To the Graduate Council:

I am submitting a thesis written by Cheryl Anne Ashburn entitled "Nicosulfuron and Rimsulfuron Dissipation in Surface Soil." I have examined the final copy of this thesis for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Master of Science, with a major in Plant and Soil Sciences.

Thomas C. Mueller, Major Professor

We have read this thesis and recommend it acceptance

Accepted for the Council:

Associate Vice Chancellor and
Dean of The Graduate School

DISSIPATION OF NICOSULFURON AND RIMSULFURON IN SURFACE SOIL

A Thesis

Presented for the

Master of Science

Degree

The University of Tennessee, Knoxville

Cheryl Anne Ashburn

December 1998

DEDICATION

This thesis is dedicated in honor of my parents
Noal and Erlene Ashburn
for their sacrifices and truly making this effort possible.
I could not have done this without their support.

ACKNOWLEDGMENTS

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

To God, with Him I can do anything,

To Dr. Tom Mueller, for his patience and guidance through both my undergraduate and graduate years,

To Dr. Bob Hayes, for his every readiness to share something new and for serving on my committee,

To Dr. Michael Mullen, for serving on my committee and for providing valuable insight,

To the Faculty and Staff of the Plant and Soil Sciences Department, for assistance throughout my studies,

To Jill Stringer, Alice Harless, Debbie Bowles, and Dawn Brown for assistance in many things,

To Todd Willan, Kent Gallaher, and Brian Corwin for their constant encouragement,

To the Breeden family, for their support,

To Edwin, Sloane, Andy, Ron, Jeff, Kathy, and Stephen for their friendship and support,

To Teffany Rich Cope, for her special friendship and encouragement,

To the Weed Science Graduate Students, Anthony Ohmes, Carrie Stiles, Eric Walker, Greg Breeden, Jimmy Summerlin, Joyce Tredaway, Rob Ellis, Robert Etheridge, and Susan Matthews, countless thanks for making my graduate school experience what it has been,

To Anita Barnett, for her hard work and dedication throughout the many hours of sample preparation and for her friendship,

To Deborah, Diane, Chrissy and Jon for all your love, prayers and support,

To my parents, Noal and Erlene Ashburn, for their love and encouragement

To Billy, for invaluable love, support, encouragement, and always believing in me

ABSTRACT

Many factors influencing herbicide dissipation have been studied; however, the effect of the presence of one herbicide on another herbicide's dissipation rate has not been extensively investigated. Field studies were established in 1997 and 1998 on a Sequatchie silt loam in Knoxville, TN. Treatments applied to tilled, bare ground included nicosulfuron (0.046 kg ai ha^{-1}), rimsulfuron (0.046 kg ai ha^{-1}), nicosulfuron (0.046 kg ai ha^{-1}) + rimsulfuron (0.046 kg ai ha^{-1}), and an untreated control. Samples (0-8 cm) were collected from 0 to 31 days after treatment (DAT) in 1997 and 1998. Laboratory studies were also conducted using the same soil. Soil was fortified at 50 ppb ($\mu g\ g^{-1}$) nicosulfuron, rimsulfuron, and nicosulfuron + rimsulfuron. Samples for the laboratory study were removed from the incubator 0, 1, 2, 3, and 7 DAT and frozen until extraction. All samples were extracted twice with 90:10 (v:v) 0.1 M aqueous ammonium carbonate/ acetone for 20 minutes. Solid phase extraction C_{18} and silica columns were used for sample cleanup and samples were analyzed using an HPLC. Neither rimsulfuron nor nicosulfuron dissipation was influenced by the presence of the other herbicide. Field studies in 1997 and 1998 determined that both herbicides alone and in mixture disappeared quickly. Rainfall within 12 hr of application in each year and a soil pH of 5.7 encouraged rapid degradation. In 1997, the half-life (DT_{50}) of nicosulfuron was 5.3 d and the DT_{50} of rimsulfuron was 3.1 d. When the two herbicides were applied in combination, the DT_{50} of nicosulfuron was 4.2 d and the rimsulfuron DT_{50} was 3.5

d. In 1998, all DT_{50} were $\leq$ 2.2 d. Rapid degradation was observed in the soil fortification experiments with DT_{50} for all treatments < 3.5 d.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

CHAPTER I

INTRODUCTION

The use of package mixtures is increasing. Often, herbicides are mixed to provide broad spectrum weed control. In the early 1990's, DuPont introduced a sulfonylurea mix (DPX-79406) which contains a 1:1 ratio of two sulfonylurea compounds: nicosulfuron and rimsulfuron. More recently, DuPont introduced Basis Gold ™ which is a three-way package mixture containing a 48:1:1 ratio of atrazine, nicosulfuron, and rimsulfuron.

Detection of herbicide residues can be achieved through a variety of analytical procedures. Some herbicides are applied at high rates and detection of these is often simple when compare to detection of herbicides applied at very low rates, e.g. sulfonylurea herbicides. For detection using high performance liquid chromatography (HPLC), lengthy sample preparation may be required. Sample clean up via solid phase extraction may also be required for success. Many factors influencing herbicide dissipation have been studied.

Temperature, moisture, and pH are all among factors known to influence herbicide dissipation rates. However, the influence of one herbicide on another's dissipation has not extensively been investigated. This study focuses on the dissipation of two sulfonylurea herbicides: nicosulfuron and rimsulfuron alone and in combination with the other.

The objectives of this study were 1.) to evaluate the dissipation of nicosulfuron and rimsulfuron alone and in combination under field conditions and

2.) to evaluate the dissipation of these herbicides and their mixture under laboratory conditions.

CHAPTER II

LITERATURE REVIEW

SULFONYLUREA HERBICIDES

The sulfonylurea herbicides were discovered by DuPont in 1975 (Beyer et al. 1986). There are over 375 sulfonylurea patents held by numerous companies, with DuPont holding most of them (Brown, 1990). The sulfonylureas are effective at low rates, typically from 4 to 32 grams ai ha^{-1} and exhibit more activity per unit of active ingredient than most other herbicides (Vencill and Banks, 1994). Mammalian toxicity is low because the target enzyme is in plants (Brown, 1990). Because they are used at low rates, environmental fate must be examined at ppb levels, which can be difficult (Marek, 1996). As a whole, the sulfonylureas are considered to be moderately mobile in soil (Ashton and Monaco, 1991). Chemically, the sulfonylureas are composed of an aryl ring, a sulfonylurea bridge, and a heterocycle containing three nitrogen (Willian,1992). Figure 1 show the general structure of the sulfonylurea herbicides.

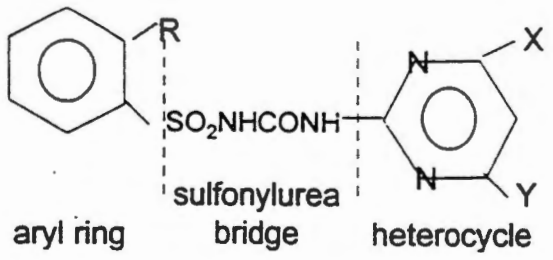

Figure 1. General Sulfonylurea Structure.

The sulfonylureas are most commonly used as postemergence herbicides; however, they do have preemergence activity. The sulfonylureas are used for weed control in agronomic and non-crop systems. Crop selectivity to these herbicides is a result of rapid biochemical degradation (Frazier, 1993). For example, rimsulfuron's selectivity is a result of unusual bridge contraction and nicosulfuron's depends on hydrolyzation of the pyrimidine ring at position five (Koeppe and Brown, 1995).

SULFONYLUREA MECHANISM OF ACTION

The sulfonylureas bind irreversibly to the ALS enzyme and inhibits ALS activity and the production of the branched chain amino acids valine, leucine, and isoleucine (Brown 1990; Ashton and Monaco, 1991). Plant death in sensitive species results from events occurs in response to ALS inhibition. The mechanism of crop selectivity varies with each sulfonylurea herbicide. The hydrolyzation of one side chains and separation of the rings resulting from a variety of reactions are the common selectivity mechanisms (Ashton and Monaco 1992). Visible signs of sulfonylurea activity include adaxial vascular reddening of leaves, leaf chlorosis, terminal bud death, and slowly developing necrosis (Brown, 1990).

SULFONYLUREA DISSIPATION

Dissipation of sulfonylureas usually follows first order kinetics, with the half-life being independent of initial concentration (Breckie and McKercher, 1989). Sulfonylureas degrade via a combination of bridge hydrolysis and microbial

degradation (Brown, 1990). However, degradation by photolysis and volatilization is also possible for some sulfonylureas (Reddy et al., 1995 and Hemmamda et al. 1994). Chemical hydrolysis and microbial degradation of sulfonylureas are affected by soil pH. Chemical hydrolysis cleaves the sulfonylurea bridge yielding sulfonamide and s-triazine derivatives (Hemmemda et al. 1994). Brown (1990) reported that degradation via chemical hydrolysis occurred more rapidly in acidic soils (~pH 5) versus alkaline soils (~pH 8). When the soil pH is near 7, microbial degradation is an important degradation mechanism (Breckie and McKercher, 1989). Sulfonylureas applied to soils of pH 6 or lower experience chemical hydrolysis as well as microbial degradation (Mueller et al., 1993). These herbicides are more persistent at higher pH (Vencill and Banks, 1994). Hemmamda and others (1994) reported this in sterile and non-sterile soil.

Brown (1990) reports a two-part dissipation model for sulfonylureas. His assumption is that this model, proposed by Hamaker and Goring, considers both microbial and chemical degradation, the two most common degradation mechanisms. In this model, the compound is subject to both types of degradation. In theory, the applied herbicide diffuses into spaces too small for microbial activity. The herbicide in these "protected spaces" is subject to hydrolytic degradation processes. Once the microbially available chemical has degraded, degradation over extended periods of time may result from hydrolysis in the protected spaces.

FACTORS INFLUENCING SULFONYLUREA DISSIPATION

Sulfonylurea dissipation is influenced not only by chemical structure, but

also by organic matter, soil pH, soil moisture and soil temperature (Breckie and McKercher, 1989 and Ahmad and Crawford, 1990). Schneiders and others (1993) reported that rimsulfuron is moderately adsorbed to soils with high clay or organic matter content. Mersie and Foy (1986) found that sulfonylurea soil mobility increases with decreasing organic matter content and increasing soil pH. Thirunarayanan and others (1985) reported inverse relations between pH and degradation half-life of sulfonylurea herbicides. Chlorsulfuron half-life in soil was 89 d and 144 d at pH levels of 6.2 and 8.1 respectively. This pH relationship is due to the increased susceptibility (250 to 1000X) of the neutral form of the sulfonylurea bridge to hydrolysis when compared to the anionic form (Brown, 1990). Brown (1990) also reports that the charge of sulfonylureas in the neutral form is not distributed uniformly throughout the molecule and therefore, results in an increased electrophilic nature of the carbonyl-carbon. Thus, it can be concluded that pH influences the rate of bridge hydrolysis via ionization effect. Studies with varying temperatures found chlorsulfuron half-life was 229 d at 10 C and 63 d at 40 C (75% of field capacity, and pH 7.7). Chlorsulfuron was more persistent in drier, cooler soil.

Sulfonylurea herbicides differ widely in their length of activity. Chlorsulfuron is persistent for periods greater than 1.5 yrs. Metsulfuron-ethyl and chlorimuron-ethyl are also among the longer residual sulfonylurea herbicides (Brown, 1990). Others dissipate rapidly and are undetectable in as few as seven days. Rimsulfuron has a half-life of 5.6 d under field conditions (Schneiders et al., 1993). Sulfonylurea degradation is more rapid in warm, moist, light-textured soils with low

pH (Beyer, 1986; Ashton and Monaco, 1991). The persistence of some sulfonylurea herbicides can damage rotational crops (Cotterill, 1992). When chlorsulfuron is applied the previous season, 99.5% of the herbicide must degrade before sugar beets can be planted without injury the following season (Brown, 1990). Herbicide labels contain guidelines for application rates and recropping intervals based on soil pH. Recropping intervals are based on the relationship between pH and hydrolysis. Some long residual sulfonylureas are not labeled for use on alkaline soils because of the lack of hydrolysis (Brown, 1990). Modifications to sulfonylureas structures produce herbicides with more rapid degradation. These short residual sulfonylureas include DPX-L5300 which is subject to rapid degradation via hydrolysis and thifensulfuron-methyl [methyl 3-[[[[(4-methoxy-6-methyl-1,3, 5-triazin-2-yl]-amino]-carbonyl]amino]sulfonyl-2-thiophenecarboxylate] which is subject to rapid microbial degradation (Brown, 1990).

NICOSULFURON

Nicosulfuron (2-[[[[(4,6-dimethoxy-2-pyrimidinyl)amino]carbonyl]amino] sulfonyl]-N,N-dimethyl-3pyridinecarboxamide) is a commonly used herbicide in corn production for control of johnsongrass (*Sorghum halepense*) and other troublesome weeds. Nicosulfuron also inhibits ALS enzyme and branched chain amino acid production. Application rates range from 35 to 70 g/ha (Herbicide Handbook, 1994). Figure 2 gives the structure for nicosulfuron. Slower nicosulfuron dissipation is observed in alkaline soils (Mekki and Leroux, 1995).

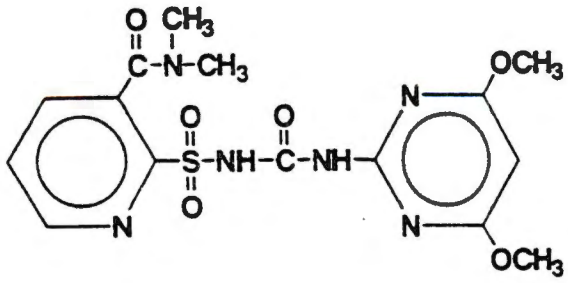

Figure 2. Nicosulfuron Structure.

The average half-life of nicosulfuron in a soil of pH 6.5 is ~21 days (Herbicide Handbook, 1994). Nicosulfuron is a white solid with a pKa of 4.3 and is soluble in water to 39,200 ppm at pH 6.85 (Herbicide Handbook, 1994).

RIMSULFURON

Rimsulfuron (*N*-[[4,6-dimethoxy-2-[pyrimidinyl)amino]carbonyl]-3-(ethylsulfonyl)-2-pyridinesulfonamide) is used for weed control in maize and potato (Kreidi, 1992). In the United States, it is used for postemergence weed control in potatoes. Rimsulfuron is active at low rates (5 to 20 g ha^{-1}), has very low potential for ground water contamination, and exhibits low mammalian toxicity (Eberlin, 1994 and Green and Green, 1993). Rimsulfuron is a white, odorless powder having a pKa of 4.0 and is soluble in water to 7300 ppm at a neutral pH (Green and Green, 1993). The structure of rimsulfuron is outlined in Figure 3.

Rimsulfuron is rapidly degraded in both alkaline and acidic soils (Mekki and Leroux 1995 and Green and Green 1993). Rimsulfuron degradation was rapid in pH 5, 7 and 9 solutions and soil (silt loam in Newark, DE) due to bridge contraction

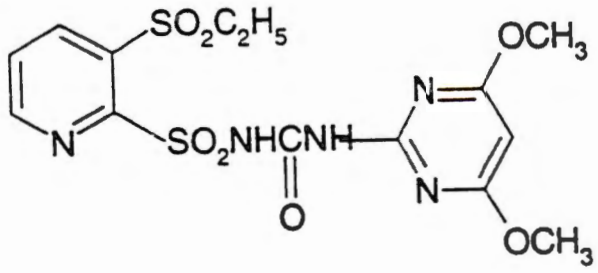

Figure 3. Rimsulfuron Structure.

Schneiders et al., 1996). Because of its rapid degradation, crop rotation limits are minimal (Leep et al. 1991 and Mekki and Leroux, 1994).

HERBICIDE INTERACTION

Although mixing of herbicides is quite common, better weed control is not always the result. Herbicides may be antagonistic or synergistic to one another. This is often the case with postemergence herbicides. Antagonism is also prevalent when quick-acting contact herbicides are mixed with slower systemic herbicides. When POST graminicides and dicot herbicides are mixed, reduced grass control often results. For example, when clethodim is mixed with pyrithiobac, reduced grass control results when compared to clethodim alone (Tredaway et. al, 1998). Changes in herbicide dissipation rate may also be possible when herbicides are mixed. Researchers in Germany have reported changes in dissipation rates when two sulfonylurea herbicides were mixed (personal communication with Mike Duffy). Synergistic relationships may be observed when sulfonylurea herbicides and organophosphate insecticides are

applied to the same crop. These interactions may result in injury to crops. Diehl and Stoller (1995) reported terbufos (S-[[(1,1-dimethylethyl) thio] methyl]O,O-diethyl phosphorodithioate) insecticide preemergence followed by nicosulfuron postemergence injured corn and reduced yield. Application method (in furrow, T-band, etc.) and formulation type (controlled release CR, granular G, etc.) proved to be factors when applying terbufos treatments preemergence followed by nicosulfuron postemergence, resulting in differing severity of synergistic response. Diehl and others (1995) reported that in-furrow applications were more injurious than surface band applications and the 15G formulation was more injurious than the 20CR formulation. Frazier and others (1993) reported that corn treated with terbufos (Counter 15G) preemergence followed by primisulfuron (2-[[[[[4,6-bis (difluoromethoxy)-2-pyrimidinyl]amino] carbonyl]amino]sulfonyl] benzoic acid) postemergence did not cause visual injury, but shoot dry weight and length were reduced. The insecticide treatment had no effect on primisulfuron metobolite profiles, but rather the increased herbicide activity resulted from decreased metabolism of primisulfuron in terbufos treated corn.

SULFONYLUREA DETECTION

Because they are used at low use rates, analytical detection of sulfonylurea herbicides to monitor environmental fate has been difficult (Marek, 1996). This is further complicated by their chemical instability (Powley and de Bernard, 1998). Various detection mechanisms have been attempted with varying success. One is plant bioassay systems. Cotterill (1992) reported that bioassays are extremely

sensitive, but lack specificity. Bioassays are cost effective, but results may be confounded by other herbicidally active compounds or non-herbicidal parameters (Amhad and Crawford, 1990). Other techniques are extraction followed by either high pressure liquid chromatograph (HPLC), gas chromatography, supercritical fluid chromatography, capillary electrophoretic techniques, or enzyme immunoassay (Smith, 1995). Unlike other herbicides, sulfonylureas cannot be directly detected by gas chromatography due to their low volatility and thermal instability (Powley and de Bernard, 1998). However, gas chromatography is a successful technique for the analysis of sulfonylureas, e.g. rimsulfuron, hydrolysis products (Marucchini and Luigetti, 1997). Cotterill (1992) evaluated metsulfuron-methyl derivatives by gas chromatography.

The most common detection mechanism for sulfonylurea analysis in soil and water is by HPLC using either ultraviolet or mass-spectrometric detection (Powley and de Bernard, 1998). HPLC analysis has also been used to detect sulfonylurea degradation residues in seeds from resistant plants (Dyer et al., 1993). Hemmemda and others (1994) analyzed hydrolysis studies via HPLC analysis. Powley and de Bernard (1998) detected nine sulfonylurea herbicides in water and soil using HPLC. Sample clean up via solid phase extraction (SPE) and concentration was successful. With modifications, detection of other sulfonylurea herbicides is possible. Solid phase extraction was used for sample cleanup by Marek and Koskinen (1996). Galletti (1995) developed an HPLC-UV method for detection of four sulfonylureas with detection limits ranging from 1 to 50 ppb. Studies investigating the dissipation of nicosulfuron and rimsulfuron without aid of

14C label were not readily documented in literature. Rather, persistence is indirectly measured as a function of length of weed control.

QUALITY ASSURANCE OF HERBICIDE DISSIPATION STUDIES

Studies to examine herbicide fate in soil are common in weed science research. Research is conducted under controlled (laboratory, incubator, etc.) or uncontrolled (field, greenhouse) conditions. Quality of studies done under uncontrolled conditions are often questionable. Blumhorst and Mueller (1996) reported several questionable points about these studies and present several pieces of information that should be included in dissipation studies.

Soil analysis should be done before herbicide application. When publishing data, it is recommended that limit of detection, recoveries, site history with respect to herbicide treatment and environmental conditions be included. Recoveries between 70 and 120% of fortified concentrations are deemed acceptable by the EPA. Storage stability of samples in freezers were also questioned and not recommended for periods > 30 d. As suggested by these authors and others, running fortified blanks are also recommended. Sampling is very important to field studies and samples should accurately be taken to the same depth at each sampling point. It is common, and expected, that herbicide concentrations increase in the sample directly following the time 0 (day of application) sample, due to the difficulty of obtaining an accurate, representative soil sample at that time.

CHAPTER III

DISSIPATION OF NICOSULFURON AND RIMSULFURON IN SURFACE SOIL[1]

ABSTRACT

Field and soil fortification studies were conducted to evaluate the half-life (DT_{50}) of nicosulfuron and rimsulfuron in surface soil. Also, the dissipation rate was evaluated with the two compounds applied simultaneously to the same plot. Field studies in 1997 and 1998 determined that both herbicides alone and in mixture disappeared quickly. In 1997, half-life of nicosulfuron was 5.3 d and the half-life of rimsulfuron was 3.1 d. When the two herbicides were applied in combination, the half-life of nicosulfuron was 4.2 d and the half-life of rimsulfuron was 3.5 d. In 1998, all half lives were ≤ 2.2 d. Rainfall on the day of application and soil pH of 5.7 encouraged rapid degradation. Rapid degradation was observed in the soil fortification experiments with all half lives <3.5 d. The presence of nicosulfuron did not influence the degradation of rimsulfuron and rimsulfuron presence did not influence nicosulfuron degradation.

Nomenclature: Nicosulfuron, (2-[[[[(4,6-dimethoxy-2-pyrimidinyl) amino] carbonyl] amino]sulfonyl]-N,N-dimethyl-3pyridinecarboxamide); Rimsulfuron (N-[[4,6-dimethoxy-2-[pyrimidinyl)amino]carbonyl]-3-(ethylsulfonyl)-2-pyridine sulfonamide).

Additional Index Words: HPLC, soil dissipation, solid phase extraction

---

[1] This chapter has been submitted for publication with C.A. Ashburn, R.M. Hayes and T.C. Mueller as authors.

INTRODUCTION

Herbicide dissipation is influenced by many factors including soil pH, climate, temperature, rainfall, etc. However, the influence given by another herbicide's presence has not been extensively studied. If two herbicides are package mixed, what happens to the dissipation rate of the two herbicides? Herbicide package mixes are becoming more common, so this is a relevant question to producers. DuPont Agricultural Products (Wilmington, Delaware) has marketed a new postemergence package mixture for weed control in corn (*Zea mays*) (Anonymous, 1997). It is a combination of nicosulfuron, rimsulfuron, and atrazine. The nicosulfuron: rimsulfuron mixture controls weeds in corn with decreased carryover potential (Doohan et. al, 1998 and Mekki and Leroux, 1993). Nicosulfuron controls of seedling and rhizome johnsongrass (*Sorghum halepense*); however, it exhibits poor control of several broadleaf weeds including common ragweed (*Ambrosia artemisiifolia*), velvetleaf (*Abutilon theophrasti*), and common cocklebur (*Xanthium strumarium*) (Dobbels and Kapusta, 1993). Rimsulfuron controls both monocot and dicot weeds (Mekki and Leroux, 1993). When mixed, these two compounds exhibit improved weed control (Mekki and Leroux, 1993). With increased atrazine restrictions possible in the future, the 1:1 mixture shows promise as an alternative to atrazine (McMullan and Blackshaw, 1995). This study focuses on the dissipation rate of the two sulfonylureas in this package mixture.

Carryover can be a problem when recropping to a crop or cover crop which is not tolerant to the previous herbicides. For this reason, persistence of

herbicides is of interest. Detection of herbicides to determine length of persistence can be achieved by a variety of techniques; however, many are lengthy and tedious. Due to the difficulty of analysis, there are few cases where analytical detection of these two herbicides are documented

Dissipation of sulfonylureas usually follows first order kinetics, with the half-life being independent of initial concentration (Breckie and McKercher, 1989). Sulfonylureas degrade via a combination of bridge hydrolysis and microbial degradation (Brown, 1990). However, degradation by photolysis and vaporization is also possible for some sulfonylureas (Reddy et al., 1995 and Hemmamda et al., 1994). Chemical hydrolysis and microbial degradation of sulfonylureas are affected by soil pH. Chemical hydrolysis cleaves the sulfonylurea bridge resulting in sulfonamide and s-triazine derivatives (Hemmemda et al. 1994). Brown (1990) reported that degradation via chemical hydrolysis occurred more rapidly in acidic soils (~pH 5) versus alkaline soils (~pH 8). When the soil pH is near 7, microbial degradation is an important degradation mechanism (Breckie and McKercher, 1989). Sulfonylureas applied to soils of pH 6 or lower experience chemical hydrolysis as well as microbial degradation (Mueller et al., 1993). These herbicides are more persistent at higher pH (Vencill and Banks, 1994). Hemmamda and others (1994) reported this in sterile and non-sterile soil.

Sulfonylurea dissipation is influenced not only by chemical structure, but also by organic matter, soil pH, and environmental conditions resulting from varying moisture and temperature combinations (Breckie and McKercher, 1989 and Ahmad and Crawford, 1990). Schneiders and others (1993) reported that

rimsulfuron is moderately adsorbed to soils with high amounts of clay or organic matter. Mersie and Foy (1986) found that sulfonylurea soil mobility increases with decreasing organic matter content and increasing soil pH. Thirunarayanan and others (1985) reported inverse relations between pH and degradation half-life of sulfonylurea herbicides. Chlorsulfuron half-life in soil was 89 d and 144 d at pH levels of 6.2 and 8.1, respectively. This pH relationship is due to increased susceptibility (250 to 1000X) of the neutral form of the sulfonylurea bridge to hydrolysis when compared to the anionic form (Brown, 1990). Brown (1990) also reports that the charge of sulfonylureas in the neutral form is not distributed uniformly throughout the molecule and therefore, results in an increased electrophilic nature of the carbonyl-carbon. Thus, it can be concluded that pH influences the rate of bridge hydrolysis via ionization effect. Studies looking at temperature found chlorsulfuron half-life was 229 d at 10 C and 63 d at 40 C (75% of field capacity, and pH 7.7). Chlorsulfuron was more persistent in drier, cooler soil.

Sulfonylurea herbicides differ widely in their duration of activity. Chlorsulfuron persists for periods greater than 1.5 yr. Metsulfuron-ethyl and chlorimuron-ethyl have even longer residual activity, while other sulfonylurea herbicides dissipate rapidly and are undetectable in as few as 7 d (Brown, 1990). Rimsulfuron has a half-life of 5.6 d under field conditions (Schneiders et al., 1993). Sulfonylurea degradation is more rapid in warm, moist, light-textured soils with low pH (Beyer, 1986 and Ashton and Monaco, 1991). The persistence of some sulfonylurea herbicides can injure rotational crops (Cotterill, 1992). When

chlorsulfuron is applied the previous season, 99.5% of the herbicide must degrade before sugar beets can be planted without injury the following season (Brown, 1990). Labels contain guidelines for application rates and recropping intervals based on soil pH. The background for these result from the relationship between pH and hydrolysis. Some long residual sulfonylureas are not labeled for use on alkaline soils because of the lack of hydrolysis (Brown, 1990). Modifications to sulfonylurea structures have resulted in herbicides which rapidly degrade. These short residual sulfonylureas include DPX-L5300 which is subject to rapid degradation via hydrolysis and thifensulfuron-methyl which is subject to rapid microbial degradation (Brown, 1990).

The objectives of this study were 1.) To determine the half-life of nicosulfuron and rimsulfuron and 2.) to examine the effect of the two herbicides applied in combination on dissipation rates.

MATERIALS AND METHODS

Field Study. Field plots were established in 1997 and 1998 on a Sequatchie silt loam. Several properties of this soil are given in Table 1. Plots were established on bare, tilled ground and were 3 m by 15 m. The study consisted of four treatments as outlined in Table 2. Treatments were applied in 1997 and 1998 to tilled, bare ground using a CO_2-backpack sprayer at 140 L ha^{-1} at 240 kPa on June 30 of each year. Application timing was chosen to simulate typical timing when these POST emergence herbicides are applied in Tennessee.

Table 1. Soil Properties.

Characteristic	Value
pH	5.7
CEC	7.0
O.M.	1.3%
Sand, %	27
Silt, %	59
Clay, %	14

Table 2. Treatments for Field Dissipation Study.

Treatment	Herbicide	Rate
1	Nicosulfuron	0.046 kg ai ha^{-1}
2	Rimsulfuron	0.046 kg ai ha^{-1}
3	Nicosulfuron Rimsulfuron	0.046 kg ai ha^{-1} 0.046 kg ai ha^{-1}
4	Untreated	

Herbicide rates were chosen in a ratio comparable to those in the Basis Gold package mixture. No surfactant was included in the spray mixture because treatments were applied to bare ground. The study utilized a randomized complete block design with four replicates.

Sample Collection. Surface soil samples were taken randomly within plots using a hand-held 8 cm core sampler. Two cores were taken per plot and composited. The sampler was cleaned between plots. The samples were put into plastic bags

and immediately frozen at -10 C until analysis. In 1997, samples were taken to a depth of 0 to 10 cm at 0, 2, 4, 7, 11, 14, 18, 31 and 60 days after treatment (DAT). Samples were taken (0-8 cm) in 1998 were 0, 1, 2, 3, 4, 7, 11, 14, 18, and 31 DAT and samples were taken to a depth of 8 cm. Both years it rained within 12 hrs after application (Appendix A, Table A-1).

Soil Fortification Research. Air dried, screened soil (50 g) taken from the field study untreated area was placed in Low Density Polyethylene (LDPE) bottles and fortified with herbicide at 50 ng g^{-1} soil basis (Table 3). Studies were completed twice with three replications and data combined for the two studies. Samples were then placed in an incubator at 30 C and removed at 0, 1, 2, 3, and 7 DAT. Samples were frozen at -10 C until analysis.

Table 3. Treatments for Soil Fortification Study.

Treatment	Herbicide	Rate
1	Nicosulfuron	50 ng g^{-1}
2	Rimsulfuron	50 ng g^{-1}
3	Nicosulfuron	50 ng g^{-1}
	Rimsulfuron	50 ng g^{-1}
4	Untreated	

Herbicide Extraction. Extraction methods were slightly modified from those of Powley and de Bernard (1998). Nicosulfuron and rimsulfuron were simultaneously extracted and analyzed using the same methodology. Field study samples were thawed and then thoroughly homogenized. Moist soil (50 g) was then placed into a 250 ml LDPE bottle. The soil was extracted with 100 ml of aqueous ammonium carbonate (0.1M) / acetone solution (90:10 v:v) by agitating on a reciprocating shaker[2] for 20 min. Samples were centrifuged in a refrigerated centrifuge (4 C) at 5000 rpm for 45 min. The supernant was decanted through glass wool into a 250 ml Erlenmeyer flask and 100 ml extracting solution were added to repeat the extraction procedure. The supernants were combined. Extraction was completed 1 d before clean up and samples were stored in a refrigerator at 4 C overnight. An aliquot of the supernant (120 ml) was placed into a clean LPDE bottle and the pH adjusted to between 3.0 and 3.5 with 85% phosphoric acid to protonate the herbicide molecule before passing through the solid phase extraction cartridge.

Sample Cleanup. Solid phase extraction, while under negative pressure at 110 kPa (± 35 kPa), was completed using a vacuum extraction manifold[3] to hold cartridges . The cartridges for the first clean up were C_{18} (2g/12 ml)[4]. The C_{18} cartridges were preconditioned with methanol (5 ml) followed by water (10 ml).

---

[2] Eberbach, Ann Arbor, MI

[3] Alltech, Deerfield, IL

[4] Varian part no.1225-6008, Varian, Sugarland TX

The sample extract was slowly passed (5 ml min^{-1}) through the individual column allowing individual droplets to form at the column base. After all of the supernant had passed, the cartridge was rinsed with water (5 ml). A graduated 13 ml centrifuge tube was placed under each cartridge. The cartridge was then eluted with 0.1% glacial acetic acid in ethyl acetate (10 ml). Samples were placed in a water bath at 35 C and dried using a stream of nitrogen gas. Samples were reconstituted in acetone (1 ml) and mixed well using a vortex mixer and ultra sonicated for 5 min. The samples were placed in the water bath and dried a second time. This process removed any excess water.

The second cleanup was with a silica cartridge (1 g/6 ml)[5] because of the high affinity sulfonylurea herbicides have for silica. Ethyl acetate (2 ml) was added to reconstitute the sample, mixed with a vortex mixer, and ultra sonicated for five minutes. Then, hexane (10 ml) was added. The silica cartridge was preconditioned with ethyl acetate (5 ml) followed by 5 ml hexane/ethyl acetate (80:20 v:v). The sample extract was then passed through the column. The test tube was rinsed with the hexane/ethyl acetate mixture (5 ml) and the rinsate was passed through the column. The herbicide was then eluted from the column with 0.5% glacial acetic acid in acetone (15 ml) into a centrifuge tube. The sample extract was dried using the water bath (35 C) and a nitrogen stream.

The sample was then reconstituted in (1 ml) acetone, vortexed, and ultra sonicated for 5 min. Potassium phosphate buffer, pH 6.2 (1 ml), was added and

---

[5] Varian part no.1225-6012, Varian, Sugarland TX

the sample reduced to < 1 ml. Samples were brought to 1 ml with buffer (6.2) and passed through a 0.45 μm syringe filter[6] into a 4-ml vial[7] . The sample was then brought to 2 ml in 6.5 buffer and injected for analysis.

Herbicide Analysis. Samples were analyzed using reverse phase high performance liquid chromatography (HPLC). The column was a Zorbax 4.6 x 250 mm SB-phenyl analytical column with a Zorbax SB-Phenyl guard cartridge[8]. All solvents were HPLC grade[9] and consisted of acetonitrile and 0.30 mM potassium phosphate buffer at either pH 2.7 or 6.2. Buffered mobile phases were adjusted to the proper pH by using 85% phosphoric acid for the pH 2.7 (2.6- 2.8) solution and 10% ammonium hydroxide for the pH 6.2 (6.1 - 6.3) solution. Flow rate was constant at 1.0 ml min^{-1}. Table 4 lists the mobile phase gradient. The concept of the gradient program was to load and concentrate the herbicide at the column head due to the initially low pH. The water soluble components were then extracted from the soil matrix. Nicosulfuron and rimsulfuron were then eluted from the column by increasing the organic solvent concentration. A tunable absorbance detector[10] was operated at 245 nm determination of nicosulfuron and rimsulfuron.

---

[6] Millipore 0.45 μm Hydrophilic PTFE/PE, from Fisher Scientific

[7] National Scientific Company, Fisher cat. no. 03-375-3G

[8] P/N 880975-912 and 820674-917, MAC MOD via Hewlett Packard

[9] Fisher Scientific, Fair Lawn, NJ and Burdick and Jackson, Muskegon, MI

[10] Waters 486 Tunable UV detector, Milford, MA

Data was captured using a computer data system[11]. Recoveries for nicosulfuron and rimsulfuron were both 70%. Herbicide concentrations were determined using an external standard technique. Analytical standards of nicosulfuron (94.5%) and rimsulfuron (99.1%) were used (DuPont Agricultural Products, Wilmington, DE). Samples were processed by each sampling interval and experimental replication identity was maintained throughout analysis. A fortified control sample was included with extraction runs as a measure of herbicide recovery.

Table 4. Mobile Phase Flow Gradient Table.

Time	Acetonitrile	30 mM Phosphate Buffer	
		pH 2.7	pH 6.5
min	----------%----------		
Initial	23	72	5
10.05	10	5	85
15.00	10	5	85
30.00	30	5	65
30.05	50	25	25
40.00	23	72	5
55.00	23	72	5
60.00	23	72	5

[11] Hewlett-Packard ChemStation, San Fernando, CA

Pump Maintenance. For proper pump operation, it is very important to never allow flow to stop completely when using buffered mobile phase. Also, pump heads should be rinsed with water each morning and evening during run periods to avoid buffer precipitation on plungers. This is done by irrigating the plunger through an access hole on the pump head.

Statistical Analysis. Data were fit to first order kinetics using SAS nonlinear (NLIN) regression procedure[12] (Appendix B). The data were regressed against time in days. Output from the NLIN procedure included first order dissipation rate constant (k) and upper and lower confidence intervals. These values were converted into days to 50% (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-(residual sums of squares/corrected total sums of squares)]

This is a conservative approach because two standard deviations are given for each rate constant (Brown et al.1996 and Zar, 1992).

RESULTS AND DISCUSSION

Field Dissipation Study. The observed half-lives of both herbicides in mixture were equivalent to the dissipation rate when applied alone (Table 5). In 1997, nicosulfuron applied alone and in a mixture with rimsulfuron had DT_{50} of 5.3 d and

[12] SAS Institute, Cary, NC

4.2 d, respectively. Rimsulfuron half-lives were 1.2 d and 2.2 d alone and in mixture, respectively (Figure 4). In 1998, there were no differences in dissipation rate between the sulfonylureas applied alone and in mixture (Figure 5). Herbicide concentration decreased over time; however, initial herbicide concentration differed by year. This can be attributed to difference in sampling technique with deeper samples taken in 1997. However, all samples were taken to a consistent depth throughout a given year. Both herbicides disappeared quickly in the field and would cause minimal problems for crop rotation. Sulfonylurea degradation is more rapid in warm, moist, light-textured soils with low pH (Beyer, 1986 and Ashton and Monaco, 1991). In both years, adequate rainfall occurred within 12 hrs of application to favor microbial degradation. Soil pH was 5.7. This would favor a combination of chemical hydrolysis and microbial degradation (Hemmemda et al. 1994). Temperature throughout the field study interval was > 16.0 C. (Appendix A, Table A-2). Another possible explanation may be that the herbicide leached below the zone of soil sampling which is beyond the scope of this study. Under different environmental conditions, nicosulfuron and rimsulfuron dissipation results may differ. However, in soils with similar properties, these results are expected.

Table 5. First order dissipation rate constants (k), calculated half-lives (DT_{50}), and 95% confidence interval (C.I.) for herbicides in surface soil from field experiments.

Year	Herbicide Treatment	r^2	k	DT_{50}	C.I.
			day^{-1}	days	days
97	Nicosulfuron Only	0.92	0.13	5.3	3.6 - 9.7
97	Nicosulfuron Mix	0.89	0.17	4.2	2.7 - 9.4
97	Rimsulfuron Only	0.95	0.22	3.1	2.3 - 5.4
97	Rimsulfuron Mix	0.85	0.20	3.5	2.0 - 13.9
98	Nicosulfuron Only	0.91	0.54	1.3	0.8 - 3.5
98	Nicosulfuron Mix	0.85	0.32	2.2	1.3 - 6.6
98	Rimsulfuron Only	0.83	0.56	1.2	0.7 - 3.8
98	Rimsulfuron Mix	0.91	0.32	2.2	1.4 - 4.2

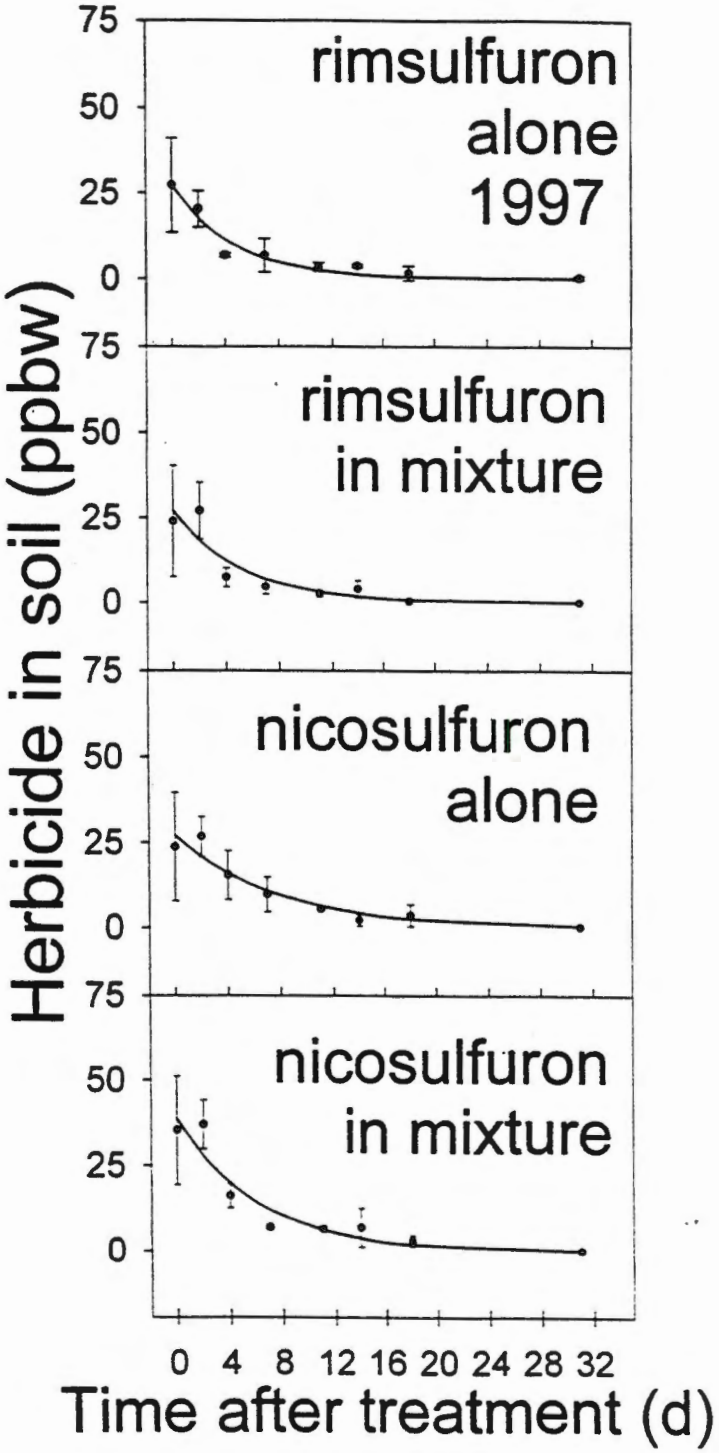

Figure 4. Concentration of Nicosulfuron and Rimsulfuron Alone and In Mixture During July 1997 in Surface Soil (0-8 cm).

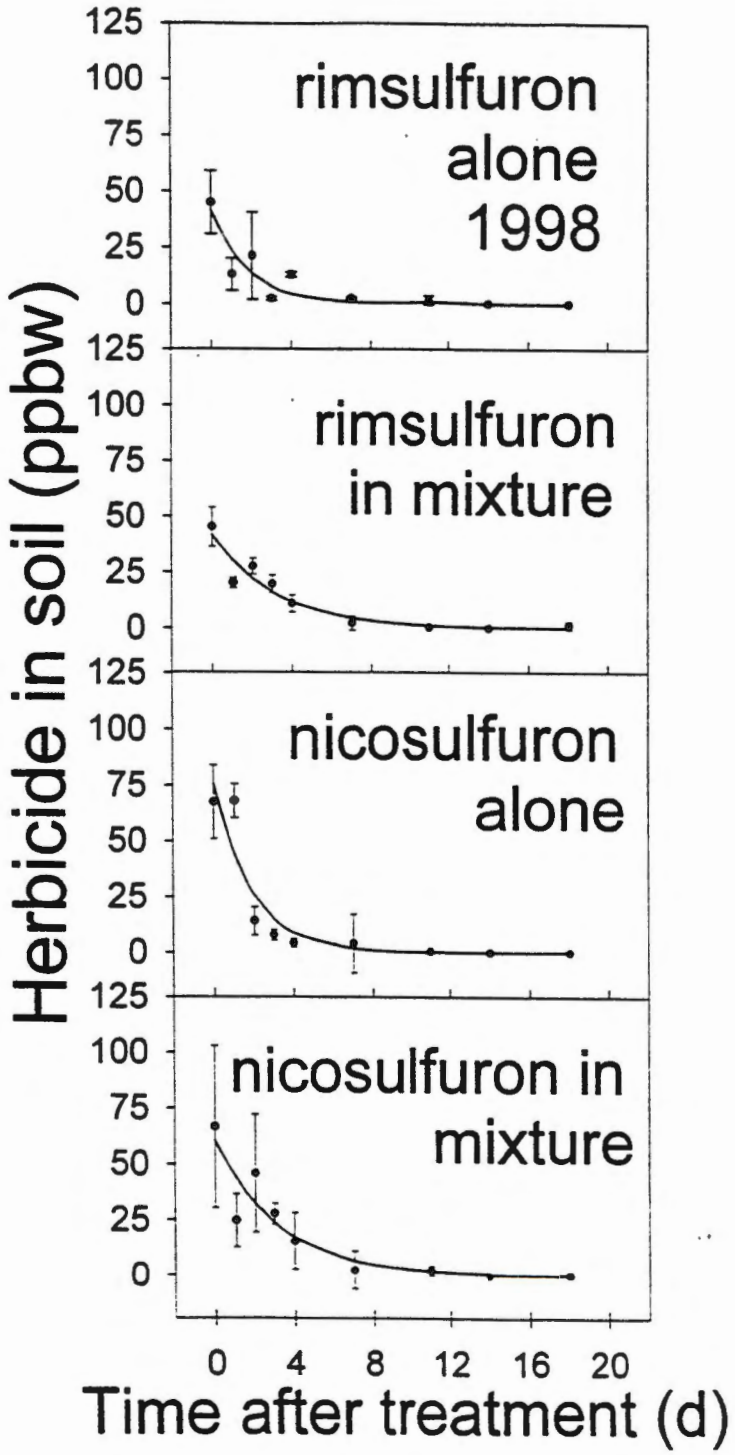

Figure 5. Concentration of Nicosulfuron and Rimsulfuron Alone and In Mixture During July 1998 in Surface Soil (0-8 cm).

Soil Fortification Study. Dissipation rates between herbicides did not differ either alone or in mixture. All treatments in the laboratory experiment followed first-order degradation with all r^2 values > 0.92 (Table 6). Dissipation in the laboratory is given in Figure 6. With pH, temperature, and moisture held constant, there were no difference in herbicide half-lives when applied alone and in mixture. Herbicide concentrations decreased rapidly with time and followed first order kinetics. Except nicosulfuron-mix 1998, herbicide DT_{50} values in the soil fortification study were smaller when compared to field study DT_{50} values. Neither herbicide was very persistent (DT_{50} < 5d). The rimsulfuron DT_{50} was shorter than the nicosulfuron DT_{50}. Temperature difference between laboratory and field experiments may explain observed differences with rimsulfuron. Nicosulfuron upper confidence levels were higher than expected. The short length of sampling period did not allow nicosulfuron concentration of reach zero.

Table 6. First-order dissipation rate constants (k), calculated half-lives (DT_{50}), and 95% confidence interval (C.I.) for herbicides in surface soil from soil fortification experiments.

Herbicide Treatment	r^2	k	DT_{50}	C.I.
		day^{-1}	days	days
Nicosulfuron Alone	0.93	0.34	2.0	1.2 - 5.9
Nicosulfuron Mix	0.92	0.30	2.3	1.4 - 7.0
Rimsulfuron Alone	0.98	1.15	0.6	0.5 - 0.9
Rimsulfuron Mix	0.99	1.53	0.45	0.4 - 0.5

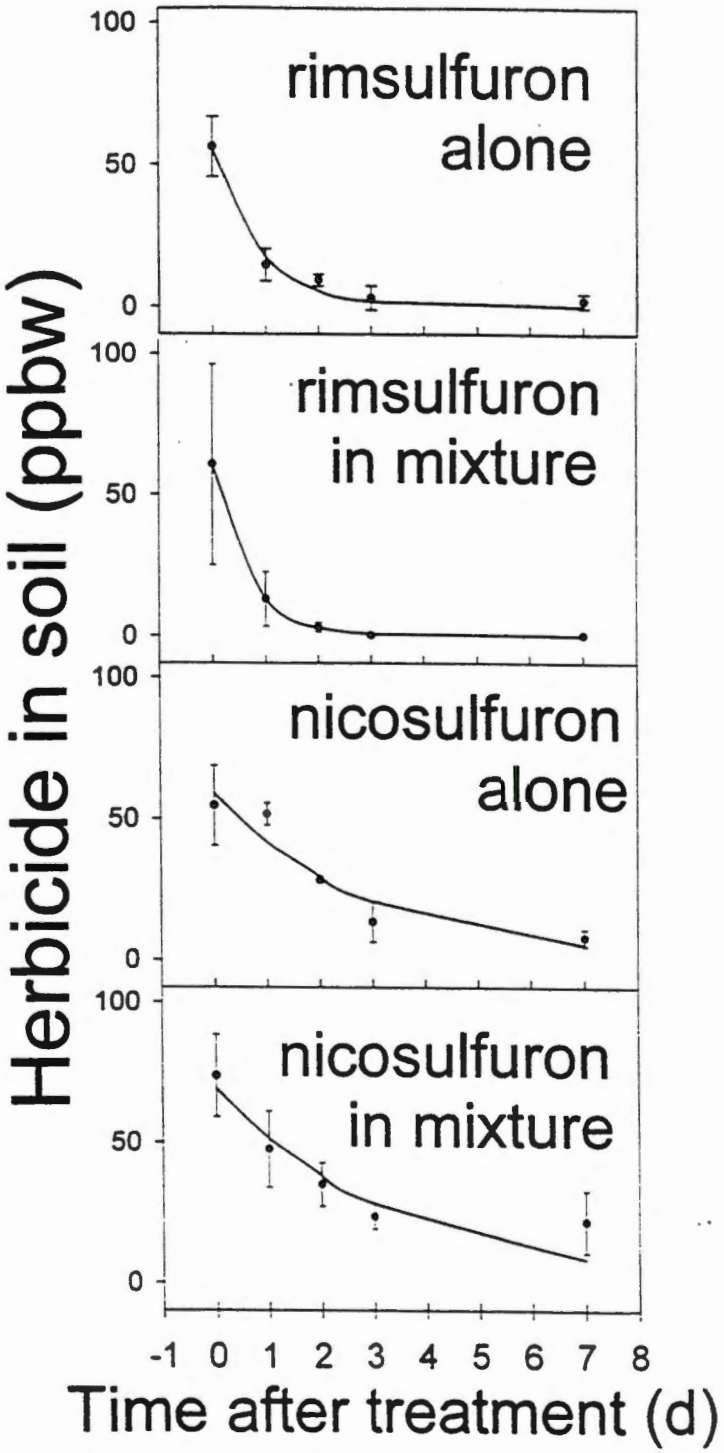

Figure 6. Concentration of Nicosulfuron and Rimsulfuron Alone and in Mixture in the Soil Fortification Study.

The presence of nicosulfuron did not influence the degradation of rimsulfuron and rimsulfuron presence did not influence nicosulfuron degradation. Half-lives for nicosulfuron were comparable to those reported at Newark, DE on a soil with 1.4% O.M. and a pH of 6.0 (Herbicide Handbook, 1994). Half-life values for rimsulfuron in this study were comparable with those previously reported (Herbicide Handbook, 1994).

LITERATURE CITED

LITERATURE CITED

Ahrens, W.H., ed. 1994. Herbicide Handbook, Seventh Edition, Weed Science Society of America. Champaign, IL 352 pp.

Amhad, I. and G. Crawford. 1990. Trace residual analysis of the herbicide chlorsulfuron in soil by gas chromotography-electron capture. J. Agric. Food Chem. 38:138-141.

Anonymous, 1997. Basis Gold Update Bulletin. Wilmington, DE.

Ashton and Monaco. 1991. Weed Science, Principles and Practices. Third Edition J. Wiley Publishers, New York. p 266-272.

Beyer, E. 1986. Sulfonylurea herbicides - Pioneering a new trend in weed control. North Central Weed Science Society Proceedings Vol. 41:137-142.

Blumhorst, M.R. and T.C. Mueller. 1997. Quality control procedures in herbicide field dissipation studies. Weed Technol.11:832-837.

Breckie, H.J. and R.B. McKercher. 1989. Soil residual properties of DPX-A7881 under laboratory conditions. Weed Sci. 37:412-418.

Brown, B.A., R.M. Hayes, D.D. Tyler, and T.C. Mueller. 1996. Effect of long term vetch (*Vicia villosa*) cover crop and tillage system on fluometuron dissipation from surface soil. Weed Sci. 44:171-175.

Brown, H.M. 1990. Mode of action, crop selectivity, and soil relations of the sulfonylurea herbicides. Pestic. Sci. 29:263-281.

Cotterill, E.G. 1992. Determination of the sulfonylurea herbicides chlorsulfuron and metsulfuron-methyl in soil, water and plant material by gas chromotography of their pentafluorobenzyl derivatives. Pestic. Sci. 34:291-

296.

Dobbels and Kapusta, 1993. Postemergence weed control in corn (*Zea mays*) with nicosulfuron combinations. Weed Technol.7:844-850.

Diehl, K.E. and E.W. Stoller. 1995. Effect of simulated rainfall, insecticide formulation, and insecticide application method on the interaction between nicosulfuron and terbufos in corn (*Zea mays*). Weed Technol.9:80-85.

Doohan, D.J., J.A. Ivany, R.P. White, and W.A. Thomas. 1998. Tolerance of early maturing corn (*Zea mays*) hybrids to DPX-79406. Weed Technol.12:41-46.

Dyer, W.E., P.W. Chee, and P.K. Fay. 1993. Rapid germination of sulfonylurea resistant *Kochia seoparia* L. accessions is associated with the elevated levels of branched chain amino acids. Weed Sci 41:18-22.

Eberlin, C.V. J.C. Whitmore, C.E. Stranger, and M.J. Guttieri. 1994. Postemergence weed control in potatoes (*Solanum tuberosum*) with rimsulfuron. Weed Technol.8:428-435.

Frazier, T.L., S.J. Nissen, D.A. Mortensen, and L.J. Meinke. 1993. The influence of terbufos on primisulfuron absorption and fate in corn. Weed Sci. 41:664-668.

Green, J.M. and J.H. Green. 1993. Surfactant structure and concentration strongly affect rimsulfuron activity. Weed Technol.7:633-640.

Hemmamda, S., M. Calmon, and J.P. Calmon. 1994. Kinetics and hydrolysis mechanism of chlorsulfuron and metsulfuron-methyl. Pestic. Sci. 40:71-76.

Kreidi, M. 1992. CATO (DPX-E9636) - A new sulfonylurea herbicide for grass and weed control in maize and potato. Abstract, 16th German Conference on

Weed Biology and Control. 13:663-666.

Koeppe, M.K. and H.M. Brown. 1995. Sulfonylurea herbicide plant metabolism and crop selectivity. Agro. Food Industry Hi. Technol.6:9-14.

Leek, G.L., J.M. Green, H.L. Palm, and S.W. Rowe. 1989. DPX-79406 - A new selective herbicide for postemergence grass control in corn. North Central Weed Science Society Proceedings: 44:11.

Leep, D.C., J.M. Green and W.C. Karl. 1991. DPX-E9636: A new herbicide for potatoes. Weed Science Society of America Abstract 1991. p.10.

Marek, L.J. 1996. LC/MS Analysis of 4-Methoxy-6-methyl-1,3,5-triazin-2-yl-containing sulfonylurea herbicides in soil. J. Agric. Food Chem. 44:3878-3881.

Marucchini, C. and R. Luigetti. 1997. Determination of N-(3-ethylsulfonyl-2-pyridinyl)-4,6-dimethoxy-2-pyridineamine in soil after treatment with rimsulfuron. Pestic. Sci. 51:12-107.

McMullan, P.M. and R.E. Blackshaw. 1995. Postemergence green foxtail (*Setaria faberi*) control in corn (*Zea mays*) in western Canada. Weed Technol.9:37-43.

Merise, W. and C.L. Foy. 1986. Adsorption, desorption, and mobility of chlorsulfuron in soils. J. Agric. Food Chem. 34:89-92.

Mekki, M. and G.D. Leroux. 1994. Activity of nicosulfuron, rimsulfuron, and their mixture on field corn (*Zea mays*), soybean (*Glycine max*), and seven weed species. Weed Technol.8:436-440.

Mueller, T.C., R.M. Hayes, and W.A. Krueger. 1993. Nicosulfuron and

primisulfuron activity in two Tennessee soils. Tennessee Farm and Home Sci. Agricultural Experiment Station, University of TN 167:17-23.

Powley, C.R. and P.A. de Bernard. 1998. Screening method for nine sulfonylurea herbicides in soil and water by liquid chromotography with ultraviolet detection. J. Agric. Food Chem. 46:514-519.

Reddy, K.N., R.M. Zablotowicz, and M.A. Locke. 1995. Chlorimuron adsorption, desorption, desorption, and degradation in soils from conventional and no-tillage systems. J. Environ. Qual. 24:760-767.

Schneiders, G.E., M.K. Koeppe, M.V. Naidu, P. Horne, A.M. Brown, and C.F. Mucha. 1996. Fate of rimsulfuron in the environment. J. of Agric. Food Chem. 41:2404-2410.

Smith, A.E. 1995. A review of the analytical methods for sulfonylureas in soil. Int. J. Environ. Anal. Chem. 59:97-106.

Thirunarayanan, K., R.L. Zimdahl, and D.E. Smika. 1985. Chlorsulfuron adsorption and degradation in soil. Weed Sci. 33:558-563.

Tredaway, J.A., M.G. Patterson, and G.R. Wehtje. 1998. Interaction of clethodim with pyrithiobac and bromoxynil applied in low volume. Weed Technol. 12:185-189.

Vencill, W.K. and P.A. Banks. 1994. Dissipation of chlorimuron in southern soils. Weed Sci. 42:625-628.

Walker, A. 1987. Herbicide persistence in soil. Rev. Weed Sci. 3:1-17.

Willian, W.T. 1992. Efficacy and phytotoxicity of DPX-79406 on johnsongrass and corn. M.S. Thesis. University of Tennessee. Knoxville, TN. 70 pp.

Zar, J. 1992. Pages 132-133 in Biostatistical Analysis, 2nd edition Prentice Hall, New York, NY.

APPENDICES

APPENDIX A

ENVIRONMENTAL CONDITIONS

Table A-1. Daily precipitation (cm) prior to and during sampling period in 1997 and 1998 at field location.

DAT	1997	1998
	----------cm----------	
-5	0.00	0.00
-4	0.00	0.00
-3	1.32	0.00
-2	0.00	0.00
-1	0.48	0.00
0	0.30	0.00
1	3.66	1.24
2	0.00	0.00
3	0.00	0.97
4	0.00	0.00
5	1.78	0.00
6	0.00	0.00
7	0.00	0.00
8	0.00	0.00
9	0.00	0.05
10	1.78	2.08
11	0.00	0.00
12	0.00	0.00
13	0.00	0.00
14	0.00	0.00
15	0.00	0.00
16	0.05	0.00
17	0.00	0.00
18	0.00	0.00
19	0.00	0.00
20	0.00	0.00
21	0.00	0.00
22	0.00	0.00
23	6.86	0.76
24	0.10	3.15
25	0.00	2.77
26	0.00	0.08
27	0.00	0.00
28	0.00	2.34
29	0.00	0.00
30	0.00	0.00
31	0.00	0.79
total	16.32	14.22

Table A-2. Maximum and minimum daily temperature (C) prior to and during sampling period in 1997 and 1998 at field location.

DAT	1997		1998	
	---------C---------			
	max	min	max	min
-5	32.2	19.4	32.2	17.8
-4	32.2	20.6	32.2	17.8
-3	30.6	21.1	32.2	20.0
-2	30.0	19.4	32.2	20.0
-1	30.0	19.4	32.2	20.6
0	28.9	20.6	31.1	21.7
1	30.0	21.1	30.6	16.7
2	30.0	19.4	28.3	16.1
3	32.8	20.0	28.3	16.7
4	35.0	18.3	29.4	18.9
5	32.2	18.9	30.0	20.0
6	26.7	14.4	30.0	17.8
7	28.3	16.1	30.6	18.9
8	27.8	16.1	30.6	20.0
9	31.1	17.8	27.8	21.1
10	28.3	18.3	30.0	19.4
11	28.9	17.2	29.4	18.3
12	30.6	19.4	29.4	17.8
13	31.1	19.4	31.1	19.4
14	31.7	20.0	30.0	20.0
15	33.3	19.4	27.8	17.8
16	33.3	19.4	31.1	18.9
17	32.2	19.4	28.9	19.4
18	32.8	18.3	30.6	16.1
19	33.3	19.4	30.6	18.3
20	34.4	20.0	32.8	17.8
21	34.4	20.6	31.1	18.3
22	33.9	22.2	32.8	18.9
23	33.9	21.1	30.6	19.4
24	32.8	20.6	28.9	19.4
25	32.2	19.4	28.3	20.0
26	32.2	19.4	28.3	18.3
27	32.8	20.0	27.8	18.9
28	31.7	22.2	27.2	18.9
29	33.9	20.0	29.4	20.6
30	31.1	20.6	29.4	20.6
31	28.9	17.2	27.2	20.0

APPENDIX B

SAS PROGRAM

Appendix B. SAS program used for data analysis.

```
data ds1;
infile 'c:\sas\datafile.DAT';
input herb $ dat ppbw stderr;
RUN;
TITLE 'Lab Study 1 Nicosulfuron-mix first-order';
PROC NLIN METHOD=MARQUARDT;
MODEL ppbw=C0*EXP(K*DAT);
PARMS C0=1000 K=-0.03;
DER.CO=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;
```

herb = herbicide name
dat = days after treatment
ppbw = herbicide concentration in parts per billion at given DAT
stderr = standard error of ppbw at given DAT

VITA

Cheryl Anne Ashburn was born in Royal Oak, Michigan on July 15, 1974. In 1980, she moved to Clarkrange, Tennessee. She graduated from Clarkrange High School in May 1992 and chose to continue her education at the University of Tennessee, Knoxville. In August 1996, she received her Bachelor of Science in Plant and Soil Science. Following graduation, she began pursuit of a Master of Science in Plant and Soil Sciences with a concentration in Weed Science. The author is a member of the Tennessee Agricultural Production Society and the Southern Weed Science Society. Following graduation, the author plans to pursue a career assisting producers.