicides may be influenced by soil depth (Mueller et al. 1992, Veeh et al. 1996). Therefore, surface soil was collected from a depth of 0 to 10 cm and subsurface soil was collected from a depth of 30 to 40 cm. The surface soil had a pH of 6.1, organic matter of 1.27%, cation exchange capacity of 5.48 cmol/kg, and sand/silt/clay percentages of 43/44/13, respectively. The subsurface soil had a pH of 5.42, organic matter of 1.01%, cation exchange capacity of 1.16 cmol/kg, and sand/silt/clay percentages of 45/37/18, respectively. Determination of soil characteristics was made using standard procedures (Chapman 1965; Gee and Bauder 1986; McLean 1982; Nelson and Sommers 1982). Soils were passed through a 2-mm screen. Seven grams of moist soil was placed in separate 20-ml glass vials. To determine microbial degradation, soils were evaluated under sterile and non-sterile conditions. The soils were sterilized by autoclaving in the vial for 30 min at 120 C. An aqueous solution (14 µg/ml) of analytical sulfentrazone (>90% purity) was prepared using sterile water and 500 µl added to the soils. Soil concentrations were 1000 ppbw. The sulfentrazone was added to the sterile soils in a laminar flow hood, and all vials were capped after herbicide fortification. Soils were incubated in the dark at a temperature of 30 C.

The experiment utilized a completely randomized design with three

treatments (sterile, non-sterile surface, and non-sterile subsurface soils) with a sampling interval of 0, 2, 4, 6, 8, 10, 12, 14, 16, 18, 20, 22, 24, 36, and 48 weeks after treatment (WAT). For each treatment-WAT combination there were four vials. Each vial was an individual experimental unit and the experiment was repeated. At each sampling interval, the respective vials were removed from the incubator and placed in a freezer at -10 C until analysis. Since the vials were a closed system allowing no gas exchange, all were vented for 10 min in a laminar flow hood every twelve weeks to prevent formation of anaerobic conditions.

Sulfentrazone analysis. Samples were analyzed using high pressure liquid chromatography (HPLC). The mobile phase was 50:50 (v/v) of acetonitrile:water+H₃PO₄ at a flow rate of 1 ml/min, a 25 cm x 4.6 mm, 5 μm LC-C₁₈ (Whatman, Clifton, NJ) was used for the separation, and adsorbance at 220 nm was measured and peak area used to determine herbicide concentration.

Field dissipation. Sulfentrazone residue was determined in each soil sample by adding 80 ml of methanol to 40 g of air-dry soil and then agitating for 16 hr on a reciprocating-action shaker (Eberbach, Ann Arbor, MI) operated at 180 rpm. The extract was then filtered through two pieces of Whatman # 1 filter paper (Whatman, Clifton, NJ) directly into 4 ml autosampler vials. A 50-μl sample was injected into the high pressure liquid chromatograph.

Microbial degradation. Vials were removed from the freezer and brought to room temperature. Fourteen ml of methanol was added to each vial, and the vials were agitated 16 hr on a reciprocating-action shaker. The methanol-soil extract

was then passed through two pieces of Whatman # 1 filter paper (Whatman, Clifton, NJ) directly into 4 ml autosampler vials. A 50- μ l sample was injected into the liquid chromatograph.

Statistical analysis. Data were empirically fit to first order kinetics using SAS nonlinear regression procedure (SAS Institute, Cary, NC)⁴. The data were regressed against time in days. Output from the nonlinear procedure included first order dissipation rate constant (k) and upper and lower confidence intervals. These values were converted into half-life or 50% disappearance time (DT_{50}) using the equation: $DT_{50} = \ln 0.50/k$ (Walker 1987). A “corrected” r^2 value was determined by the formula:

$$r^2 = [1 - (\text{residual sums of squares} / \text{corrected total sums of squares})]$$

For the degradation study, confidence intervals for the two runs were compared. If the confidence intervals overlapped, then dissipation rate was not different. This is a conservative approach because two standard deviations are given for each rate constant (Brown et al. 1996).

For both the field and degradation figures, sulfentrazone concentration was plotted over time with each individual data point with error bars representing the mean and standard error, while the line represents the predicted values (Figures 2, 3, and 4, respectively).

Results and Discussion

Field dissipation. In 1995, samples were only taken through 77 days. First-

⁴All SAS programs are in Appendix C.

order kinetics empirically fit sulfentrazone dissipation under field conditions, with $r^2 = 0.87$ (Table 5). Variation among replications within a sampling period, indicated by the error bars, was large, probably due to sampling technique (Figure 2). Dissipation was generally slow, as indicated by the gradual decline in sulfentrazone concentration with time (Figure 2). The half-life (DT_{50}) in 1995 was 113 d (Table 5). This half-life agrees with previously reported information (FMC Corp. 1989).

In 1995, rainfall from study initiation to end of the sampling period to cotton recropping was approximately 118 cm, which was slightly below normal for the year. For the three months after sulfentrazone application, rainfall was below normal. This led to slower dissipation rates, and a longer half-life (113 d). In 1996, cotton injury was observed in the 1995 sulfentrazone plots (Table 6).

In 1996, first-order kinetics empirically fit sulfentrazone dissipation under field conditions, with $r^2 = 0.90$ (Table 5). In general, dissipation was initially rapid followed by a gradual decline over time (Figure 2). The half-life (DT_{50}) in 1996 was 25 d (Table 5). This half-life was considerably shorter than 1995 and to that previously reported (FMC Corp. 1989).

Total rainfall in 1996 was approximately 31 cm more than 1995. For the three months after sulfentrazone application, rainfall was above normal. Above normal moisture conditions may possibly be conducive to more rapid chemical and microbial degradation (Basham and Lavy 1987). With more rain, sulfentrazone could have possibly moved below the sampling zone. However, application was

not proceeded by a heavy rain (<2.5 cm) and with a soil pH of 6.1, which is below the pKa (6.56), there should have been minimal movement due to increased adsorption (Grey et al. 1997). The cotton field assay in 1997 supported this dissipation rate, indicating no differences among the sulfentrazone treatments and the untreated check (Table 6).

In 1997, there were two locations in which the study was initiated at separate times. First-order kinetics empirically fit sulfentrazone dissipation under field conditions, with $r^2 = 0.89$ (Table 5). In general, dissipation was initially rapid followed by a gradual decline over time (Figure 3). The half-life (DT_{50}) at location one was 24 d (Table 5). This half-life was considerably shorter than 1995 and to that previously reported (FMC Corp. 1989), but almost identical to 1996. Location two was initiated approximately 45 d after location one. First-order kinetics empirically fit sulfentrazone dissipation under field conditions, with $r^2 = 0.82$ (Table 5). In general, dissipation at location two (Figure 3) resembled 1995 (Figure 2) with a gradual decline over time. The half-life (DT_{50}) at location two was 85 d (Table 5). This half-life was much closer to 1995 than that of 1996 or location one of 1997.

In 1997, location one was initiated the second week of May and received approximately 10 cm of rain (>5 cm for one event) between day 0 and day 14, the most for any location in this research. This amount of rain over a short period of time (2 weeks) most probably is the reason for the substantial drop in sulfentrazone concentration from 0 DAT to 14 DAT (Figure 3). Sulfentrazone

may have gone below the sampling depth. Rainfall data for May, June, and July of 1997 are comparable to the same three months in 1996 which would indicate a possible trend in dissipation rate and rainfall (Table 4). Dissipation curves (Figures 2 and 3, respectively) and half-lives (Table 5) for 1996 and 1997 at location one are similar which could support this trend.

In 1997, rainfall at location two was approximately 116 cm, which was similar to the total rainfall observed in 1995 (Table 4). In 1998, as in 1996, cotton injury was observed in both sulfentrazone plots (Table 6).

In summary, sulfentrazone half-life was negatively correlated to rainfall collected 0 to 90 DAT (-0.99 $p < 0.02$). In 1995 and 1997 (location two) had similar rainfall patterns and amounts (Table 4). For both years, dissipation was similar with regards to rate (Figures 2 and 3, respectively) and half-life (Table 5). As a result cotton carryover injury was observed the following years at both the 420 and 840 g/ha rates (Table 6). The conclusion that can be drawn from 1995 and 1997 (location two) is that under conditions that are conducive to slower dissipation, half-lives will be extended which increases the potential for carryover if rotating to sensitive crops the following year. In contrast, heavier rainfall was observed in 1996 and 1997 at location one (Table 4). For both of the studies, dissipation rate (Figures 2 and 3, respectively) and half-life (Table 5) were similar. No cotton carryover injury was observed in 1997. These data indicate that rainfall affected sulfentrazone dissipation in the field.

Microbial degradation. Statistical analysis indicated no difference between the two runs, therefore data were combined and analyzed. Combined data were

then fit to first order kinetics using SAS nonlinear regression procedure.

First-order kinetics empirically fit the sulfentrazone degradation for all three treatments under controlled conditions (Table 7). Differences in degradation rates between treatments were determined by the comparison of the confidence intervals around the first-order rate constant (Brown et al. 1994). If the confidence intervals overlapped, they were not different at the 5% significance level (Brown et al. 1994).

These soils had no previous exposure to sulfentrazone. Degradation was slower in autoclaved (sterile) soil than in nonautoclaved (nonsterile) soil (Figure 4). The half-life of the sterile soil was 198 d, while half-lives for the surface and sub-surface were 93 d and 102 d, respectively (Table 7). Sulfentrazone degradation in sub-surface soil was similar to surface soil.

This increase in persistence in autoclaved soil indicated that microbial degradation was an important sulfentrazone dissipation mechanism from the soil. Microbial populations or their activity were not measured in this research. Half-lives of the surface and sub-surface were similar to those observed under 1995 and 1997 (location two) field conditions, which were years for normal moisture conditions (Table 5). Half-lives were also similar to that previously reported (FMC Corp. 1989). Although the observed degradation under sterile conditions was slower (Figure 4), data did empirically fit first-order kinetics ($r^2 = 0.79$), indicating that microbial degradation is not the only dissipation mechanism. Chemical degradation appears to be involved in the dissipation of sulfentrazone, also.

In general, data from these studies indicate that rainfall, microbial degradation and chemical degradation are all important mechanisms of sulfentrazone dissipation.

PART IV

Sulfentrazone Adsorption and Mobility in Surface Soil⁵

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Introduction

Organic compounds can be adsorbed to the soil colloid surface and absorbed into soil organic matter. Since both of these processes usually occur to some degree, the term sorption is used to refer to this phenomenon. Organic compounds that are absorbed are considered unavailable. Therefore, adsorption is one of the main factors controlling soil solution concentration (Walker 1980). Herbicide adsorption maybe affected by organic matter, clay content and pH (Loux and Reese 1992; Mueller et al. 1992). Due to these variations, herbicide rates sometimes vary according to soil type and are generally lower for soils with low clay or low organic matter compared to high clay or organic soils (Calvert 1980; Carringer et al. 1975; Mueller and Banks 1991; Mueller et al. 1992; Peter and Weber 1985; Walker 1980).

Herbicide availability under varying soil pH is due to the possibility of herbicides to be charged or neutral (Loux and Reese 1992; Schneiders et al. 1993; Talbert and Fletchall 1965). Previous research indicated that sulfentrazone adsorption is related to pH and soil type regardless of concentration (Grey et al. 1997).

Sulfentrazone has a water solubility of 110 $\mu\text{g/g}$ at pH 6.0, 780 $\mu\text{g/g}$ at pH 7.0, and 1600 $\mu\text{g/g}$ at pH 7.5 and a vapor pressure of 1×10^{-9} mm Hg at 25 C (FMC Corp. 1989). This indicates that sulfentrazone solubility increases with increasing pH and has low volatility.

Herbicide mobility is both an agronomic and environmental concern. Agronomically, soil-applied herbicides that readily move in the soil can result in decreased weed control. From an environmental perspective, herbicides that

readily move in the soil may be a potential groundwater contaminant due to vertical movement through the soil profile. Mobility has been studied using soil columns (Fleming et al. 1992; Mueller and Banks 1991; Peter and Weber 1985). Mobility of herbicides is often influenced by properties of that particular herbicide and the soil to which it was applied (Grey et al. 1997). Soil structure influences water flow (Jarvis and Messing, 1995). Soils with coarse texture usually have increased flow of percolating water. This can influence the amount of time the herbicide has to adsorb to soil colloids or organic compounds. This research could be useful as an indirect measurement of movement potential of sulfentrazone.

The objectives of this research were to evaluate the adsorption of sulfentrazone using a modified slurry technique and its mobility in seven soils under saturated conditions. This work has not been previously reported in the literature.

Materials and Methods

Experimental soils. Soils were collected from the 0- to 10-cm depth from seven locations in five states. Soils used were from Sequatchie loam (fine-loamy, siliceous, thermic Humic Hapudult), Drummer silt loam (fine-silty, mixed, mesic Typic Haplaquolls), Malden loamy sand (coarse-sandy, mixed, thermic Typic Udipsamments), Bosket fine sandy loam (fine-loamy, mixed, thermic Mollic Hapludalfs), Commerce silty clay loam (fine-silty, mixed, nonacid, thermic Aeric Fluvaquents), Harkey clay loam (coarse-silty, mixed, calcareous, thermic Typic

Torrifluent), and Dothan loamy sand (coarse-sandy, mixed, Plinthic Kandiudults) series. Soil analysis conducted to characterize the soils included soil pH (McLean 1982), organic matter content (Nelson and Sommers 1982), cation exchange capacity (CEC) (Chapman 1965), and particle size analysis (Gee and Bauder 1986) (Table 1).

Adsorption. Herbicide adsorption in each soil (Table 1) was evaluated using a modified slurry technique (Talbert and Fletchall 1965). Soil was screened through a 2-mm screen, and 10 g was added to 50-ml plastic screw top centrifuge tubes. Twenty ml of 0.01 M CaCl_2 solution containing either 0 or 1 μg per ml of analytical sulfentrazone was added to each tube. Tubes were capped and placed on a reciprocating shaker that was operated at 180 rpm at 25 C for 24 h. After 24 h equilibration, samples were centrifuged at 12 000 g for 10 min. The samples were filtered through two pieces of qualitative filter paper to remove particulates. Sulfentrazone concentrations in the supernatant were determined by high pressure liquid chromatography (HPLC). Centrifuge tubes containing no soil were included to account for any sulfentrazone adsorption to the tube. Although there was >95% recovery, there was an average of 60 ppbw (6% of initial) of sulfentrazone adsorbed to centrifuge tubes, therefore the average concentration in the fortified control tubes containing no soil was used to determine adsorption distribution coefficients (K_d). An adsorption distribution coefficient (K_d), which is the ratio of the amount of herbicide adsorbed (g/g soil) to the amount remaining in solution ($\mu\text{g}/\text{ml}$), was calculated for each sample.

Mobility. Mobility of sulfentrazone was evaluated as described in methods by Mueller and Banks (1991). The 7.6 cm diameter PVC columns consisted of six 4.5 cm sections, giving a total packed soil column length of 27 cm and total volume of 1231 cm³. The total column length was 40 cm, with the extra 13 cm above the packed soil to facilitate the addition of water. The bottom of the PVC pipe was capped with a standard PVC 7.6 cm diameter cap. The cap, prior to placing on the pipe, had fifteen 0.44 cm holes drilled in it and was lined with glass wool. This allowed for ease of water movement, while maintaining the soil column integrity.

The columns were packed by adding small amounts of soil to the column while it was agitated manually. After packing each column, the soil bulk density (g/cm³) was determined and used to calculate porosity by the relationship [1 - (bulk density/particle density)] (Brady 1990) (Table 1). Glass wool was placed on the soil surface on top of the packed column to minimize surface disturbance, and one pour volume of water was added to the top of each column to completely saturate it (Table 1). The columns were drained completely before sulfentrazone was applied.

After the soil column drained, the surface glass wool was removed and sulfentrazone dissolved in methanol was uniformly applied to the soil surface of each column. Two ml of 200 ug/ml of analytical sulfentrazone solution was applied. This was the equivalent of approximately 1 kg/ha of sulfentrazone. The methanol was allowed to evaporate prior to replacing the glass wool on the soil surface. One pore volume of water was added to each column using the same

procedure previously described to saturate the columns. The leachate was collected in a reservoir below each column.

After 24 h, all columns were placed in the freezer at -10 C, while the leachate was placed in 250 ml bottles and placed in the refrigerator at 4 C until columns were analyzed. Forty-eight hours later the frozen columns were removed, cut into the six sections and air-dried. A 40 g sample from each section (air-dried and passed through a 2 mm screen) was placed in a 250 ml bottle and placed in the freezer until chemical analysis.

Sulfentrazone analysis. Samples were analyzed using high pressure liquid chromatography (HPLC). The mobile phase was 50:50 (v/v) of acetonitrile:water+H₃PO₄ at a flow rate of 1 ml/min, a 25 cm x 4.6 mm, 5 μm LC-C₁₈ (Whatman, Clifton, NJ) was used for the separation, and adsorbance at 220 nm was measured and peak area used to determine herbicide concentration.

Adsorption analysis. Centrifuge tubes were removed from centrifuge and the aqueous supernatant was passed through two pieces of filter paper into HPLC vials.

Mobility analysis. Sulfentrazone residue was determined by adding 80 ml of methanol to 40 grams of soil for each sample and agitating for 16 hours on a reciprocating shaker (Eberbach, Ann Arbor, MI) operated at 180 rpm. The extract was then filtered through two pieces of Whatman # 1 filter paper (Whatman, Clifton, NJ) directly into 4 ml autosampler vials. A 50-μl sample was injected into the high pressure liquid chromatograph.

Statistical analysis. The adsorption experiment used a completely randomized design with four replications per treatment and the experiment was repeated. Data were subjected to analysis of variance and means were separated by procedure mixed in SAS. Multiple correlation and regression analyzes were run on adsorption data.

The mobility experiment used a completely randomized design with three replications per treatment and the experiment was repeated. Data among runs were sorted by section and subjected to analysis of variance and means separation using general linear model procedure in SAS. Data within a particular soil were analyzed among section using mixed procedure in SAS.

Data analysis indicated no treatment interactions between experiments. Data were pooled across the two experiments examining sulfentrazone adsorption and pooled across the two experiments examining sulfentrazone mobility. Adsorption data are plotted against pH and organic matter (Figure 5). Mobility data are presented in vertical bar format based on percent sulfentrazone concentration at a certain depth (cm) with error bars on each column (Figures 6 through 12).

A distribution value (DV) was determined for each soil in the mobility study (Jones et al. 1990). This value incorporated distance of sulfentrazone movement in the column and concentration of sulfentrazone at each distance. This value was derived by multiplying the percent sulfentrazone in each 4.5 cm section by the depth (cm) to the center of that section. The leachate reservoir was included as a section because sulfentrazone was detected in two of the soils

examined. A higher DV indicated more movement down the column in sulfentrazone concentration. These values were then correlated to Kd and various soil characteristics (Table 8).

Results and Discussion

Adsorption. Sulfentrazone adsorption to a Bosket sandy loam and Dothan loamy sand soils were similar (Table 1). The Malden loamy sand and Commerce silty clay loam soils were similar (Table 1). For all other treatments sulfentrazone adsorption was different (Table 1). Sulfentrazone adsorption decreased with increasing pH and decreasing organic matter (Figure 5). Figure 5 has two points on the pH graph that depart from the regression line, the Drummer silt loam and Malden loamy sand. The Drummer silt loam is high because organic matter content strongly influences sulfentrazone adsorption. The Malden loamy sand is low possibly due to low organic matter content and high sand content. The simple regression model poorly explained the data from all seven soils with r^2 values for pH and organic matter below 50% (Figure 5).

Sulfentrazone adsorption was positively correlated to organic matter and the distribution value (Table 8). Sulfentrazone was negatively correlated to pH (Table 8). The Kd values listed in Table 1 support this with larger Kd values at lower pH and higher organic matter content. The Malden loamy sand is the only one that does not follow this trend (Table 1). The most probable reason for this would be the Malden loamy sand properties. Adsorption is influenced by soil properties including organic matter and texture (Grey et al. 1997; Mueller et al. 1992). The

Malden loamy sand soil contained 81% sand and 1.1% organic matter, which leaves very little surface area for sulfentrazone adsorption. Low adsorption from the Malden loamy sand as a reflection of potential movement is indicated in the mobility data. These data agree with previously reported data, which indicated a correlation between organic matter and pH (Grey et al. 1997).

Since adsorption was correlated with pH and organic matter content, a multiple regression analysis was run to see how much these two variables explained adsorption. The analysis indicated that pH and organic matter could explain 97% of adsorption. The estimated regression equation was $K_d = 1.33 + 0.348 \cdot OM - 0.255 \cdot pH$.

Adsorption influences soil solution concentration which is important for a soil applied herbicide because of availability to be adsorbed by plants and/or leachability from the target site. The negative correlation between K_d and DV indicates that as adsorption decreases movement increases. Therefore, in a high organic matter soil such as the Drummer silt loam (Table 1), sulfentrazone would be more tightly adsorbed which could decrease weed control. This relationship was observed in a previous study (Wehtje et al. 1995). In contrast, a soil with a high pH such as the Harkey clay loam (Table 1), sulfentrazone would be less adsorbed, therefore increasing availability for plant uptake and/or potential leaching.

Mobility. Differences in bulk densities resulted in different pore volumes for each soil (Table 1). The water added after application under saturated conditions represented a high-mobility scenario.

The distribution value (DV) was negatively correlated to adsorption; therefore, as adsorption increases the DV decreases (Table 8). Sulfentrazone movement was limited in the Sequatchie loam and Drummer silt loam (Figures 6 and 7, respectively). In the Sequatchie loam sulfentrazone was concentrated in the 0-9 cm layers ($P < 0.05$). The distribution values (DV) for the Sequatchie loam and Drummer silt loam were 5.75 and 2.25, respectively (Table 1). The common characteristics of these two soils are that they are both loams (medium texture) and have low pH (Table 1).

Sulfentrazone moved throughout the Bosket sandy loam indicated by a DV of 20.24 (Table 1). Sulfentrazone was concentrated at the 22.5 and 27 cm depths (Figure 8). The highest concentration section was different from the other sections ($P < 0.05$). The Bosket sandy loam contained more sand than the previously discussed loams and had a pH of 7.5 (Table 1).

Sulfentrazone also moved throughout the Dothan and Malden loamy sands with a similar pattern of movement (Figures 9 and 10, respectively). However, the relative movement was less, indicated by DVs of 15.4 and 14.6, respectively (Table 1). These two soils had high sand content, low organic matter content, and pH around 6 (Table 1). In the Dothan loamy sand, sulfentrazone was equally distributed at the 18, 22.5, and 27 cm depths, respectively ($P > 0.05$) (Figure 9). These concentrations were higher than the upper three sections of the column ($P < 0.05$). In the Malden loamy sand, sulfentrazone had the highest concentration at the 18 cm depth ($P < 0.05$) (Figure 10).

Movement was detected throughout the Harkey clay loam and Commerce silty

clay loam (Figures 11 and 12, respectively). Sulfentrazone was also detected in the leachate of both soils. In the Harkey clay loam sulfentrazone was equally distributed at the 9, 13.5 and 18 cm depths, respectively ($P>0.05$) (Figure 11). Only a small amount of sulfentrazone was detected in the leachate and relative movement was low with a DV of 13.7 (Table 1). In the Commerce silty clay loam sulfentrazone was equally distributed through the 22.5, 27 cm depths and the leachate reservoir, respectively ($P>0.05$) (Figure 12). Relative movement of sulfentrazone in this soil was high with a DV of 21.5 (Table 1). Both of these soils are loams with similar pH and organic matter content (Table 1). The difference in DV was possibly due to the differing soil textures. The Commerce silty clay loam had a lower clay content than the Harkey clay loam (Table 1).

Sulfentrazone adsorption was positively correlated to organic matter and negatively correlated to pH (Table 8). Previous data also suggests that sulfentrazone is influenced by soil texture (Grey et al. 1997). The amount of time the herbicide has to adsorb to clay particles and organic matter may be an important factor in a herbicide's potential for leaching, depending on adsorption kinetics. Through observation, water movement through the columns varied with texture. More rapid water movement was observed in the Bosket sandy loam, Malden loamy sand and the Dothan loamy sand than in the other soils evaluated (data not shown).

Sulfentrazone mobility in the Sequatchie loam and Drummer silt loam was limited to the top 9 cm of the columns. The factors observed, slow water movement, medium texture, low pH, and highest amount of adsorption for the

soils evaluated, would suggest that this is a plausible scenario for sulfentrazone movement under these conditions. The Bosket sandy loam had both high pH and coarse texture (Table 1). However, it did contain an agronomically normal amount of soil organic matter. The combination of a high pH resulting in low adsorption (Table 1) and observed rapid flow of water due to coarse texture resulted in sulfentrazone mobility throughout the column which suggests that pH and texture were the dominant factors.

The Dothan loamy sand and Malden loamy sand both had low organic matter and low clay content, which would indicate little surface area for sulfentrazone adsorption. This, in combination with the rapid movement of water through the column, supports the fact that sulfentrazone was relatively mobile through these soils. Adsorption data indicate moderate adsorption for the Dothan loamy sand ($K_d = 0.45$) which had a pH of 6.1. The Malden loamy sand had a pH of 5.7, but had low adsorption ($K_d = 0.23$). This did not follow the adsorption trend established by the other soils based on pH (Table 1). However, the similarity in mobility of these two soils suggests that texture, in particular sand content, is an indication of potential in sulfentrazone movement through the soil.

The Harkey clay loam and Commerce silty clay loam share similarities which include texture, pH and organic matter content (Table 1). Mobility data indicate that sulfentrazone movement was similar in these two soil (Figures 11 and 12). Sulfentrazone came through both columns and was detected in the leachate. These data supports the adsorption values determined for these two soils, which were the lowest of the seven evaluated (Table 1), indicating that a higher pH

influences adsorption and mobility of sulfentrazone more than texture. However, texture still plays a role when differentiating where sulfentrazone will concentrate at high pH. This was indicated by the concentration of sulfentrazone in the upper sections of the Harkey clay loam, which had higher clay content compared to the bottom layers of the Commerce silty clay loam, which had low clay content (Table 1).

Sulfentrazone adsorption and mobility follow what appears to be certain trends based on soil properties, in particular pH and texture. However, data suggests that in isolated incidents (Malden loamy sand) sulfentrazone behavior can contradict generalized trends.

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APPENDICES

Appendix A

Figures

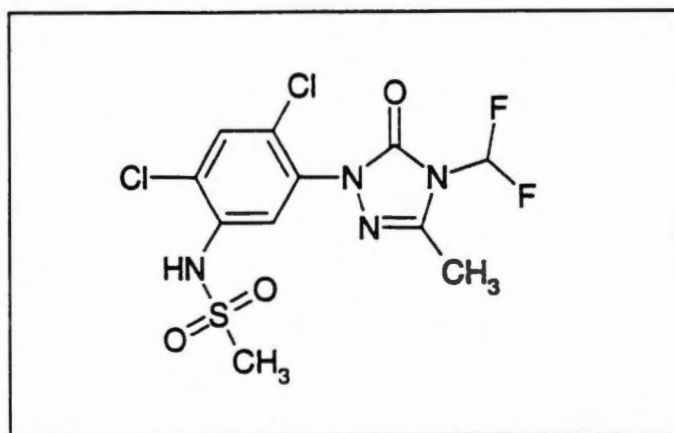


Figure 1. Sulfentrazone, *N*-{2,4-dichloro-5-[4-(difluoromethyl)-4,5-dihydro-3-methyl-5-oxo-1*H*-1,2,4-triazol-1-yl]phenyl}methanesulfonamide (Ahrens 1998).

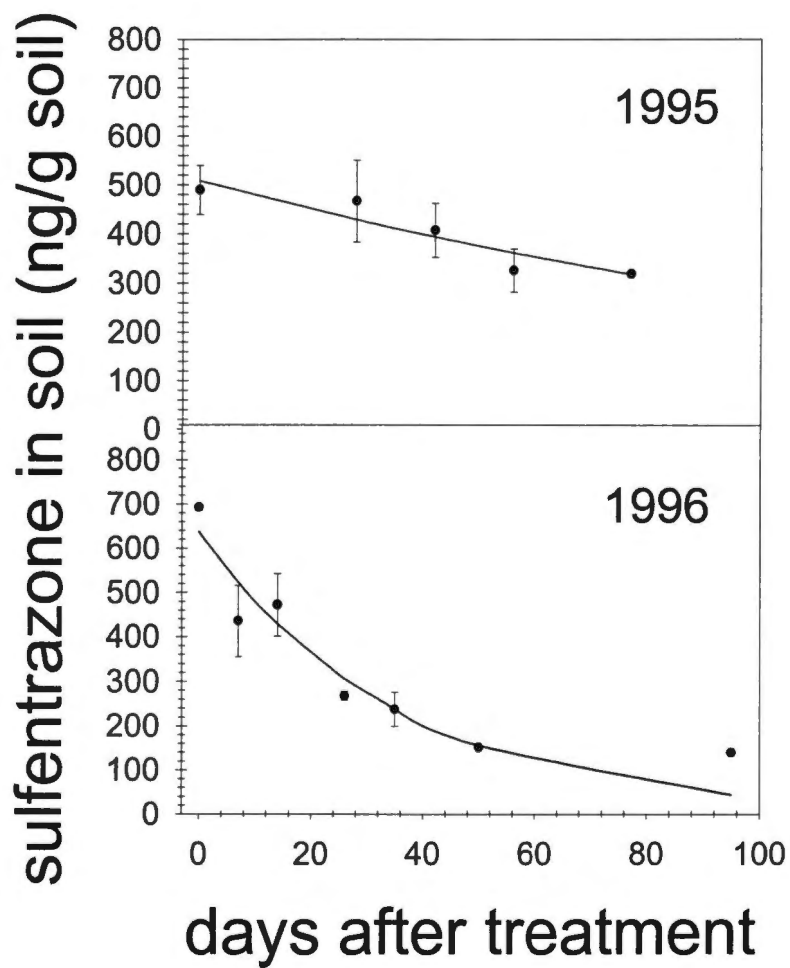


Figure 2. Sulfentrazone concentration over time for 1995 and 1996 field dissipation studies. Data points are means of four replications \pm one standard error. The line represents the first-order regression equation. Rate constants, calculated half-lives, and r^2 are in Table 5.

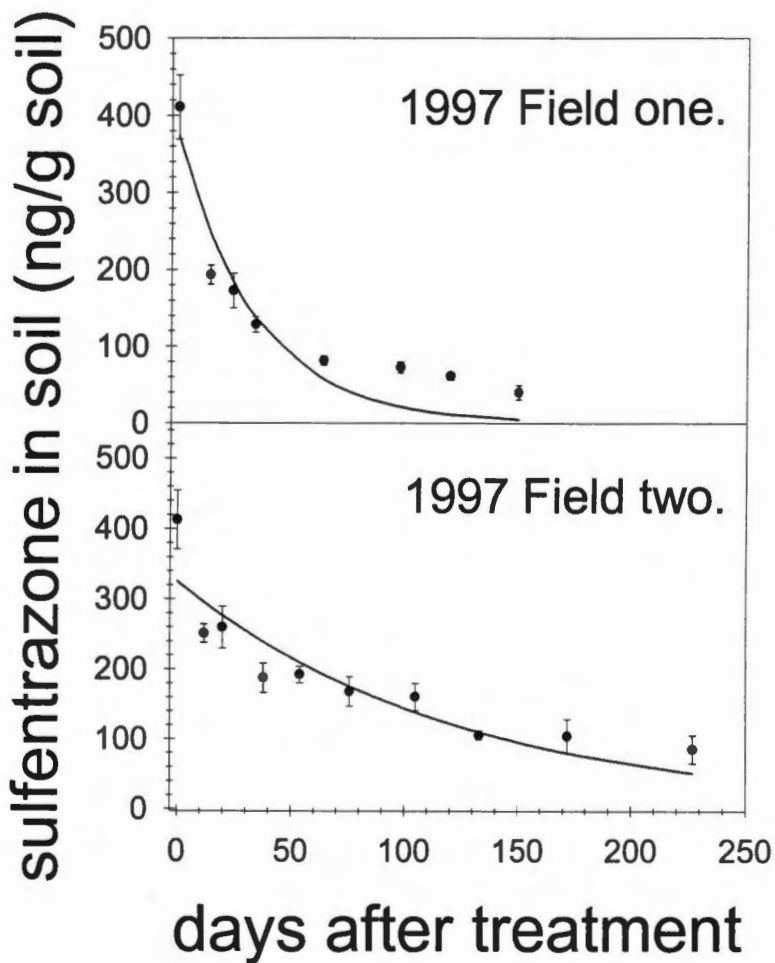


Figure 3. Sulfentrazone concentration over time for 1997 locations one and two field dissipation studies. Data points are means of four replications \pm one standard error. The line represents the first-order regression equation. Rate constants, calculated half-lives, and r^2 are in Table 5.

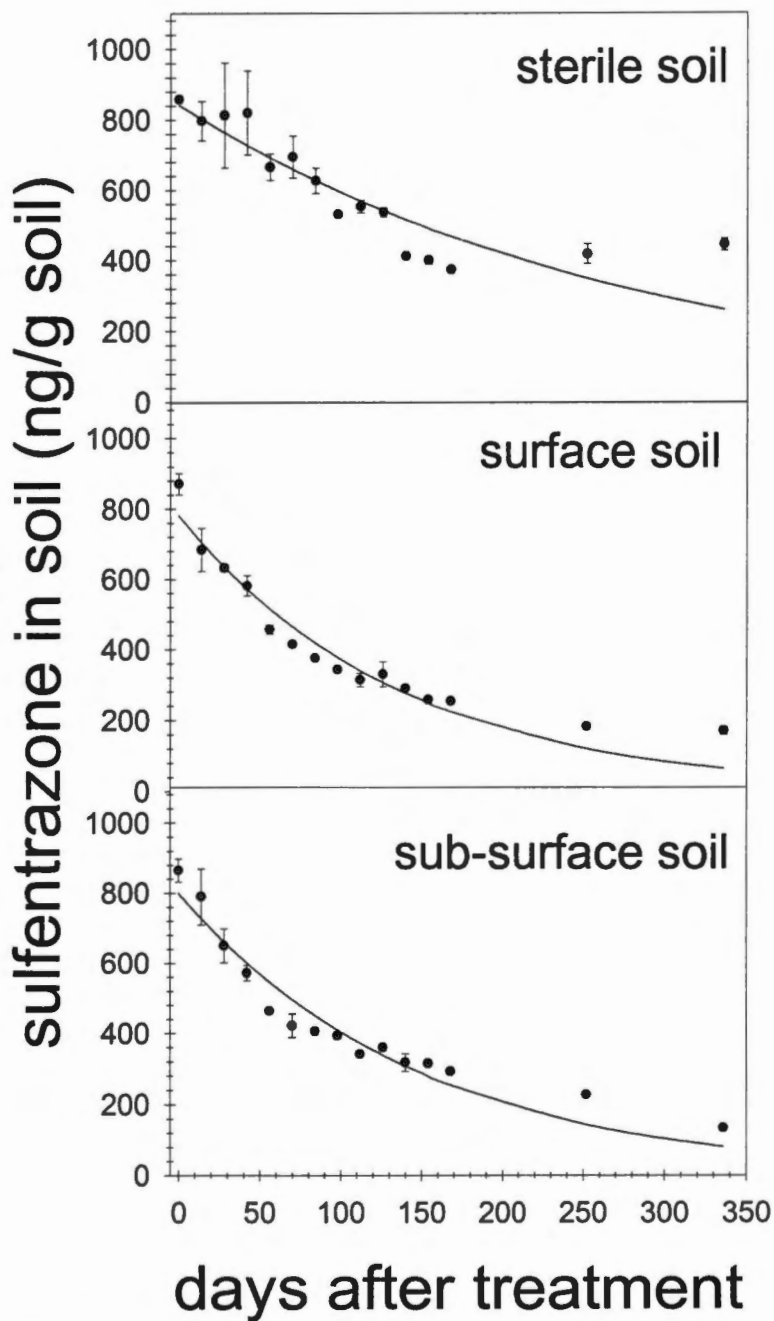


Figure 4. Sulfentrazone concentration over time for the degradation study. Data points are the means of the two runs \pm standard error. The line represents the first-order regression equation. Degradation rate constants (k), 95% confidence levels, half-lives (DT_{50}) and r^2 are in Table 7.

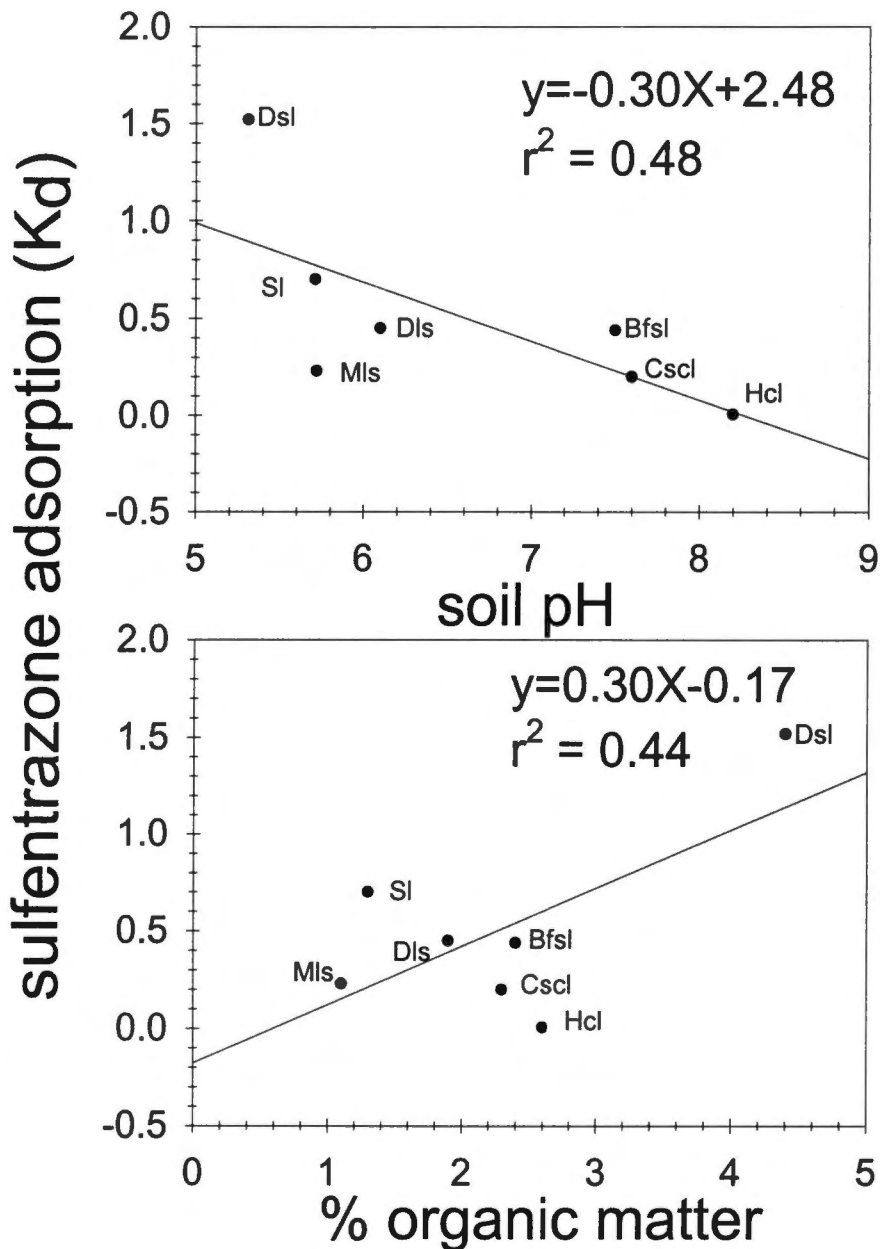


Figure 5. Sulfentrazone adsorption as influenced by pH and organic matter of the seven soils evaluated. Plotted according to increasing pH and organic matter of the individual soils from Table 1. Letters beside each point represent soil series: Drummer silt loam (Dsl), Sequatchie loam (SI), Malden loamy sand (Mls), Bosket fine sandy loam (Bfsl), Commerce silty clay loam (Cscl), Harkey clay loam (Hcl), and Dothan loamy sand (Dls).

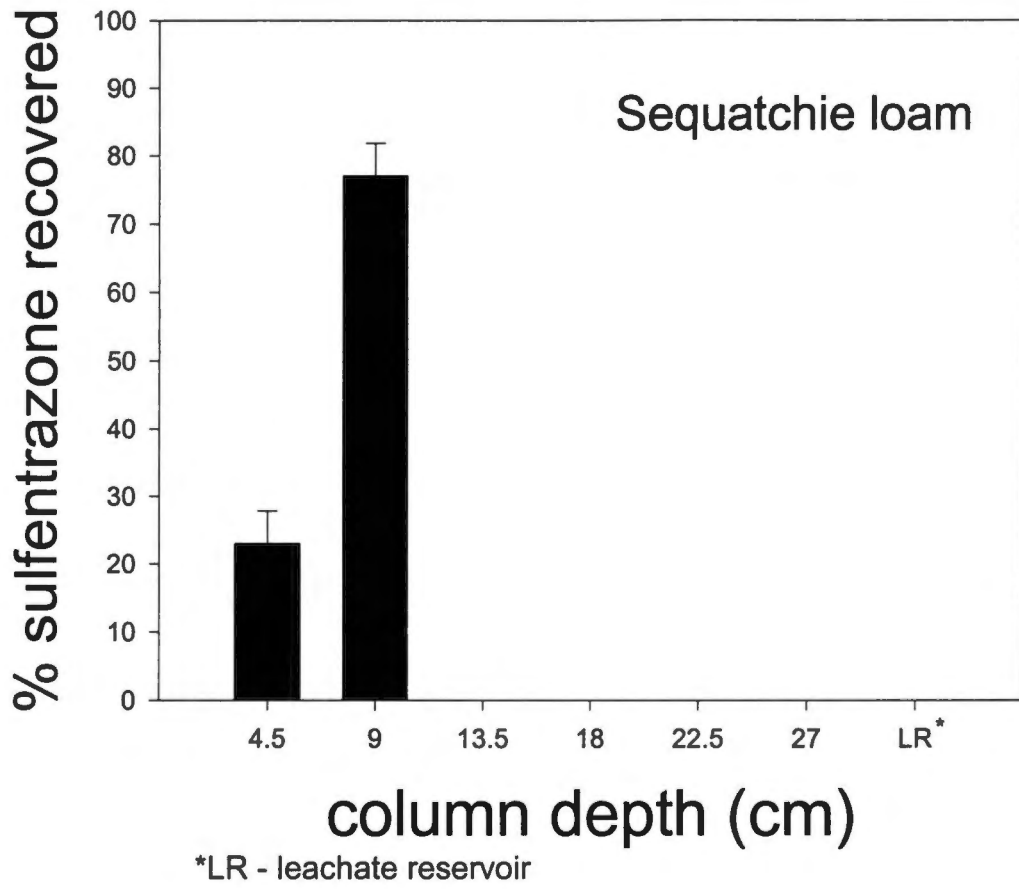


Figure 6. Mobility of sulfentrazone through packed columns with surface soil from Sequatchie loam series.

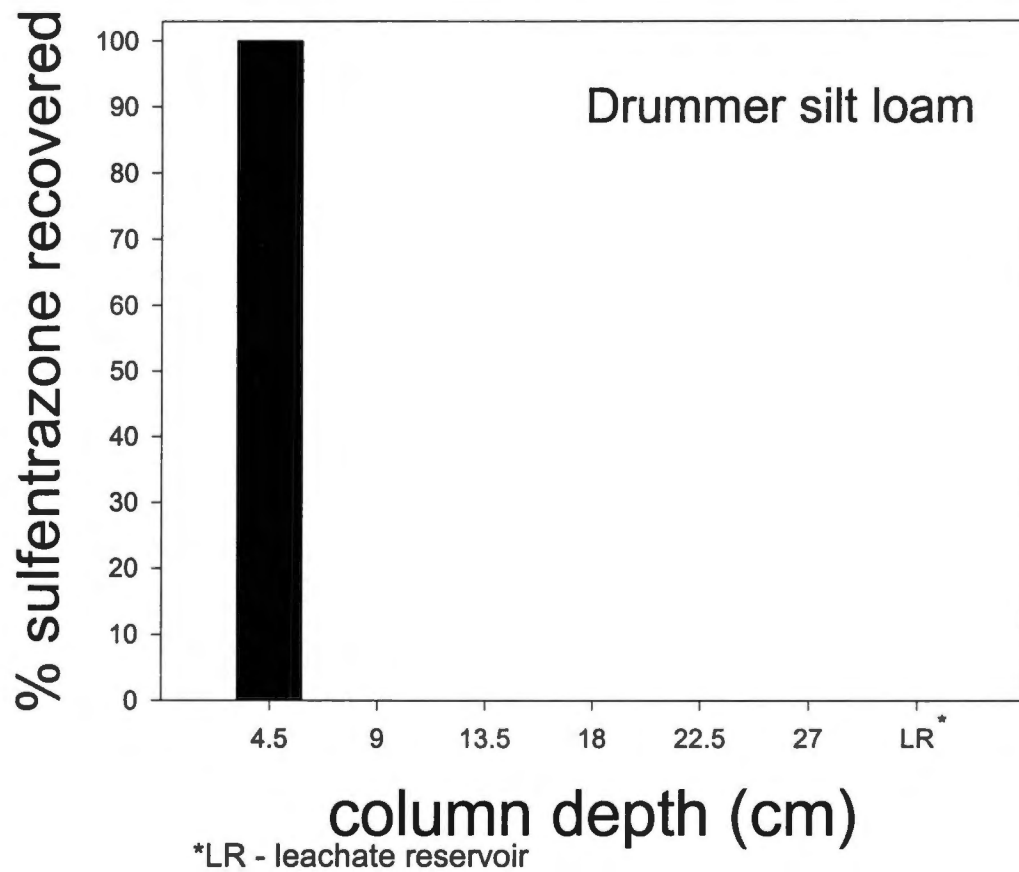


Figure 7. Movement of sulfentrazone through packed columns with surface soil from Drummer silt loam series.

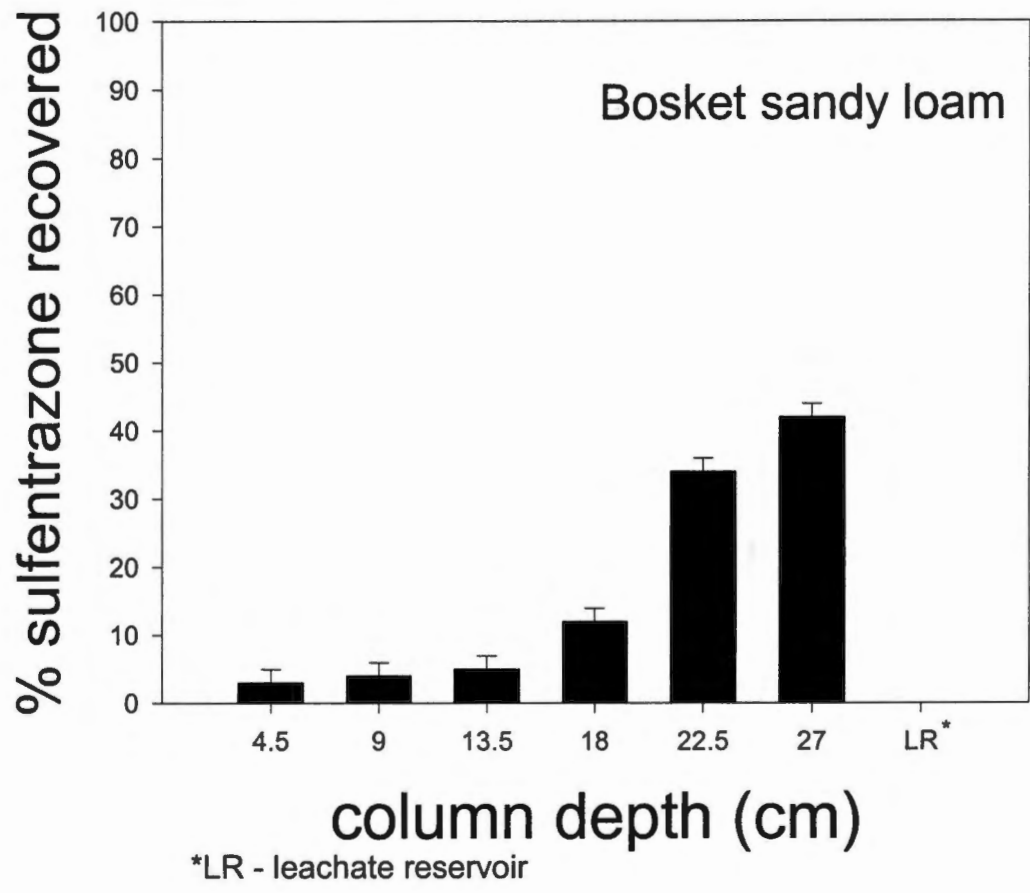


Figure 8. Mobility of sulfentrazone through packed columns with surface soil from Bosket sandy loam series.

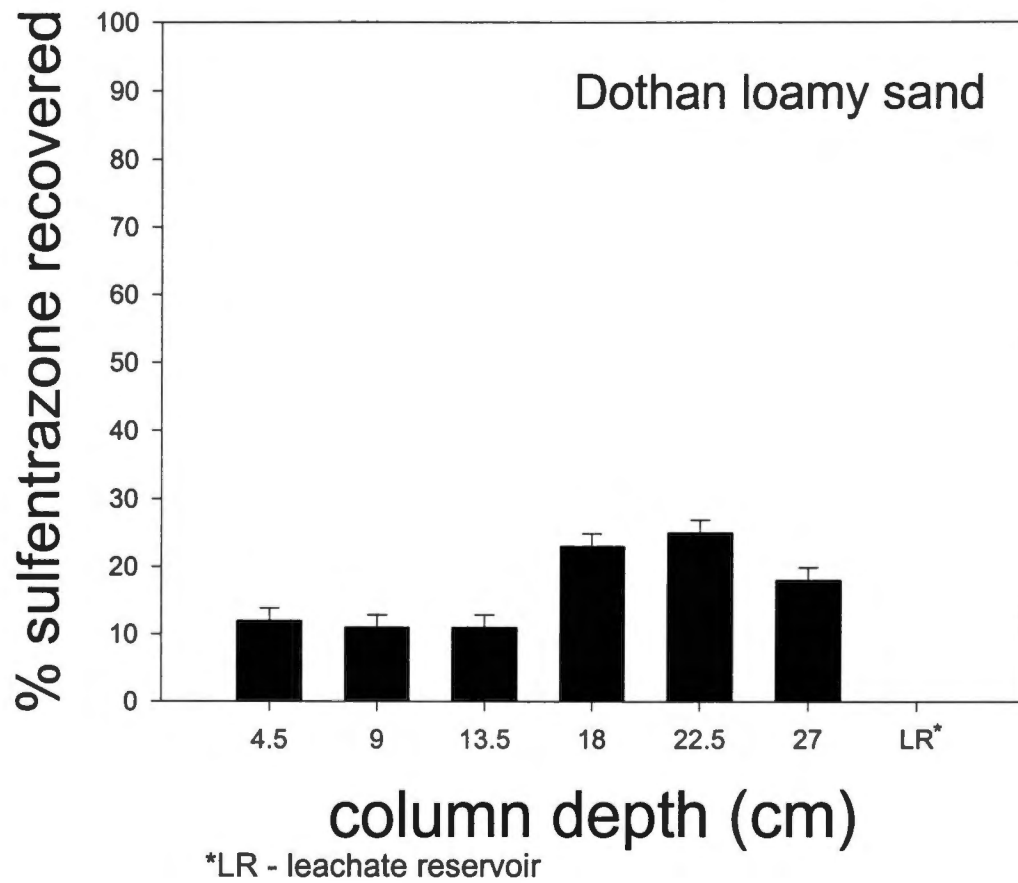


Figure 9. Mobility of sulfentrazone through packed columns with surface soil from Dothan loamy sand series.

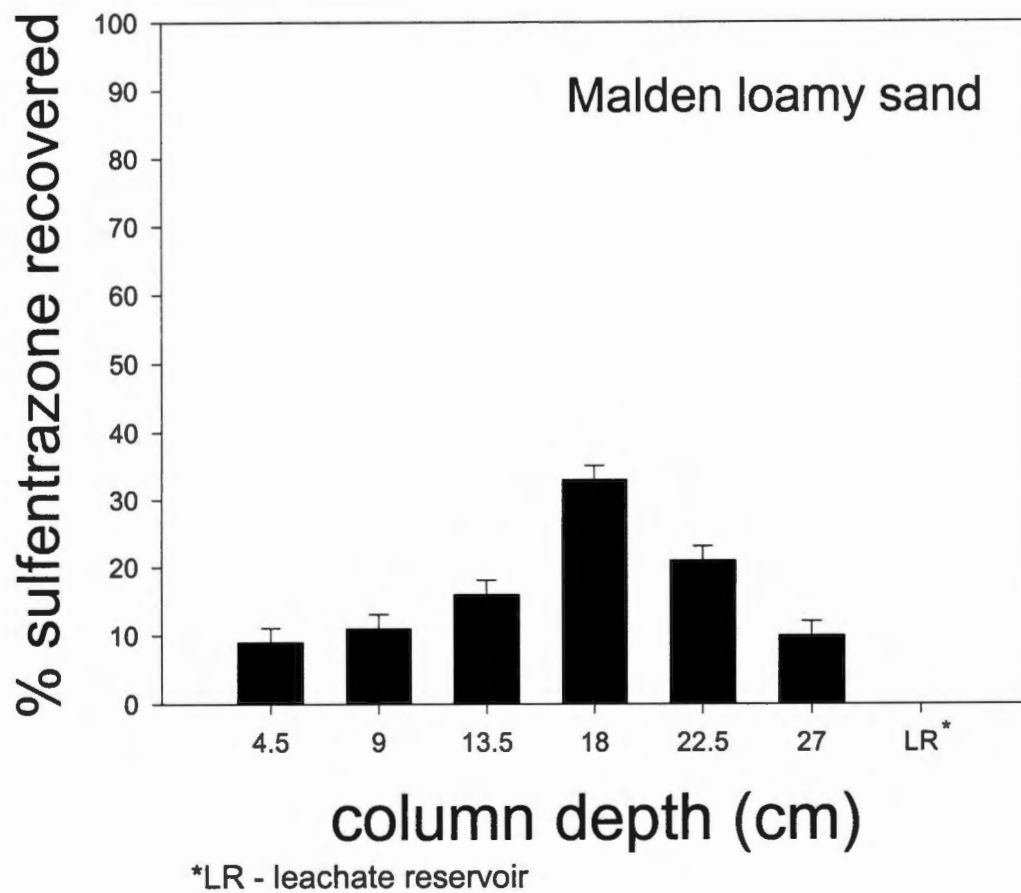


Figure 10. Mobility of sulfentrazone through packed columns with surface soil from Malden loamy sand series.

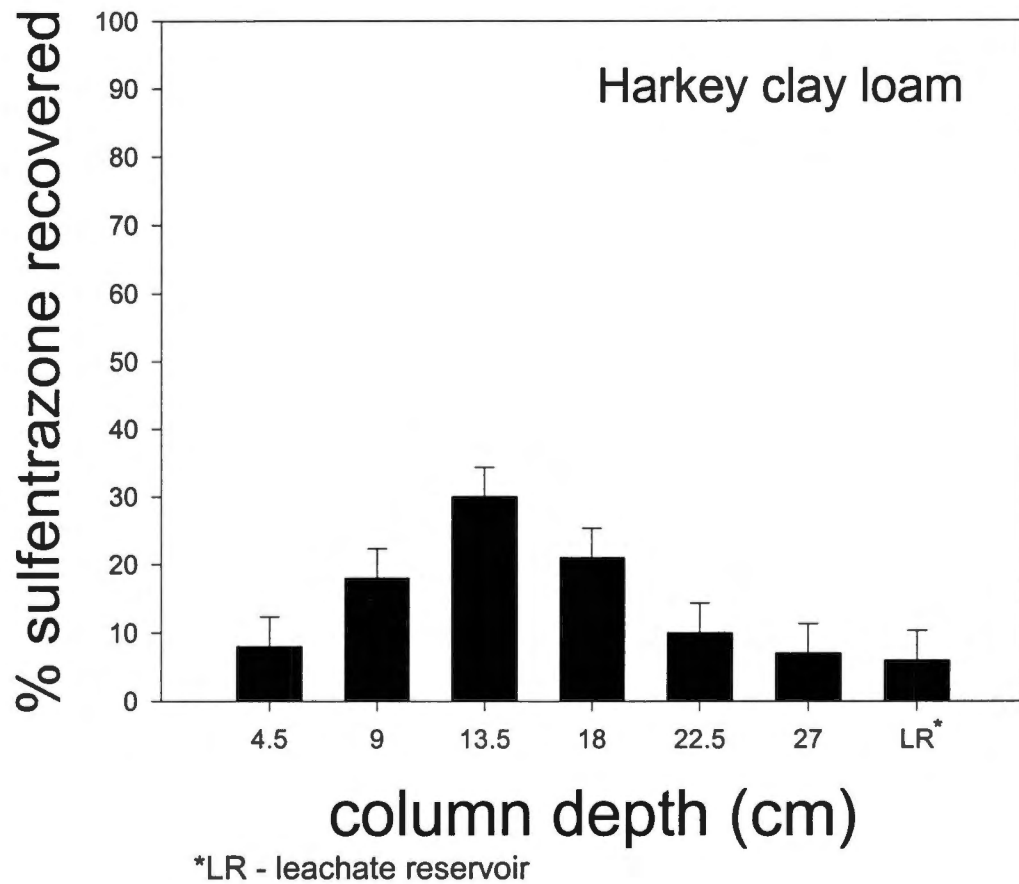


Figure 11. Mobility of sulfentrazone through packed columns with surface soil from Harkey clay loam series.

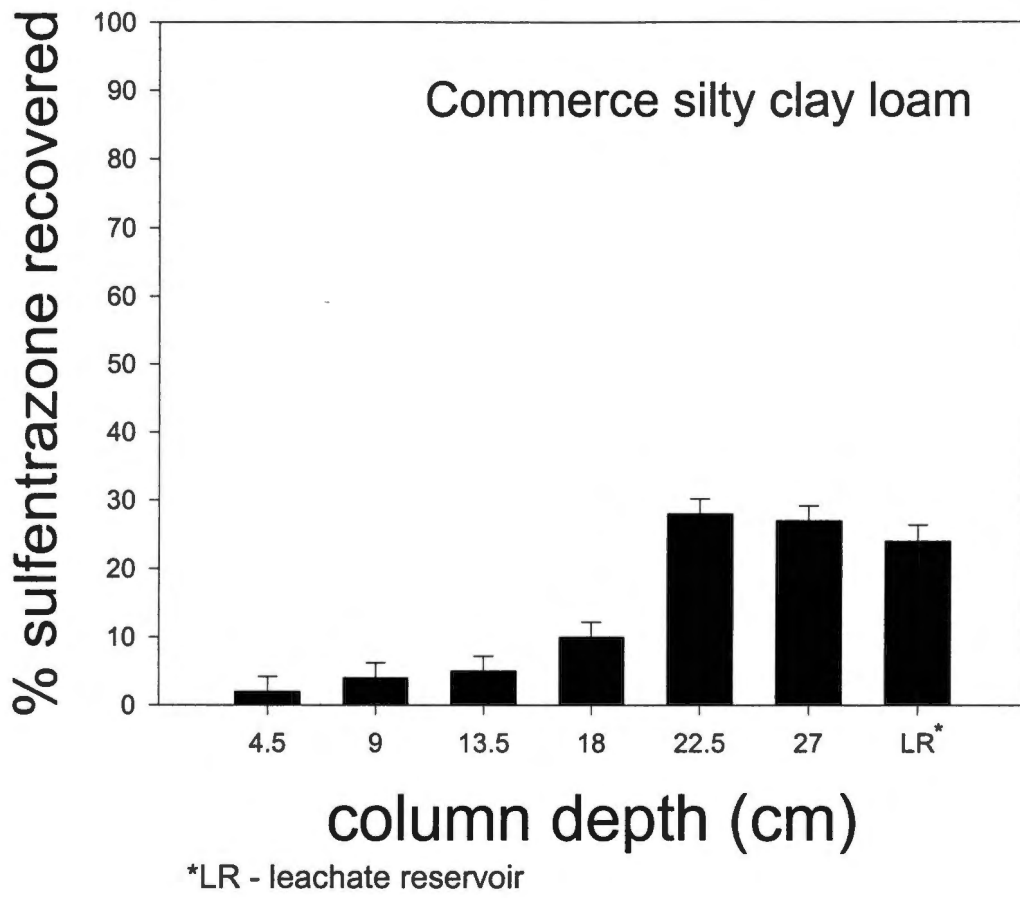


Figure 12. Mobility of sulfentrazone through packed columns with surface soil from Commerce silty clay loam series.

Appendix B

Tables

Table 1. Characteristics of the seven soils examined in the sulfentrazone method, adsorption, and mobility experiments.

| State | Series | Texture | pH ^a | OM ^b | Sand ^c | Silt ^c | Clay ^c | CEC ^d | Bulk Density | Pore Volume ^e | Kd ^f | DV ^g |
|------------|------------|-----------------|-----------------|-----------------|-------------------|-------------------|-------------------|------------------|-------------------|--------------------------|-----------------|-----------------|
| | | | | % | % | | | cmol/kg | g/cm ³ | ml | | |
| Tennessee | Sequatchie | loam | 5.71 | 1.27 | 43 | 44 | 13 | 9.3 | 1.46 | 550 | 0.70 | 5.75 |
| Illinois | Drummer | silt loam | 5.31 | 4.42 | 14 | 61 | 25 | 21.8 | 1.38 | 590 | 1.52 | 2.25 |
| Missouri | Malden | loamy sand | 5.72 | 1.08 | 81 | 15 | 4 | 3.8 | 1.62 | 480 | 0.23* | 14.60 |
| Missouri | Bosket | fine sandy loam | 7.46 | 2.37 | 61 | 33 | 6 | 5.8 | 1.50 | 540 | 0.44** | 20.24 |
| Missouri | Commerce | silty clay loam | 7.61 | 2.25 | 25 | 60 | 15 | 13.9 | 1.43 | 570 | 0.20* | 21.52 |
| New Mexico | Harkey | clay loam | 8.24 | 2.56 | 30 | 32 | 38 | 25.3 | 1.37 | 590 | 0.01 | 13.69 |
| Florida | Dothan | loamy sand | 6.07 | 1.87 | 82 | 13 | 5 | 4.8 | 1.58 | 500 | 0.45** | 15.40 |

^a pH was determined using a 1:2 soil:water ratio (McLean 1982).

^b Organic matter was determined using LECOTM carbon analyzer (Nelson and Sommers 1982).

^c Particle analysis was determined using hydrometer method (Gee and Bauder 1986).

^d Cation exchange capacity was determined using distillation method (Chapman 1965).

^e Bulk density in packed soil column was determined and used to calculate porosity by the relationship $[1 - (\text{bulk density}/\text{particle density})]$ (Brady 1990).

^f Distribution coefficients (Kd) of sulfentrazone adsorption, ratio of amount adsorbed to amount in solution.

^g Distribution values (DV) of sulfentrazone leaching, % sulfentrazone remaining in each section multiplied by distance to center of that section.

* Kd values for these two soils did not differ at the 5% level.

** Kd values for these two soils did not differ at the 5% level.

Table 2. Solvent systems, retention times, and capacity factor (k) for sulfentrazone.

| Mobile phase | Solvent ratio (v/v) | Retention time, min | K ^a |
|--------------------|------------------------|------------------------|----------------|
| Acetonitrile-water | 80+20 | 3.72 | 0.62 |
| Acetonitrile-water | 70+30 | 4.06 | 0.77 |
| Acetonitrile-water | 60+40 | 5.48 | 1.38 |
| Acetonitrile-water | 55+45 | 6.65 | 1.89 |
| Acetonitrile-water | 50+50 | 7.76 | 2.37 |
| Acetonitrile-water | 40+60 | 14.90 | 5.48 |
| MeOH-water | 70+30 | 5.73 | 1.49 |
| MeOH-water | 60+40 | 8.35 | 2.63 |

^a Capacity factors for sulfentrazone: t_0 for system = 2.3 min.

Table 3. Recovery of sulfentrazone from seven soils with methanol extraction, isocratic mobile phase, ultraviolet detection^a

| Series | Detection conc., | | |
|------------|------------------|---------|--------|
| | ng/g soil | Rec., % | RSD, % |
| Sequatchie | 880 | 93 | 0.34 |
| Drummer | 931 | 98 | 6.0 |
| Malden | 835 | 88 | 16.0 |
| Bosket | 980 | 103 | 26.3 |
| Commerce | 913 | 96 | 14.5 |
| Harkey | 938 | 99 | 11.0 |
| Dothan | 885 | 93 | 8.2 |

^a Initial concentration was 950 ng/g soil.

Table 4. Monthly rainfall from study initiation to cotton recropping for each year.

| Month | 1995 ^a | 1996 ^b | 1997 ^c | 1997 ^d |
|-----------|-------------------|-------------------|-------------------|-------------------|
| | cm | | | |
| May | 1.37 | 6.73 | 10.36 | . |
| June | 9.04 | 6.78 | 14.15 | 0.30 |
| July | 3.66 | 14.33 | 14.22 | 14.22 |
| August | 3.33 | 9.80 | 2.67 | 2.67 |
| September | 5.21 | 9.19 | 6.50 | 6.50 |
| October | 9.65 | 3.10 | 6.55 | 6.55 |
| November | 15.14 | 17.04 | 6.05 | 6.05 |
| December | 6.05 | 14.83 | 7.47 | 7.47 |
| January | 21.06 | 13.13 | 12.29 | 12.29 |
| February | 9.50 | 10.74 | 8.41 | 8.41 |
| March | 11.94 | 16.48 | 11.38 | 11.38 |
| April | 11.46 | 12.93 | 30.02 | 30.02 |
| May | 8.00 | 13.92 | 10.24 | 10.24 |
| Total | 117.90 | 149.00 | 140.31 | 116.10 |

^a Study initiation: May 23

^b Study initiation: May 22

^c Study initiation for location one: May 15

^d Study initiation for location two: June 30

Table 5. First-order dissipation rate constants (k) and half-lives (DT₅₀) of sulfentrazone in soil under field conditions.

| Year | k ± SE ^a | DT ₅₀ | r ² |
|----------|---------------------|------------------|----------------|
| 1995 | 0.0061 ± 0.001 | 113.0 | 0.87 |
| 1996 | 0.0282 ± 0.005 | 25 | 0.90 |
| 1997 one | 0.0294 ± 0.006 | 24 | 0.89 |
| 1997 two | 0.0082 ± 0.001 | 85 | 0.82 |

^a First-order rate constant ± standard error.

Table 6. Cotton field assay recropped into sulfentrazone treatments.

| Treatment | Rate | Injury ^a | | |
|---------------|--------------|---------------------|------|-------------------|
| | | 1996 | 1997 | 1998 ^b |
| Sulfentrazone | 420 g/ha | 11.0 | 15.8 | 13.4 |
| Sulfentrazone | 840 g/ha | 8.2 | 15.3 | 10.8 |
| Untreated | No herbicide | 20.1 | 15.1 | 16.6 |
| | LSD | 2.8 | 1.5 | 1.6 |

^a Cotton injury as a function of height reduction.

^b Field location two.

Table 7. First-order degradation rate constants (k) and half-lives (DT₅₀) of sulfentrazone in Tennessee soil held for 336 days at 30 C.

| Treatment | k ± SE ^a | C. I. ^b | DT ₅₀ | r ² |
|-------------|---------------------|--------------------|------------------|----------------|
| sterile | 0.0035 ± 0.0005 | (148,296) | 198 | 0.79 |
| surface | 0.0074 ± 0.0006 | (79,114) | 93 | 0.94 |
| sub-surface | 0.0068 ± 0.006 | (86,125) | 102 | 0.93 |

^a Rate constant ± standard error.

^b Lower and upper limits of 95% confidence interval.

Table 8. Correlation coefficients of various experimental parameters. Significance at the 5% level indicated by one asterisk (*) and at the 10% level indicated by two asterisks (**).

| | CEC | OM | pH | Sand | Silt | Clay | K _d |
|--------------------|--------|---------|---------|---------|---------|---------|----------------|
| Distribution value | -0.373 | -0.629 | 0.674** | 0.388 | -0.305 | -0.377 | -0.770* |
| CEC | | 0.696** | 0.325 | -0.843* | 0.563 | 0.970* | 0.207 |
| OM | | | -0.162 | -0.785* | 0.731** | 0.580 | 0.801* |
| pH | | | | -0.180 | -0.010 | 0.381 | -0.693** |
| Sand | | | | | -0.913* | -0.769* | -0.392 |
| Silt | | | | | | 0.441 | 0.500 |
| Clay | | | | | | | -0.078 |

Appendix C
SAS Programs

Program 1. SAS nonlinear procedure used to determine dissipation rate constants in the field and laboratory studies.

```
data ds1;
infile 'c:\sas\filename.DAT';
input herb $ dat ppbw stderr;
Inc=log(ppbw);
RUN;
TITLE 'title';
PROC NLIN METHOD=MARQUARDT;
MODEL ppbw=C0*EXP(K*DAT);
PARMS C0=1000 K=-0.03;
DER.C0=EXP (K*DAT);
DER.K=DAT*(C0*EXP(K*DAT));
OUTPUT OUT=STAT1 P=PRED R=RESID;
PROC PRINT; VAR herb DAT ppbw stderr PRED RESID;
RUN;
```

Program 2. SAS mixed procedure used to determine differences in adsorption.

```
data one; input soil$ kd; title 'sulfentrazone adsorption';  
cards;  
data  
;  
proc mixed;  
class soil;  
model kd=soil;  
lsmeans soil/pdiff;  
run;
```

Program 3. SAS correlation procedure used to determine correlations of various variables with adsorption (K_d) and distribution values (DV).

```
data one; input soil$ dv cec om pH kd sand silt clay;
title 'adsorption correlation';
cards;
tn 5.75 9.3 2.47 5.71 0.70 39 46 15
il 2.25 21.8 4.42 5.31 1.52 14 61 25
bs 14.60 3.8 1.08 5.72 0.23 81 15 4
yz 20.24 5.8 2.37 7.46 0.44 61 33 6
nm 13.69 25.3 2.56 8.24 0.01 30 32 38
tb 21.52 13.9 2.25 7.46 0.20 25 60 15
fl 15.40 4.8 1.87 6.07 0.45 82 13 5
;
proc corr;
var dv cec om pH kd sand silt clay;
run;
```

Program 4. SAS regression procedure used to determine relationship of pH and organic matter to K_d .

```
data one; input pH kd;
cards;
;
proc reg;
model kd = pH/p clm;
output out=rrr p=pkd r=rkd;
run;
proc plot;
plot rkd*pH/vref=0;
plot kd*pH;
run;
proc univariate normal plot;
var rkd;
run;
```

Program 5. SAS general linear procedure used to determine if there were differences within a section between runs.

```
data one; input rep section run mobility; title 'sulfentrazone mobile';  
cards;  
;  
proc sort; by section rep run;  
proc glm;  
class rep run;  
model mobility= rep run; by section;  
means run/lsd;  
run;
```

Program 6. SAS mixed procedure use to determine mean separation between sections within a particular soil.

```
data one; input run section mobility; title 'sulfentrazone mobile';  
cards;  
;  
proc mixed;  
class run section;  
model mobility=section;  
random run*section;  
lsmeans section/pdiff;  
run;
```


Program 7. SAS regression procedure used for multiple regression test of adsorption data.

```
data one; input soil$ dv cec om pH kd sand silt clay;
title 'adsorption regression';
cards;
tn 5.75 9.3 2.47 5.71 0.70 39 46 15
il 2.25 21.8 4.42 5.31 1.52 14 61 25
bs 14.60 3.8 1.08 5.72 0.23 81 15 4
yz 20.24 5.8 2.37 7.46 0.44 61 33 6
nm 13.69 25.3 2.56 8.24 0.01 30 32 38
tb 21.52 13.9 2.25 7.46 0.20 25 60 15
fl 15.40 4.8 1.87 6.07 0.45 82 13 5
;
proc reg;
model kd = om pH/ ss1 ss2 pcorr2 stb spec;
output out=ppp p=pkd r=rkd l95=lkd u95=ukd;
run;
```

VITA

Anthony Ohmes was born in Charleston, Missouri, on June 6, 1972. He grew up on a row crop and produce farm. This farm experience lead the author to a career in agriculture. In 1990, he attended Southeast Missouri State University for 1 year. In 1991, he enrolled at the University of Missouri and was awarded a Bachelor of Science degree in 1994 and a Master of Science degree in 1996. In 1996, Anthony moved to Knoxville, Tennessee to pursue a doctorate degree under the direction of Dr. Thomas C. Mueller in the department of Plant and Soil Sciences at The University of Tennessee. Upon graduation in May 1999, the author will begin work at the University of Missouri-Delta Center in the area of Weed Science.

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