ABSTRACT

HIXSON, ADAM CHARLES. Soil Properties Affect Simazine and Saflufenacil Fate, Behavior, and Performance. (Under the direction of Drs. Fred H. Yelverton and Jerome B. Weber.)

Considerable concern exists about pesticide losses and contamination of groundwater with intensely managed turfgrass systems. Triazine herbicides such as simazine are subject to moderate mobility in the sandy soils commonly found beneath turfgrass systems in coastal regions of the southeastern U.S. Experiments were conducted to investigate the influence of soil organic matter and microorganisms on degradation and sorption of ^{14}C-simazine [6-chloro-*N*,*N'*-diethyl-1,3,5-triazine-2,4-diamine] in soils from turfgrass systems of widely varying ages that have differing levels of organic matter. ^{14}C Binding was related to organic matter content, with 58, 83, and 78% of applied ^{14}C bound in soils from 4, 21, and 99 yr old turfgrass systems after 16 weeks of incubation, respectively. Release of $^{14}CO_2$, presumably resulting from biological degradation and cleavage of the triazine ring, was the primary fate of ^{14}C-simazine with 73, 77, and 54% of ^{14}C applied released from the three types of soils. ^{14}C binding was evident to a greater soil depth with the older turfgrass systems. Sorption characteristics of the herbicides simazine and *S*-metolachlor were determined on five soils from bermudagrass systems of increasing ages. Sorption of both herbicides was greatest on the surface soil from the oldest turfgrass soil system and decreased with age of the system. Sorption decreased as soil depth increased, and simazine sorbed more to subsoil of the oldest system when compared to *S*-metolachlor. Herbicide sorption and organic matter levels were directly related to turfgrass soil system age.

Saflufenacil [*N'*-[2-chloro-4-fluoro-5-(3-methyl-2,6-dioxo-4-(trifluoromethyl)-3,6-dihydro-1(2*H*)-pyrimidinyl)benzoyl]-*N*-isopropyl-*N*-methylsulfamide], a new herbicide discovered by BASF, is targeted for contact and residual broadleaf weed control in select crop and non-crop areas. To determine bioactivity in soil, varying rates of saflufenacil were applied preplant incorporated to 29 different soils and then seeded with canola (*Brassica napus* L.). Saflufenacil bioactivity was highly correlated to organic matter (r = 0.85) and humic matter (r = 0.81) and less correlated to cation exchange capacity (r = 0.49). Stepwise regression analysis suggests that organic matter, humic matter, and sand together are the best predictors (r^2 = 0.77) for estimating the residual activity of saflufenacil. Wash-off characteristics of saflufenacil and four other herbicides from five crop residues under simulated rainfall (32, 64, and 127 mm) on two soils were also determined. Saflufenacil easily washed off all crop residues with a majority of herbicide washed off with the first 32 mm of simulated rainfall. In general, sweet almond = sweet orange > wheat = soybean > corn in wash-off ability across all herbicides. Among herbicides, saflufenacil > mesotrione > isoxaflutole > oxyfluorfen > flumioxazin in wash-off ability across all crop residues. In subsequent experiments, we examined the leaching and sorption/desorption patterns of saflufenacil. Saflufenacil had a mobility index (MI) of 12.7 and was the most mobile herbicide in Candor loamy sand, followed by mesotrione (MI = 5.8), atrazine (MI = 3.0), isoxaflutole (MI = 2.8), flumioxazin (MI = 1.4), and oxyfluorfen (MI = 1.3). Saflufenacil was most mobile through Dundee silt loam and mobility was inversely related to percent organic matter and humic matter. Saflufenacil sorption (K_d) on nine selected soils also showed strong correlation to organic matter and humic matter content. As expected, there was a positive correlation between MI and K_d. Finally, growth chamber and greenhouse

studies were conducted to determine soybean ‘Hutcheson’ response to selective placement of saflufenacil-treated soil. In general, shoot only and shoot + seed exposure resulted in less plant injury, height reduction, and dry weight reduction. Shoot exposure resulted in blackening (necrosis) of the stem at the soil surface, while root exposure caused leaf chlorosis with no stem necrosis.

Soil Properties Affect Simazine and Saflufenacil Fate, Behavior, and Performance

by
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DEDICATION

Dedicated to my wife and family.

Their patience, encouragement, and support have allowed me to achieve my goals.

BIOGRAPHY

Adam Hixson was born and raised in the central Texas town of China Spring. Following high school, he obtained his B.S. degree in Entomology from Texas A&M University. At Texas A&M he was a member of the Fightin' Texas Aggie Band and Corps of Cadets. After receiving his degree in Entomology at Texas A&M University, he accepted a graduate research assistantship at the University of Florida under the direction of Dr. William Crow at the University of Florida. His Master's research focused on plant-parasitic nematode population dynamics in seashore paspalum. Upon finishing his Master's degree, he decided to broaden his knowledgebase by pursuing a Ph.D. degree in Turfgrass Weed Science with Dr. Fred Yelverton at North Carolina State University. During his Ph.D., Adam researched the role of soil organic matter and microbial degradation in determining fate of pesticides in turfgrass systems. Adam took on the sole responsibility of handling herbicide-soil interaction research with a developmental herbicide (saflufenacil) looking at correlating soil properties to efficacy, wash-off from crop residue, and comparing relative soil mobility against commercially available herbicides. His research incorporated agronomy, weed science, soil chemistry, soil microbiology, soil physics, and herbicide chemistry and used all of these to address major environmental concerns in turfgrass and agronomic systems. Adam was the recipient of the 2007 Golf Course Superintendents Association Watson Fellowship, 2008 Musser International Turfgrass Foundation Award of Excellence, and 2008 Weed Science of North Carolina Outstanding Ph.D. student. Adam enjoys watching college sports, and spending time with his wife, Kelly, and son, Chase.

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To my wonderful family, your love and support throughout my many years pursuing my graduate degrees is more appreciated than you can imagine. My dad planted the 'seeking knowledge' seed in me at a young age. That seed has developed into the profession that I enjoy today. I thank my mom for all her emotional support and always believing in me. Thanks to my brother and Seema for all their love and advice. To my favorite mother-in-law and father-in-law, I appreciate your humor, emotional support, and most importantly, the willingness to allow your wonderful daughter to spend the rest of her life with me.

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TABLE OF CONTENTS

LIST OF FIGURES

DEGRADATION AND OTHER DISSIPATION PATHWAYS OF SIMAZINE IN A TURFGRASS SYSTEM CHRONOSEQUENCE

SORPTION OF SIMAZINE AND *S*-METOLACHLOR TO SOILS FROM A CHRONOSEQUENCE OF TURFGRASS SYSTEMS

SOIL PROPERTIES INFLUENCE EFFICACY OF SAFLUFENACIL

WASH-OFF OF SAFLUFENACIL AND OTHER HERBICIDES FROM CROP RESIDUES

SAFLUFENACIL SORPTION, DESORPTION, AND MOBILITY IN SOIL

LIST OF TABLES

SOIL PROPERTIES INFLUENCE EFFICACY OF SAFLUFENACIL

WASH-OFF OF SAFLUFENACIL AND OTHER HERBICIDES FROM CROP RESIDUES

SAFLUFENACIL SORPTION, DESORPTION, AND MOBILITY IN SOIL

INFLUENCE OF SAFLUFENACIL SOIL PLACEMENT ON SOYBEAN (*GLYCINE MAX*) TOLERANCE

INTRODUCTION AND LITERATURE REVIEW

Pesticide Fate in Turfgrass Soil Systems. Over 20 million hectares, approximately 15% of cropland area, is managed as turfgrasses in the United States (Qian and Follett 2002). Turfgrass areas, including golf courses, sports fields, and home lawns, are prominent components of the urban landscape (Beard and Green 1994). High visual and functional expectations of turfgrass systems coupled with optimal environments for weeds, insects, and pathogens leads to increased need for pesticides and fertilizers in these areas. About two billion kilograms of pesticides are used each year in the United States with agricultural usage accounting for approximately 77% (Aspelin and Grube 1999). In recent years, public concern that turfgrass areas are environmentally unsafe due to intensive use of these pesticides and irrigation has increased (Balogh and Anderson 1992; Kenna 1995). Increased sensitivity of advanced analytical techniques make it possible to detect pesticides in groundwater and surface water at concentrations (parts per quadrillion (ppq)) whose presence would not have been discovered using earlier methodology. This has led to the recent detection of many pesticides in soil, groundwater, and surface water (Barbash et al. 2001; Ritter 1990; Williams et al. 1988).

Pesticides applied to turfgrass systems are subject to several fates including, plant uptake, photodegradation, volatilization, sorption onto soil particles such as clay and organic matter (OM), microbial and chemical degradation, and solubilization by water (Branham 1994; Cummings 2004; Gardner et al. 2000; Horst et al. 1996; Hurto et al. 1979). The relative importance of each process is controlled by the chemistry of the pesticide and environmental variables such as temperature, moisture content, and soil characteristics. One

might expect that pesticide dissipation is more rapid in turfgrass than in production agriculture systems due to greater soil microbial activity (Gardner et al. 2000; Gold et al. 1988; Horst et al. 1996; Hurto et al. 1979; Shi et al. 2006; Smith and Paul 1988). Turfgrass soils, however, generally have higher levels of OM (Bandaranayake et al. 2003; Qian and Follett 2002) for which pesticides may be irreversibly sorbed onto OM and reduce bioavailability (Blumhorst and Weber 1994; Novak et al. 1997, Weber et al. 1993).

Pesticides broken down into simpler components can be more easily consumed by soil bacteria, fungi, and other microorganisms and used as energy sources. Soil microorganisms residing in highly maintained soil environments such as turfgrass systems must respond to numerous disturbances. In newly created turfgrass systems, soil microbes are exposed to significant soil disturbance and associated adjustments in soil physical and chemical properties due to construction and establishment (Clark and Paul 1970). The prevailing disturbances may include partial replacement of surface soil with the subsoil or sand from an external source, soil compaction and an abrupt change in landscape cover. As turfgrass systems age, soil microbes will be progressively challenged by changing environments associated with long-term management practices. As major management components, fertilization and pesticide applications may have considerable impacts on soil and soil microbial community. Bossio et al. (1998) reported that soil environmental disturbances would change microbial community composition over time, possibly influencing soil processes, such as nutrient cycling and pesticide disappearance.

Turfgrass soil systems are not tilled, and the grass canopy grows continuously, uninterrupted by harvest and/or crop removal. High mowing frequency requirements

associated with turfgrass maintenance results in constant deposition of leaf clippings on the turfgrass. Consequently, as plant material decomposes, soil OM is likely to accumulate (Bandaranayake et al. 2003; Qian and Follett 2002; Shi et al. 2006). Soil OM levels greatly influence sorption, downward movement, and bioavailability of pesticides (Blumhorst and Weber 1992; Gerritse et al. 1996; Novak et al. 1997; Weber et al. 1993). A turfgrass chronosequence represents a practical system to evaluate how temporal changes in soil microbial properties and carbon mineralization affects soil OM levels and pesticide fate in turfgrass soils.

The physicochemical properties of a pesticide govern its behavior and ultimately its biological activity. Pesticide properties such as molecular size, ionizability, water solubility, lipophilicity, polarity, charge distribution, and volatility are all key properties, which determine the fate of pesticides in soil (Pignatello and Xing 1996; Senesi 1992; Weber 1972; Weber et al. 1993). In addition, soil physical and chemical properties such as bulk density, clay content, OM content, cation exchange capacity, and pH can greatly affect pesticide fate (Hatzinger and Alexander 1995; Piatt and Brusseau 1998). Although sorption to mineral, non-organic soil components such as clay particles does occur (Ball and Roberts 1991a, 1991b; Mader et al. 1997), it is thought that sorption to soil OM is the dominant process in the sequestration of most pesticides (Alexander 2000; Hatzinger and Alexander 1997; Nam et al. 1998; Weber et al. 1993). Sorption is probably the most important interaction between soil and pesticides because it controls the amount of pesticide in the soil solution.

Herbicide performance may be influenced by the complex dynamic soil system. Herbicide availability in soil for uptake by plants and thus its efficacy and subsequent

performance, depends on the soil sorption capacity and the strength of affinity between the herbicide molecule and exchange sites on soil particle surfaces (Bailey and White 1970; Calvert 1980; Harper 1994; Peter and Weber 1985; Weber 1970). Many investigators have studied the effects of OM, humic matter (HM), clay, pH, specific surface area, water holding capacity, and cation exchange capacity (CEC) on herbicide activity (Corbin et al.1971; Weber et al. 1993; Wolcott 1970; Blumhorst et al. 1990; Harrison et al. 1976). Among these soil properties, OM was consistently the factor with the most significant affect on herbicide activity (Parochetti 1973; Rahman and Matthews 1979; Sheets et al. 1962; Weber et al. 1987). Herbicide bioactivity has also been inversely correlated with HM and soil clay mineral content (Blumhorst et al. 1990; Harper 1994; Peter and Weber 1985; Weber 1970). Soil pH indirectly affects sorption of ionizable herbicides through its effect on the properties of particle surfaces and the herbicide (Corbin et al. 1971). Cation exchange capacity is the sum of positive charges of sorbed cations that a soil can sorb, and is directly related to OM and clay mineral content. Therefore, CEC can often be inversely correlated with herbicide bioactivity (Kerr et al. 2004).

Turfgrass soils generally have high levels of OM for which pesticides may be immobilized by sorption onto OM rendering the pesticide unavailable for microbial degradation, plant uptake, and leaching. Taking into account the differences in OM and microbial activity, one might think that pesticide fate in turfgrasses would be unlike agronomic systems (Branham 1994; Cummings 2004). Information concerning these differences would allow for a better understanding on the mechanisms of pesticides behavior in turfgrass systems.

Simazine and *S*-Metolachlor. Currently, over 70 agricultural pesticides, including simazine [6-chloro-*N,N'*-diethyl-1,3,5-triazine-2,4-diamine] and *S*-metolachlor {2-chloro –*N*-(2-ethyl-6-methylphenyl)-*N*-[(1*S*)-2-methoxy-1-methyethyl]acetamide} have been found in groundwater of 38 states, most at low to very low concentrations (Barbash et al. 2001; Ritter 1990; Williams et al. 1988; Ying et al. 2005). A combination of high aqueous solubility, low sorption, and long persistence of selected pesticides in both soil and water leads to possible contamination of drinking water.

Simazine is a weak base (pK_a = 1.62) with a low water solubility (3.5 mg L^{-1} at 20 °C) and long soil persistence (60-186 d) (Senseman 2007). Long persistence of herbicides is important for obtaining season-long weed control, but this may increase concerns over environmental contamination, especially in groundwater and surface water. Weakly basic herbicides, such as atrazine (pK_a = 1.7) and simazine (pK_a = 1.6), become protonated as soil solution pH approaches their pK_a values. These pesticides can behave similar to cations such as K^+ or Ca^{2+} and become adsorbed to clay particles and/or OM (Weber 1994). Sorption of *s*-triazines to OM is governed by hydrogen bonding and proton transfer between *s*-triazines and acid groups of humic substances especially in a hydrophobic environment where hydrogen bonds with water molecules are not dominant (Martin-Neto et al. 1994). Although simazine and atrazine are moderately sorbed to soil, there are many reports of their presence in groundwater, primarily due to their long persistence (Barbash et al. 2001). Simazine and other *s*-triazines have been termed recalcitrant, but many researchers have determined that

microbial degradation is the primary process aiding in the dissipation of simazine in soil (Kaufman et al. 1965; Kaufman and Kearney 1970).

S-metolachlor is a nonionizable, moderately aqueous soluble (488 mg L^{-1}) acetamide herbicide used for the control of grasses, sedges, and many broadleaf weeds when applied preemergence in many crops, including turfgrass. Non-ionic pesticides, such as *S*-metolachlor, can be sorbed to soil by Van der Waals forces, ligand exchange, charge-transfer complexes, hydrophobic partitioning, covalent bonding, and sequestration or combinations of these reactions (Berry and Boyd 1985; Dec and Bollag 1997). Soil sorption of metolachlor has been correlated with high clay and/or OM contents, with low to moderate mobility in most soils (Kozak et al. 1983; Obrigawithch et al. 1981; Peter and Weber 1985; Rao et al. 1986; Wood et al. 1987). Metolachlor leaches readily in sandy soils, and has been detected in groundwater probably due to intensive use in soybeans and corn (Braverman et al. 1986; Huang and Frink 1989; Maas et al. 1995).

Saflufenacil and Environmental Fate. A new herbicide, saflufenacil [*N*′-[2-chloro-4-fluoro-5-(3-methyl-2,6-dioxo-4-(trifluoromethyl)-3,6-dihydro-1(2*H*)-pyrimidinyl)benzoyl]-*N*-isopropyl-*N*-methylsulfamide] (Figure 1) has recently been introduced to be applied preemergence (PRE), preplant incorporated (PPI), and/or postemergence (POST) for broadleaf weed control in many crops and non-cropland areas. Saflufenacil is a moderately acidic, highly aqueous soluble herbicide with a pK_a value of 4.4 and an aqueous solubility of 30 mg L^{-1} at pH 5 and 2100 mg L^{-1} at pH 7, and a vapor pressure of 2.0×10^{-14} Pa at 25 °C

(BASF Agricultural Products 2008). Changing water solubility with solution pH indicates that saflufenacil is likely to easily dissolve in neutral to alkaline soil solution.

Saflufenacil inhibits protoporphyrinogen oxidase in the chlorophyll biosynthetic pathway and has potential for use in several crops. It controls many weeds by inhibiting protoporphyrinogen oxidase to induce massive accumulation of porphyrins and to enhance peroxidation of membrane lipids, which leads to irreversible damage of the membrane function and structure of susceptible plants (BASF Agricultural Products 2008; Duke et al. 1991). Saflufenacil is targeted for use in field corn (*Zea mays* L.) and grain sorghum (*Sorghum vulgare* PERS.), providing season long control of troublesome and herbicide-resistant broadleaf weeds such as tall waterhemp [*Amaranthus tuberculatus* (Moq.) Sauer], giant ragweed (*Ambrosia trifida* L.), and horseweed [*Conyza canadensis* (L.) Cronq.]. It also has potential for use in soybean [*Glycine max* (L.) Merr.] weed management, despite the possibility for saflufenacil to injure soybeans based on varietal difference in sensitivity. There is also interest for saflufenacil to be used in cereal crops, aquatic environments, tree fruit and nut crops, vines, and rights-of-way. Understanding the behavior of saflufenacil in soil will lead to a better ability to predict rates needed for sufficient weed control and tolerance of desirable crops. With the introduction a new soil- and POST-applied herbicide much research must be performed to determine its bioactivity in soil, mobility characteristics, sorption/desorption, retention by crop residues, and location of plant uptake.

Soil bioactivity of other acidic herbicides such as 2,4-D, oryzalin, chlorsulfuron, metsulfuron, and sulfentrazone were inversely related to OM and directly related to soil pH (Anderson 1985; Anderson and Barrett 1985; Jorgensen and Hamner 1948; Kerr et al., 2004;

Weber et al., 1974). Acidic herbicides are repelled by clays under neutral conditions but sorbed through physical bonding mechanisms under acidic conditions when the compounds are in the molecular form (Bailey and White 1970; Frissel and Bolt 1962; Grey et al. 1997; Weber et al. 1993). For this reason, increasing soil pH causes more acidic herbicide anions to remain in soil solution which are then available for plant uptake or dissipation. With a pK_a value less than five, saflufenacil will be primarily in the anionic form in almost all agricultural soils resulting in small pH effect on soil bioactivity.

Herbicide mobility is both an agronomic and environmental concern. Agronomically, soil-applied herbicides that readily move through the soil profile can result in reduced longevity of weed control. Herbicides that are highly mobile in soil may be a potential groundwater contaminant due to vertical movement through the soil profile. Mobility has been studied using soil columns numerous times (Fleming et al. 1992; Keller et al. 1998; Mueller and Banks 1991; Ohmes and Mueller 2007; Peter and Weber 1985). Herbicide mobility is highly influenced by both soil and herbicide properties (Grey et al. 1997). Coarse textured soils such as sands or loamy sands may have increased flow of percolating water which can affect the residence time the herbicide has to sorb to soil colloids and/or OM.

With the increasing adoption of no-till and reduced tillage cropping systems, crop residues remaining on the soil surface from year to year has increased resulting in reduced amounts of herbicide actually reaching the soil surface. Several studies on best management practices have shown distinct advantages of minimum or no-tillage systems (Banks and Robinson 1982; Dao 1991, 1995). Plant residue left on the soil surface reduces soil erosion as well as nutrient and pesticide loss in runoff, conserves soil moisture and may also offer

other benefits such as improved physical properties of soil, increased soil organic carbon (Blevins and Frye 1993) and enhanced microbial populations and soil enzyme activities (Wagner et al. 1995). Plant residues suppress weed germination and emergence of many weeds (Liebl et al. 1992; Teasdale et al. 1991; Teasdale and Daughtry 1993) by altering the light, temperature, and moisture conditions under the mulch (Teasdale and Mohler 1993).

Plant residues often form nearly impenetrable mats covering a large proportion of the soil surface area, and have a strong affinity for retaining herbicides (Banks and Robinson 1986; Reddy et al. 1995a,b; Reddy and Locke 1996). In addition, higher OM levels in the soil surface may bind soil-applied herbicides, contribute to a lessened efficacy and require a higher application rate. Several workers have reported that plant residues intercepted and retained a significant portion of applied herbicides (Banks and Robinson 1982; Banks and Robinson 1986; Ghadiri et al. 1984). Depending on how strongly the intercepted herbicide is retained by the residue, wash-off may be slow. Gradual transmission to the soil may provide extended weed control. Cover crop residue at the soil surface may also sorb a portion of herbicide dissolved in runoff water before it leaves the field, thus, offering an additional environmental benefit beyond reduced erosion. However, herbicide residues persistent beyond the crop season have potential to injure rotational crops, especially vegetables (Johnson and Talbert 1993). An advantage to herbicide interception by crop residues is the continued slow-release and increased efficiency of these herbicides leading to a potential reduction in postemergence chemical inputs as gradual desorption from the straw mulch may provide extended control of second flushes of weed emergence and growth (Dao 1991). Research on corn and wheat (*Triticum aestivum* L.) has shown that crop residue is capable of

greater retention of applied chemicals when compared with the soil surface layer (Boyd et al. 1990; Dao 1995). Herbicide binding can be weak or strong depending on the type and degree of decomposition of cover crop residue. Increased herbicide retention by plant residue not only reduces the amount reaching the soil (affecting weed control) but also prolongs herbicide persistence. The latter could provide season long control from herbicide desorbed from plant residues over a period of time.

For new soil-applied herbicides such as saflufenacil, the site of uptake in plants may be an important factor in determining whether saflufenacil would be more phytotoxic when incorporated into the soil, or when applied to the soil surface. The roots and shoots of plants are the primary absorptive tissues of soil active herbicides (Bromilow and Chamberlain 1995). In either case, the effective absorptive tissue is the relatively young/immature tissue. For roots, it is the root hairs that are particularly effective in herbicide absorption. As either shoot or root tissue matures the outer layers become thickened and form a barrier to absorption of herbicides as well as other compounds. Herbicides whose main site of entry is through the roots may have little effect when applied to the soil surface unless they are moved into the root zone by rainfall or tillage. Some soil applied herbicides are absorbed by plant roots but not shoots, while others are absorbed by plant shoots and less by roots. Therefore, placement of the herbicide in the soil with respect to the site of uptake will influence herbicide efficacy and crop tolerance (Eshel and Prendeville 1967; McLean et al, 2001; Narsaiah and Harvey 1977; Prendeville et al. 1967; Walker 1973). For practical purposes soil applied herbicides are rarely found in phytotoxic concentrations in soil deeper than approximately 7.5 cm. Plants with the bulk of their root systems deeper than 7.5 cm

normally are not greatly affected by these herbicides. Soil active herbicides that are absorbed primarily by the shoots (grass coleoptile, broadleaf hypocotyl or epicotyl) of germinating seedlings must be in the zone of soil above the seed when the shoots grow through this zone to be effective.

Soil active herbicides come in contact with the plant through one of three processes, mass flow, contact, or diffusion (Crafts and Yamaguchi 1959; Shone et al. 1974). With mass flow, herbicide molecules are carried along with soil moisture as the plant absorbs water. Contact simply implies that plants come in contact with herbicides in the soil by the roots or shoots growing into the herbicide. The diffusion process is one in which molecules move from an area of high concentration to an area of lower concentration. For any of these three mechanisms to function adequately, soil moisture is required. Soil moisture is required for the plant to be actively growing and absorbing water. Thus, activity of soil applied herbicides is enhanced by good soil moisture conditions and reduced by limited soil moisture.

Some classes of soil applied herbicides including the triazines are absorbed by the roots of plants but not the shoots. It has been reported that such herbicides as simazine and diuron are more effective when applied early in the season to allow some leaching before germination begins (Hartley 1964). Differential placement of simazine with respect to the absorptive tissue of plants is a technique used to achieve selectivity. Simazine placed on the soil surface in tree plantings is moved into the top few inches of soil with rainfall where it is absorbed by the shallow root system of germinating weeds resulting in their control (Majek and Welker 1990). The bulk of the root system of established trees is much deeper in the soil

than one or two inches and hence the tree root system does not come in contact with the simazine resulting in no absorption of the herbicide and no damage.

Weed control effectiveness of and crop tolerance to many dinitroanilines and chloroacetamides is dependent upon herbicide placement in the soil (Appleby and Valverde 1989; Roggenbuck and Penner 1987). For example, trifluralin is registered for control of unemerged weeds in corn when applied after the corn has developed two leaves. By the two leaf stage the shoots of corn and weeds have a well developed outer layer that prevents absorption of any trifluralin that may contact the shoot. Since trifluralin is very immobile in the soil it does not move deeply enough into the soil to come in contact with the immature (meristematic) portions of the root system of established corn or weeds. In contrast the shoots of germinating weed seedlings absorb trifluralin from the surface soil and are controlled. Propachlor and alachlor have been determined to be primarily shoot absorbed in the soil (Knake and Wax 1968). As a result, leaching of these herbicides below the weed seed zone significantly reduces efficacy. Cotton (*Gossypium hirsutum* L.) and corn tolerance to alachlor was based primarily on depth protection and is not a result from a metabolism to nontoxic forms within the plant (Eshel 1969; Narsaiah and Harvey 1977). Other studies also reported that soil placement of herbicides had a large effect on tolerance of peas and field beans (Eshel et al. 1975; Glasgow and Dicks 1980). Therefore, saflufenacil soil placement and/or crop planting depth could be major factors in determining crop tolerance and adequate weed control.

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DEGRADATION AND OTHER DISSIPATION PATHWAYS OF SIMAZINE IN A TURFGRASS SYSTEM CHRONOSEQUENCE

(Formatted for submission to Crop Science)

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Abbreviations: CEC, cation exchange capacity; HM, humic matter; OM, organic matter; SMBC, soil microbial biomass carbon

ABSTRACT: Triazine herbicides such as simazine are moderately mobile in the sandy soils commonly found beneath turfgrass in coastal regions of the southeastern United States. We investigated the influence of soil organic matter on the binding and degradation of ^{14}C-simazine in soils from turfgrass systems of varying ages (4, 21, and 99 yrs.). Soil cores were removed from turfgrass systems, partitioned into two depths (0-5 and 5-15 cm). Small amounts of the partitioned soil cores were placed in microcosms and conditioned as nonstrerile or sterile. For each of seven sampling intervals, ^{14}C was separated into three different pools, bound, extractable, and $^{14}CO_2$. At 16 weeks after treatment, 52, 70 and 71% of applied ^{14}C-simazine was bound to organic matter in the sterile, surface soil from the 4, 21 and 99 year-old turfgrass systems, respectively. Binding of ^{14}C to organic matter was limited in the non-sterile, surface soil by microorganisms degrading ^{14}C-simazine to $^{14}CO_2$ before binding occurred. Bound ^{14}C and $^{14}CO_2$ production was lower in subsurface soils from the younger turfgrass systems (4 and 21 yrs.), but similar to surface soil in the oldest turfgrass system (99 yrs.). ^{14}C-simazine half-life was significantly lower in non-sterile soil samples, ranging from 0.9 to 5.8 weeks, compared to sterile soil (3.7 to 35.3 weeks) where little degradation occurred and dissipation was primarily a result of binding to soil particles. As turfgrass systems age and soil organic matter levels increase, potential for simazine leaching into groundwater decreases.

Turfgrass areas, including golf courses, sports fields, and home lawns are prominent components of the urban landscape (Beard and Green, 1994). Multiple turfgrass pests and pathogens can reduce the aesthetic appeal and even playability of some turfgrass areas. High expectations coupled with optimal environments for weeds, insects, and pathogens leads to increased need for pesticides and fertilizers in these areas. Recreational uses and close proximity to homes results in frequent public exposure to turfgrass areas. This closeness leads to public concern that turfgrass areas are environmentally unsafe due to intensive use of these chemicals and irrigation (Balogh and Anderson, 1992; Kenna, 1995).

In addition, increased sensitivity of modern analytical techniques make it possible to detect pesticides in groundwater and surface water at concentrations (parts per trillion (ppt)) whose presence would not have been discovered using earlier methodology. This has led to the recent detection of many pesticides in soil, groundwater, and surface water (Barbash et al., 2001; Cohen et al., 1984; Ritter, 1990; Williams et al., 1988). Potential for leaching into groundwater together with increased opportunity for human exposure has led to extreme scrutiny of pesticides applied to turfgrass areas.

Pesticides applied to turfgrass are subject to several fates including, plant uptake, photodegradation, volatilization, sorption onto soil particles including clay and organic matter (OM), microbial and chemical degradation, and solubilization by water (Branham, 1994; Cummings, 2004; Gardner et al., 2000; Horst et al., 1996; Hurto et al., 1979). The relative importance of each process is controlled by the chemistry of the pesticide and environmental variables such as temperature, moisture content, and soil characteristics. In turfgrass soil systems pesticide dissipation has been primarily attributed to greater soil

microbial activity leading to high levels of mineralization to CO_2 and H_2O (Gardner et al., 2000; Gold et al., 1988; Horst et al., 1996; Hurto et al., 1979; Shi et al., 2006; Smith and Paul, 1988). Soils with turfgrass, however, generally have higher levels of OM (Bandaranayake et al., 2003; Qian and Follett, 2002) possibly resulting in increased pesticide sorption and reduced bioavailability. Numerous studies with agronomic soils has proven that increasing levels of OM result in greater pesticide sorption (Blumhorst and Weber, 1994; Novak et al., 1997, Weber et al., 1993), but little research has been performed to correlate higher soil sorption to pesticide bioavailability in soil. Taking into account the differences in soil OM content and microbial activity, one would assume that pesticide fate in turfgrass would be unlike agronomic systems.

Simazine (Figure 1), a highly-used herbicide is found in groundwater of several states (Barbash et al., 2001; Ritter, 1990; Williams et al., 1988). Simazine is a weak base (pK_a = 1.6) with a low water solubility (3.5 mg L^{-1} at 20 °C) and a long soil persistence (60-186 d) (Senseman, 2007). Long persistence of a herbicide is important for obtaining good weed control, but this may increase concerns over environmental contamination, especially in ground and surface water. Simazine remains in molecular from at high pH causing it to be more persistent by allowing more to remain in soil solution (Weber et al., 1993). Increase bioaccessibility leads to increased mineralization by soil microorganisms, hence, decreasing persistence. Simazine and other *s*-triazines are considered to be recalcitrant, however, many researchers have concluded that microbial degradation is the primary process aiding in the dissipation of these herbicides in soil (Kaufman et al., 1965; Kaufman and Kearney, 1970). In addition to microbial degradation, persistence decreases at low soil pH as simazine

becomes protonated and irreversibly sorbed to soil particles by cation exchange (Weber et al., 1993).

Distinct from agronomic soil systems, turfgrass soil systems are not tilled and the grass canopy grows continuously, uninterrupted by harvest. Frequent mowing necessary for turfgrass maintenance results in constant deposition of leaf clippings to the soil surface. This combined with optimal environmental conditions for microbial growth and activity causes surface soil OM to rapidly accumulate in turfgrass areas over time as plant material decomposes (Bandaranayake et al., 2003; Qian and Follett, 2002; Shi et al., 2006). Previous research has verified that soil OM levels greatly influence sorption and bioavailability of pesticides (Blumhorst and Weber, 1992; Weber et al., 1993). With increased levels of OM, higher, more diverse soil microbial populations can be supported, possibly causing certain pesticides to be broken down quicker (Clark and Paul, 1970; Smith and Paul, 1988). Furthermore, older turfgrass systems have also been exposed to repeated applications of many pesticides possibly causing soil microorganisms to become acclimated to them.

Although numerous research exsists concerning pesticide leaching in turfgrass soil systems (Branham 1994; Cummings 2004), this is the first report of the effects of turfgrass soil system age and soil microorganisms on simazine environmental fate. A turfgrass chronosequence was used to evaluate temporal changes in soil microbial properties and carbon mineralization can affect simazine fate. We hypothesized that despite the possible impacts of soil disturbance during construction and subsequent long-term management practices, soil microbial biomass, activity, and rates of carbon mineralization would increase

with soil OM as turfgrass systems age and thus change the bioavailability and degradation of simazine.

The objectives of this experiment were (i) to evaluate the change in degradation kinetics of simazine as turfgrass systems age, and (ii) to compare dissipation pathways of simazine in turfgrass systems and adjacent natural ecosystems.

MATERIALS AND METHODS

Turfgrass Sites

Three golf courses and their adjacent native pine areas near or in the city of Wilmington, North Carolina were selected. Each site was within a 20-kilometer radius of one another. The turfgrass systems were established in 1905, 1983, and 2000 and thus 99, 21, and 4 years-old, respectively, when soil samples were taken (Figure 2). All sites contained were planted to hybrid bermudagrass (*Cynodon dactylon* (L.) Pers. × *C. transvaalensis* Burtt-Davy), a warm-season perennial. The oldest site had been replanted to different bermudagrass varieties numerous times, but constant turfgrass cover was maintained from time of establishment on all courses. All sites received annual applications of simazine in the fall for the control of winter annual grass and broadleaf weeds. Early records of the 99-year-old site were not available, but simazine was not applied prior to its introduction in 1956 (Cremlyn, 1990). All sites were constructed on undeveloped land that was previously native pine forests. Therefore, resulting in a native, undisturbed immediately

adjacent to each turfgrass area. These undisturbed zones represented a reasonable reference for the highly managed turfgrass systems and therefore were included to assess differences in simazine environmental fate. Since the soils in this region are almost uniformly deep sands, the disturbance during fairway construction had little affect on soil texture.

Experimental Soils

Prior to fall applications of simazine, soils were sampled from three individual fairways from each golf course in September and October 2004. Fifteen intact cores (5-cm-diameter × 15-cm-length) were taken from each fairway. Five cores from each fairway were combined and represented a replication for a total of three replications per turfgrass system age. Soil cores were obtained in an identical manner from the adjacent native pine areas. The bagged intact soil cores were placed on ice and transported to the lab. The cores were then sectioned into 0–5 and 5–15 cm depths. Soil from each depth was sieved (< 4 mm) to remove roots and plant residues, bagged and stored at 4 °C for later use. Soils included were: Kenansville sand (loamy, siliceous, subactive, Arenic Hapludults) (4 yr.), Lakeland sand (thermic, coated Typic Quartzipsamments) (21 yrs.), and Baymeade sand (loamy, siliceous, semiactive, thermic Arenic Hapludults) (99 yrs.). Particle size was determined by the hydrometer method (Gee and Orr, 2002). Soil pH was determined by glass electrode with reference buffers on a 1:1 soil to water mixture (Peech, 1965). Effective CEC was measured using the summation of exchangeable cations procedure described by Mehlich (1984a). Percent soil OM was determined by the colorimetric Walkley-Black procedure (Nelson and Sommers, 1982). Percent humic matter (HM) was quantified by photometric determination

(Mehlich, 1984b). Total soil C and N were determined using the dry combustion method with a CHN analyzer (Carbon-Hydrogen-Nitrogen Analyzer, PerkinElmer Inc., Waltham, MA).

Herbicide

^{14}C-ring-labeled simazine [98.7% purity, specific activity (1.8 MBq mg^{-1})] and formulated simazine (PRINCEP® 4L) stock solution was prepared in methanol. From the stock solutions, a 49.6 µM radiolabeled solution was prepared in distilled water so that a 1-mL aliquot would deliver 48,000 dpm (0.02 µCi, or 0.8 kBq) to 80 or 96 grams of soil. Enough simazine solution and distilled water was added to all soils to obtain a concentration equal to twice the labeled field rate of 2.24 kg ai ha^{-1} mixed to a depth of 7.5 cm. The simazine solution added to the soil resulted in moisture content equal to 55% of field capacity.

Simazine Degradation Kinetics

A factorial design with soil treatments (sterile and non-sterile), soil depths (0-5 and 5-15 cm), and turfgrass system ages (4, 21, and 99 yrs.) as variables was used. Each factorial treatment combination had three replicates and the entire experiment was repeated. Soil was sterilized by autoclaving for 30 minutes on three consecutive days and sterility was monitored throughout the experiment by measuring CO_2 produced. Each soil microcosm consisted of eight 20-ml glass scintillation vials containing ~12 g soil (dry wt. equiv.) and one containing 10 ml 0.5 M NaOH as an alkaline trap to absorb respired CO_2 and $^{14}CO_2$

within a 1-L mason jar (Figure 3). Due to high OM, only 10 g soil from the 0-5 cm soil depth of the oldest site (99 yrs.) was used. Therefore, sterile and non-sterile sample units consisted of eight scintillation vials, totaling 80 or 96 g of soil. Distilled water was added to the jars to maintain high relative humidity and minimize soil water loss through the duration of the experiment. Three jars containing eight empty scintillation vials and one alkaline trap were used as controls. All the soil samples were adjusted to a moisture content of 40% field capacity and preincubated at room temperature (~24 ºC) for 3 days before simazine addition. Glass jars were sealed and placed in a constant temperature room in the dark at 25 ± 2 ºC.

Two additional 20-ml vials of each soil were used for measurement of soil microbial biomass C (SMBC). Soil microbial biomass C was measured using a fumigation-extraction method (Vance et al. 1987). Organic C in fumigated and unfumigated extracts was measured with a total organic C analyzer (Shimadzu® TOC-5000(A) total organic carbon analyzer, Shimadzu Corporation, Nakagyo-ku, Kyoto 604-8511, Japan). Soil microbial biomass C was then calculated by dividing difference of total extractable C between fumigated and unfumigated samples by the conversion factor 0.45 (Vance et al. 1987).

Ten- or 12-gram soil samples were analyzed at 0, 1, 2, 4, 6, 9, 12, and 16 weeks after treatment. During this incubation time, microcosms were aerated and the NaOH traps changed twice weekly for the first four weeks and once a week, thereafter. At each sampling time, NaOH traps were removed and sealed for later analysis. Subsequently, 50 ml of methanol was added to each soil sample, shaken vigorously for four hours on a rotary shaker, and using suction filtered through glass fiber filter paper. Extracts were rotary evaporated to dryness and redissolved in methanol, transferred to 15-ml volumetric test tubes, and brought

to 10 ml. One milliliter of this extract was added to 10 ml of liquid scintillation cocktail and analyzed by liquid scintillation counting (LSC). Five milliliters of extract was dried under nitrogen and resuspended in 500 µl of methanol. Subsequently, 250 µl of the extracts was spotted onto silica gel thin layer chromatography (TLC) plates (20 by 20 cm) and developed to 16 cm for chromatographic separation of ^{14}C-metabolites and parent compound. Solvent system used was chloroform:acetic acid:methanol:water (70:10:15:5 by volume). Plates were partitioned into 20 0.8-cm lanes. A standard that contained 5 µCi ^{14}C-simazine ml^{-1} was spotted on the first lane of each plate. Every other lane for a total of ten lanes received a single replicate of each soil at each time period for the two runs of the study. The plates were dried in a drying oven at 60 °C for an hour and radioactive quantities, positions, and corresponding R_f values were determined by scanning TLC plates with a radiochromatogram scanner. Radioactive peaks were integrated with WinScan software with smoothing set to 13-point cubic and background excluded from the peak area calculation. Peaks below 1% of total radioactivity were rejected (Askew and Wilcut, 2002). The parent herbicide was identified by comparing the R_f value with corresponding standard.

Bound residue formation was quantified by subjecting duplicate 1-g air-dried solvent extracted soil samples to combustion in a biological oxidizer (Model OX300 Biological Material Oxidizer, R. J. Harvey Instrument Corp., Hillsdale, NJ) with evolved $^{14}CO_2$ trapped in scintillation cocktail and subsequent ^{14}C determined by LSC. To quantify the extent of ^{14}C-simazine mineralization to $^{14}CO_2$ by soil microorganisms, a 1 ml aliquot of the NaOH trapping solution was added to 15 ml of scintillation cocktail and assayed via LSC. Organic C mineralization was measured by detecting total CO_2 produced through acid titration with

HCl. Sterility was monitored throughout the experiment by radioactive isotope assay and titration of NaOH traps to detect any $^{14}CO_2$ or total CO_2 produced.

Using the data collected, simazine half-life values were calculated for each soil. The half-life of a chemical may be defined several ways. It is often conveniently defined as the time required for 50% of the chemical to disappear or become undetectable. This is not a true kinetic half-life (where 50% of the compound has been changed to something else) and depends on many parameters including volatilization, binding to soil constituents, plant uptake, leaching, and degradation. Therefore, even if no degradation occurs, a half-life can be calculated if 50% or more of the applied compound becomes undetectable for any of the above reasons. In this study only binding to the soil, mineralization to $^{14}CO_2$, and degradation into metabolites contributed to the dissipation of the applied chemical. The half-lives presented in this study reflect the time required for 50% of the parent compound to degrade or become unextractable with methanol.

Data Analyses

Analyses of variance (ANOVA) were performed using a General Linear Models procedure (Proc GLM) in SAS. Statistical analyses were performed separately on bound ^{14}C, $^{14}CO_2$, and percent extractable ^{14}C-simazine. Simazine degradation rate constants for each soil were calculated using first-order kinetics, $C = C_0\, e^{-kt}$, where C is the amount of simazine ($\mu g\ kg^{-1}$ soil) at time t, C_0 is the amount of simazine ($\mu g\ kg^{-1}$ soil) at time zero, k is the rate constant ($week^{-1}$), and t is time (week). Degradation rate constants were estimated by linear regression from transformed first-order rate equations, $\ln C_0/C = -kt$. Calculated half-life

values ($t_{½}$) were determined using the equation $t_{½} = \ln(2)/k$ (Walker 1987) and are presented with standard errors (Table 2). Figures are plotted using the average value of the six replications for each observation. Error bars represent the standard error of the data associated with that observation.

RESULTS

Turfgrass soil contained an average of 95% sand, 2% silt and 3% clay, very similar to the adjacent native pine soil that consisted of 92% sand, 4% silt and 4% clay. Soil organic matter and humic matter levels increased as turfgrass soil systems matured and decreased with increasing soil depth (Table 1). Soil pH was lowest in the native pine area and oldest turfgrass soil system (99 yrs.) (Table 1). Soil microbial biomass C was higher in the surface soil of all locations with highest SMBC in the 21 yrs. and 99 yrs. turfgrass soil systems (Table 1). The soil C:N ratio decreased with increasing turfgrass system age (Table 1). Higher soil C:N ratios indicate unstable organic matter and competition among microorganisms for available soil nitrogen while lower C:N ratios indicate nutrients are in excess of microbial needs.

Total recoverable radioactivity was divided into three pools: (i) extractable ^{14}C removed from the soil by methanol; (ii) bound ^{14}C not removed by methanol; and (iii) $^{14}CO_2$ produced by mineralization. Total recovery of the three ^{14}C pools combined ranged from 86.7 to 103.4% and averaged 94.2. Recoveries were normalized to 100% by equally distributing the difference between the three pools.

^{14}C-simazine added to sterile soil resulted in high levels of bound ^{14}C. The bound ^{14}C was related to OM content, with 52% (4 yrs.), 70% (21 yrs.) and 71% (99 yrs.) of applied ^{14}C-simazine bound in surface soils after 16 weeks of incubation (Figure 4A). Likewise, ^{14}C-simazine binding in subsurface soil followed a similar trend with 36% (4 yrs.), 52% (21 yrs.), and 63% (99 yrs.) after 16 weeks of incubation (Figure 4B). Although the trend was similar, increase in soil depth caused a decrease in binding in all turfgrass soils. Highest binding in both soil depths occurred in native pine soils due to low pH causing protonation of simazine and binding to negative sites on soil particles. Results from sterilized soil show that extractable ^{14}C-simazine was less as turfgrass systems aged, and lowest in soils from pine areas (Figure 4C and 4D).

When non-sterile surface soil was examined, bound ^{14}C-simazine residues were much lower in all soils except the native pines (Figure 5A). The reduction in amount of bound ^{14}C-residues could be a result of rapid removal of ^{14}C-simazine from soil solution by soil microorganisms before the herbicide had an opportunity to interact with soil particles. Release of $^{14}CO_2$, presumably from biological degradation was the primary route ^{14}C-simazine reduction, as 77% (4 yrs.), 87% (21 yrs.) and 69% (99 yrs.) was released from the three surface soils after 16 weeks of incubation (Figure 5E). The mineralization rate increased rapidly at the beginning of the incubations in surface soils, reaching a steady state after eight weeks (Figure 6A). ^{14}C-simazine mineralization in soil from the native pine forest was low, with less than 20% of the applied ^{14}C-simazine mineralized. With extractable ^{14}C-simazine < 9%, bound ^{14}C still accounted for 18% (4 yrs.), 11% (21 yrs.), and 22% (99 yrs.) of applied ^{14}C even after 16 weeks of incubation (Figure 5A and 5C).

^{14}C binding was slightly lower in nonsterile subsurface soil from the 4-year-old turfgrass system due to low OM content and resulting utilization by microorganisms (Figure 5B). In the 4 and 21-year-old turfgrass systems, soil depth had a large impact on the microbial degradation of ^{14}C-simazine, with much lower $^{14}CO_2$ produced in the subsurface versus surface soil (Figure 5E and 5F). Low binding and little $^{14}CO_2$ production in subsurface soil from the 4 and 21-year-old turfgrass systems caused the extractable fraction to remain close to 50% after six weeks of incubation (Figure 5D). If simazine is able to move below the 5-cm depth in the soil profile, degradation may be delayed. Microbial degradation of ^{14}C-simazine estimated by $^{14}CO_2$ evolution was similar at both depths in the oldest turfgrass system (99 yrs.), indicating that the accumulation of OM over time is crucial in the fate of pesticides in managed turfgrass systems (Figure 5E and 5F). $^{14}CO_2$ evolved from pine area soils was very low throughout the experiment indicating very little biological degradation (Figure 5E and 5F).

^{14}C-simazine mineralization rates were inversely related to the age and OM level of the turfgrass system. The highest rates of ^{14}C-simazine mineralization occurred in the surface soil of the 4 and 21-year-old turfgrass system (Figure 6A). Lower OM amounts in these two turfgrass systems led to less binding and more bioavailable simazine. A previous study showed that bioavailability to *Pseudomonas* sp. was closely correlated to the total amounts of ^{14}C-simazine sequentially extracted by aqueous and methanol solutions (Regitano et al. 2006). This correlation verifies the relationship between methanol extractable ^{14}C-simazine and $^{14}CO_2$ production in this study. Less ^{14}C-simazine mineralization occurred in soil from the surface of the 99-year-old turfgrass system and the

native pine areas surrounding the turfgrass systems (Figure 6A). Reasons for lower mineralization was two-fold; higher OM levels and low soil pH in both soils resulted in less bioavailable ^{14}C-simazine, and soil microorganisms in the native pine areas had no previous exposure to simazine. Low soil pH (< 6) results in more simazine occurring in the protonated form leading to sorption to negatively charged soil particles (Weber et al., 1993).

^{14}C-Simazine mineralization in the surface soils showed little to zero lag phase at the beginning of the incubations followed by rapid mineralization (4, 21, and 99-year-old soil) (Figure 6A). Mineralization rate in surface soils reached a maximum between one and four weeks of incubation, corresponding to a mineralization of 4 to 8% of the applied ^{14}C-simazine per week. The mineralization rate then decreased rapidly reaching a steady state similar to the kinetics of total organic carbon mineralization (Figure 6 and 7). Little to zero initial lag phase followed by rapid mineralization could correspond to the quick growth of the microbial population and previous adaptation to the mineralization of the ^{14}C-simazine ring. The low and constant mineralization rates observed in the native pine soil indicated the absence of a specific microflora adapted to simazine-ring mineralization. The kinetics of total soil organic C mineralized revealed the innate microbial activity of each soil (Figure 7). No lag time was found in the total respiration, and the respiration rate was constant throughout the 16 weeks of incubation (Figure 7). These kinetics were not related with those of the ^{14}C-simazine mineralization.

Repeated yearly applications to the turfgrass soils could explain the rapid mineralization of ^{14}C-simazine. Enhanced degradation of pesticides in soil following

repeated application of the same pesticide has been reported numerous times (Roeth, 1986; Walker and Welch, 1992). Although little research exists concerning enhanced degradation of simazine, rapid mineralization of the triazine-ring of atrazine has been demonstrated after microbial enrichment during laboratory experiments (Gschwind, 1992; Mandelbaum et al., 1993, 1995; Radosevich et al., 1995).

Different rates of ^{14}C-simazine mineralization seem to be related to differences in the physicochemical properties of the soils. Although soil texture was similar in all soils, soil pH and OM differed among soils. ^{14}C-simazine mineralization decreased when OM increased and soil pH decreased. Previous studies with atrazine and simazine have shown that sorption increased with OM content (Barriuso and Calvet, 1992; Novak et al., 1997) and atrazine bioavailability for microbial degradation decreased when sorption and bound residue formation increased (Barriuso et al., 1994, Miller et al., 1997).

Half-life values were significantly lower in non-sterile soil, ranging from 0.9 to 5.8 weeks, compared to sterile soil (3.7 to 35.3 weeks) where little degradation occurred and disappearance was primarily a result of binding to soil particles (Table 2). As expected, lower OM levels and microbial activity associated with subsurface soil resulted in higher half-life values in both non-sterile and sterile soil. Higher half-life values occurred in the 99-year-old turfgrass system due to the presence of bound ^{14}C-residues that was inaccessible to soil microorganisms (Table 2; Figure 4 and 5).

DISCUSSION

In all soils, two competitive degradation processes were proposed: rapid dissipation through ring cleavage and mineralization in soils receiving simazine previously and more progressive dissipation through bound residues. Sorption of most organic compounds to OM is time-dependent and increases with exposure time (Xing and Pignatello, 1996). These results indicate that simazine and OM interactions are an important determinant of simazine leaching potential. As turfgrass systems age and OM levels increase, the potential for simazine leaching into groundwater decreases even though biological degradation rates may be lower.

Our results could be interpreted two ways. The first interpretation is that simazine bioavailability (soil microorganisms only) is dependent on the level of OM and soil pH in turfgrass soil systems. Thus, simazine bioavailability in surface soil (0-5 cm) decreases with time as turfgrass establishment period increases. This occurrence can explain why microbial degradation measured by $^{14}CO_2$ production is lower in the surface soil of the oldest bermudagrass system (Figure 5E).

Secondly, we could say energy source choice is more diverse in older turfgrass systems leading to less microbial degradation. Hypothetically there are less food choices for soil microorganisms in younger turfgrass soil systems with less OM. With fewer energy source choices, simazine becomes a primary energy source and is therefore degraded more quickly. Realistically, simazine fate in turfgrass soil systems is probably a combination of both proposed interpretations. Higher bioavailability and less food choice in younger

turfgrass systems equate to more microbial degradation and plant uptake, and although small, may increase the opportunity for leaching into groundwater. Our research results with simazine and bermudagrass substantiate previous claims that turfgrasses reduce pesticide runoff and potential for groundwater contamination (Branham, 1994; Branham and Wehner, 1985; Niemczyk et al., 1988; Niemczyk and Krause, 1994; Niemczyk and Krueger, 1987).

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Table 1. Characteristics of soils from two depths (0-5 and 5-15 cm) at three different aged bermudagrass systems and adjacent native pine forest.†

Location	Soil Series	Soil C‡	Soil N‡	Soil C:N	OM§	HM¶	Sand#	Clay#	CEC††	pH‡‡	SMBC§§
		mg C g^{-1}	mg N g^{-1}				%		cmol kg^{-1}	1:1	µg C g^{-1}
0-5 cm depth											
Native pines	Mixed¶¶	21.8	1.2	19.0	3.5	2.6	92	2	6.0	4.6	427
4-yr turf	Kenansville	16.6	1.2	14.3	1.8	0.4	96	2	7.1	6.3	447
21-yr turf	Lakeland	24.6	2.2	11.4	4.1	1.5	96	2	7.7	6.0	658
99-yr turf	Baymeade	39.0	3.5	11.1	4.5	2.7	92	2	9.7	5.4	510
5-15 cm depth											
Native pines	Mixed¶¶	14.3	6.7	2.1	2.6	1.1	94	2	6.1	4.7	164
4-yr turf	Kenansville	1.0	0.1	13.1	0.4	0.3	96	2	3.6	6.2	67
21-yr turf	Lakeland	9.0	0.6	14.5	1.3	0.6	94	2	5.6	6.3	96
99-yr turf	Baymeade	9.6	0.8	12.5	1.7	1.1	94	2	7.7	5.8	188

† Abbreviations: OM, organic matter; HM, humic matter; CEC, cation exchange capacity; SMBC, soil microbial biomass carbon.

‡ Soil C and N determined using a CHN analyzer.

§ Organic matter was determined using the Walkley-Black procedure (Nelson and Sommers 1982).

Table 1. (continued)

¶ Humic matter was determined by photometric determination (Mehlich 1984b).

Particle analysis was determined using the hydrometer method (Gee and Orr 2002).

†† Cation-exchange capacity was determined using the summation of exchangeable cations procedure (Mehlich 1984a).

‡‡ pH was determined using a 1:1 soil:distilled water ration (Peech 1965).

§§ Soil microbial biomass carbon determined by fumigation-extraction (Vance et al. 1987)

¶¶ Soil was removed from native pine areas adjacent to each turfgrass system and mixed.

Table 2. First-order degradation of simazine in nonsterile and sterile laboratory soil microcosms containing soils from two depths (0-5 and 5-15) at three different aged bermudagrass systems and adjacent native pine forests.

Location	Nonsterile			Sterile		
	k†,‡	R^2	Half-life	k†,‡	R^2	Half-life
	week		weeks	week		weeks
			0-5 cm depth			
4-yr. turf	0.317 (0.022)	0.98	2.2	0.041 (0.004)	0.95	17.0
21-yr. turf	0.774 (0.096)	0.96	0.9	0.090 (0.015)	0.88	7.7
99-yr. turf	0.240 (0.031)	0.91	2.9	0.114 (0.006)	0.99	6.1
Native pines	0.343 (0.059)	0.89	2.0	0.188 (0.014)	0.97	3.7
			5-15 cm depth			
4-yr. turf	0.119 (0.011)	0.95	5.8	0.020 (0.005)	0.75	35.3
21-yr. turf	0.498 (0.040)	0.98	1.4	0.040 (0.007)	0.88	17.1
99-yr. turf	0.154 (0.006)	0.99	4.5	0.067 (0.008)	0.94	10.3
Native pines	0.237 (0.021)	0.96	2.9	0.113 (0.013)	0.94	6.1

† Values in parentheses are asymptotic standard errors.

‡ First-order degradation rate constant, k is the slope of the plot of ln C (simazine concentration at time t) versus t (incubation time).

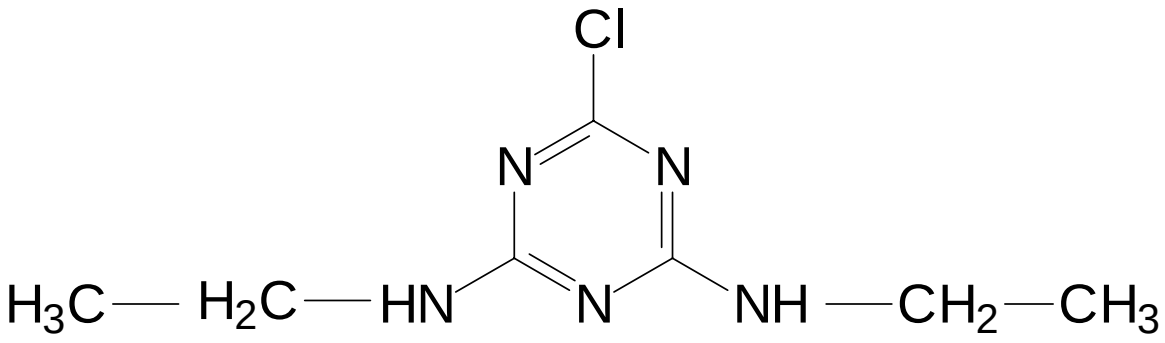


Figure 1. Simazine chemical structure.

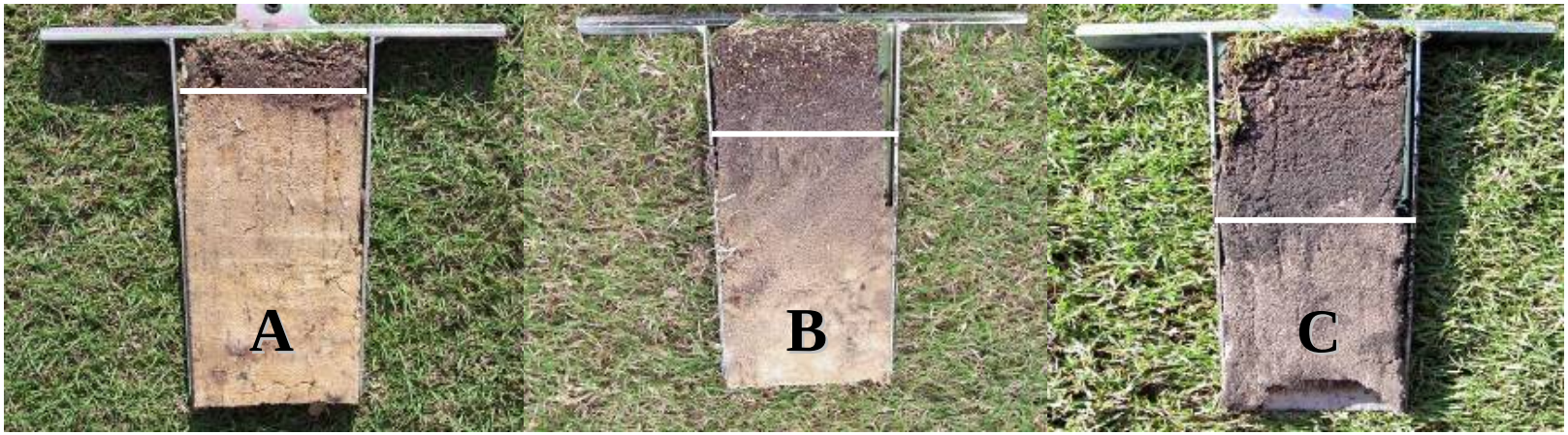


Figure 2. Soil profiles from the different aged bermudagrass systems: 4 years after establishment, (A); 21 years after establishment, (B); and 99 years after establishment, (C).

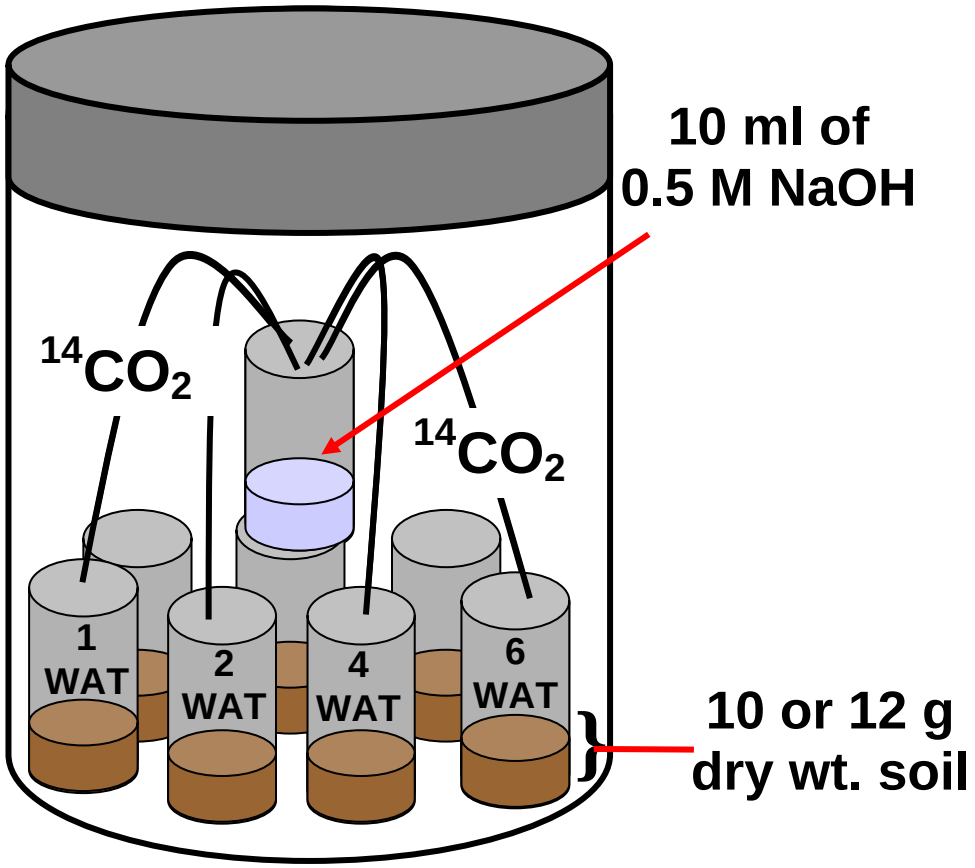


Figure 3. Schematic of soil microcosm used to measure microbial degradation kinetics of simazine.

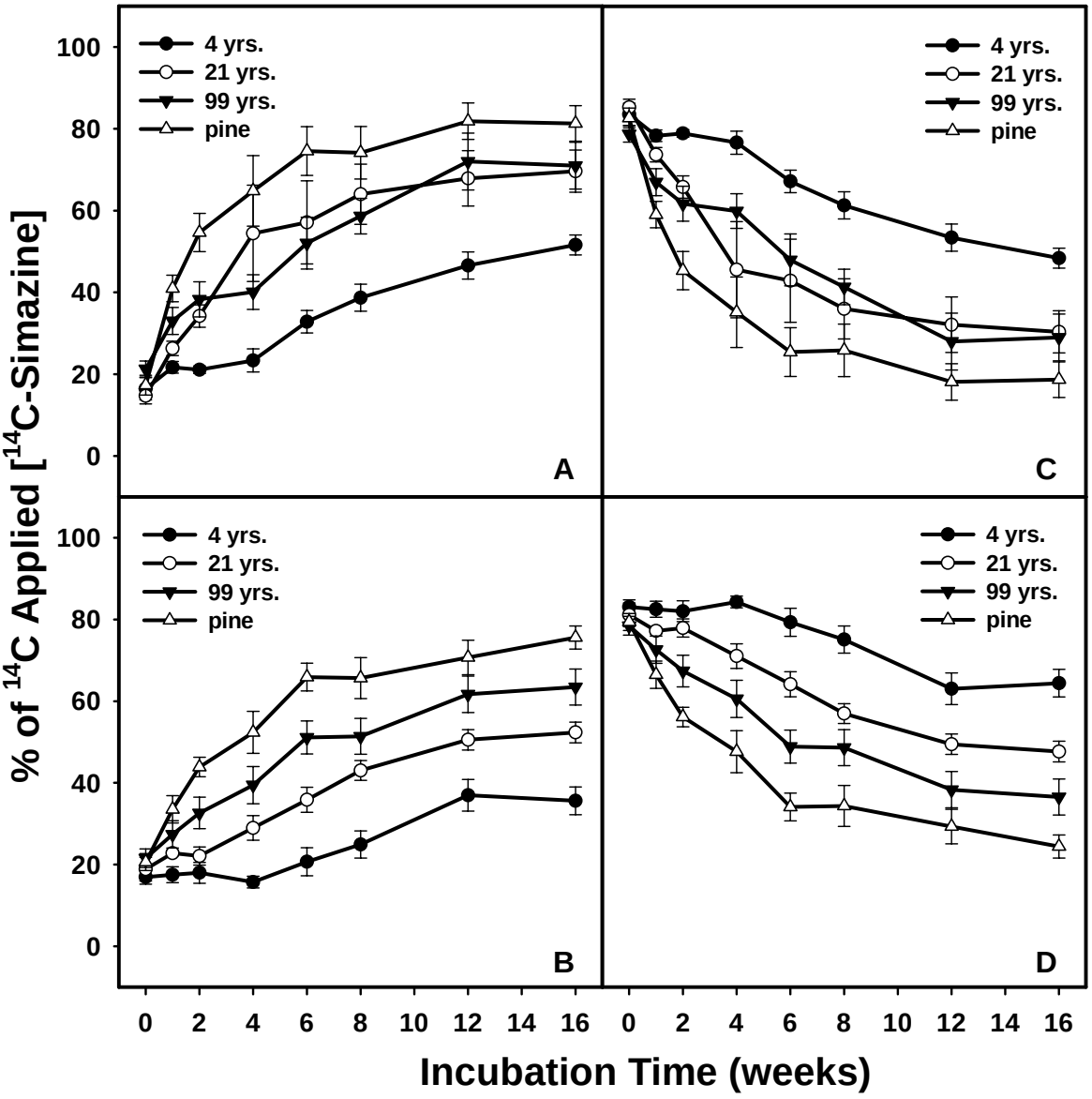
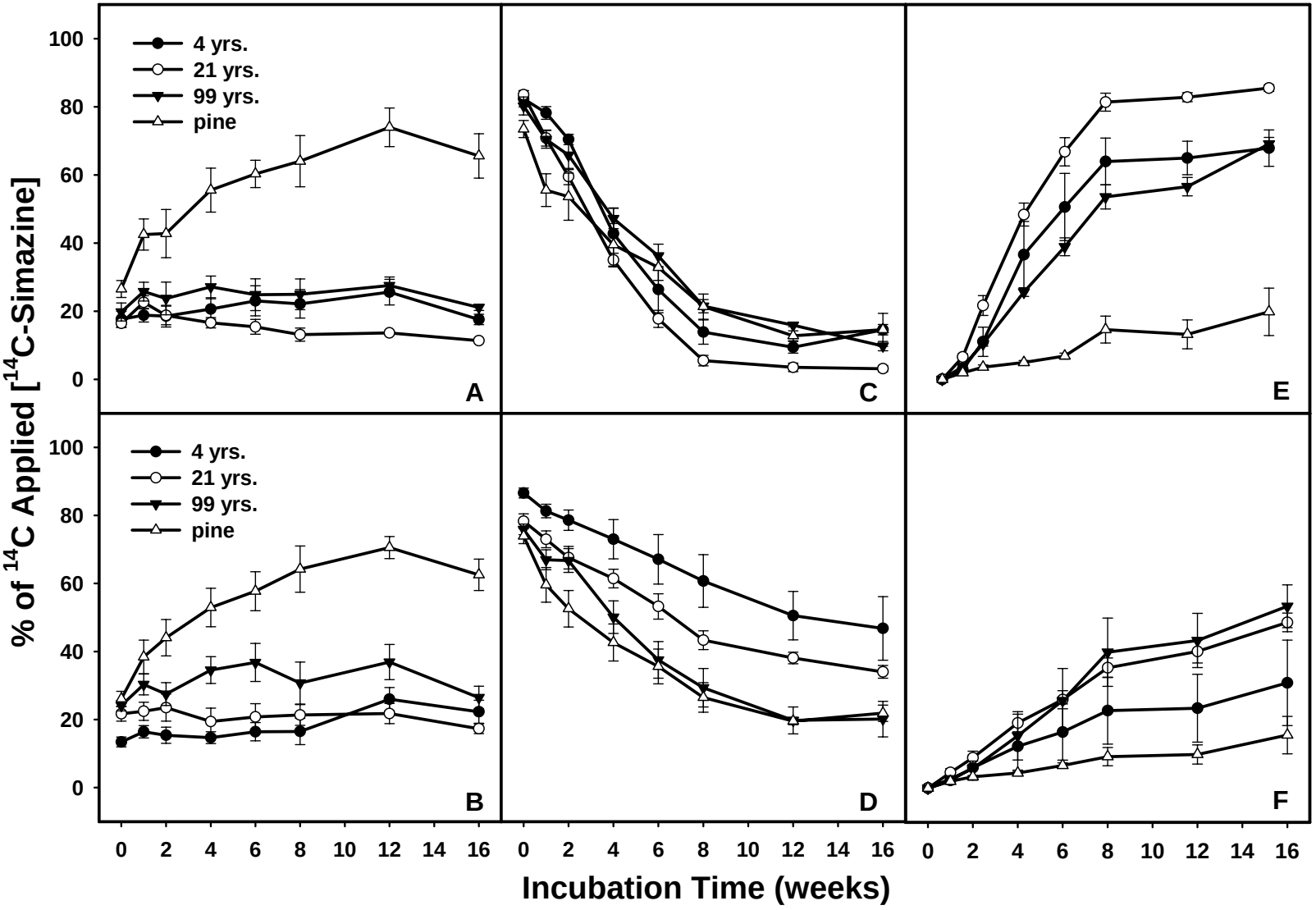


Figure 4. Formation of bound (A, B) and extractable (C, D) ^{14}C-simazine in sterilized soil samples from the 0 – 5 cm-depth (A, C) and 5 – 15 cm-depth (B, D) during laboratory incubations at 25 ± 2 °C. Bars represent standard errors (n=6).

Figure 5. Formation of bound ^{14}C (A, B), extractable ^{14}C (C, D), and cumulative $^{14}CO_2$ (E, F) in non-sterilized soil samples from the 0 – 5 cm-depth (A, C, E) and 5 – 15 cm-depth (B, D, F) during laboratory incubation at 25 ± 2 °C. Bars represent standard errors (n=6).


4 yrs.
21 yrs.
99 yrs.
pine
A
B
C
D
E
F
% of ^{14}C Applied [^{14}C-Simazine]
Incubation Time (weeks)
0
20
40
60
80
100
0 2 4 6 8 10 12 14 16

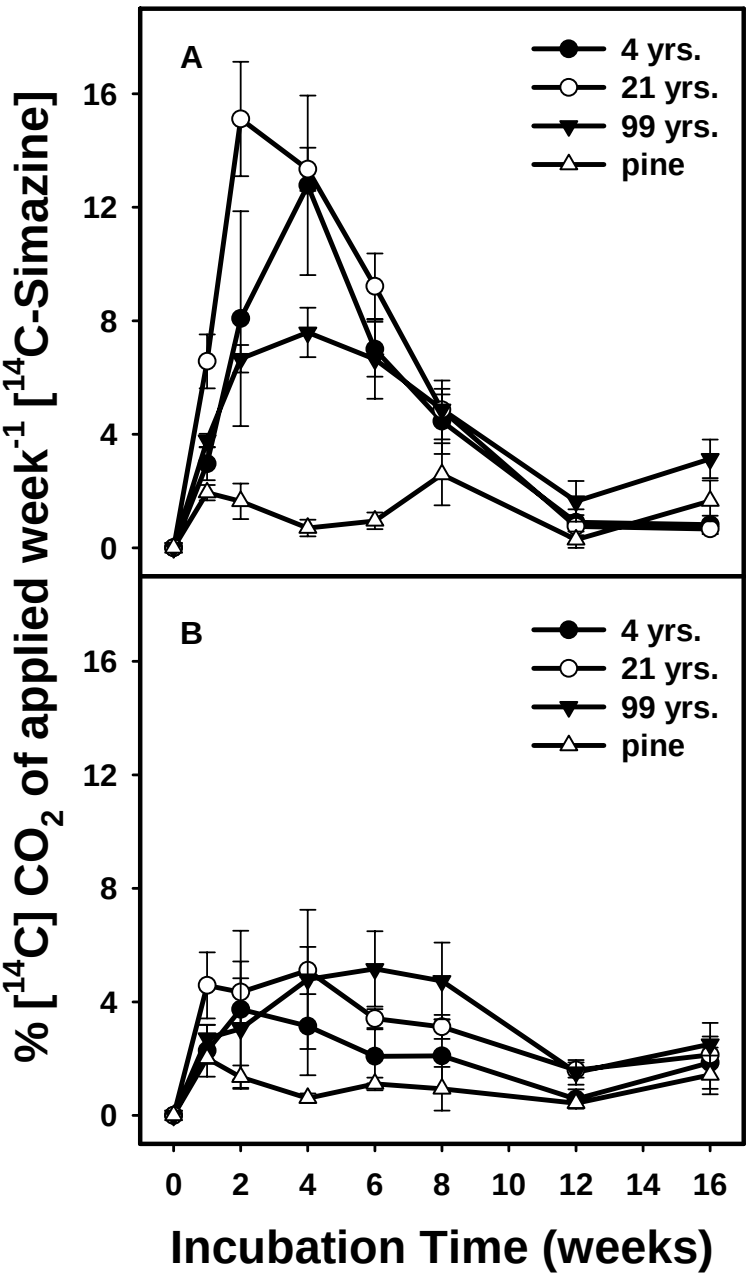


Figure 6. $^{14}CO_2$ respiration rate (A, B) of ^{14}C-simazine in soil samples from the 0-5 cm-depth (A) and 5-15 cm-depth (B) during laboratory incubations at 25 ± 2 °C. Bars represent standard errors (n=6).

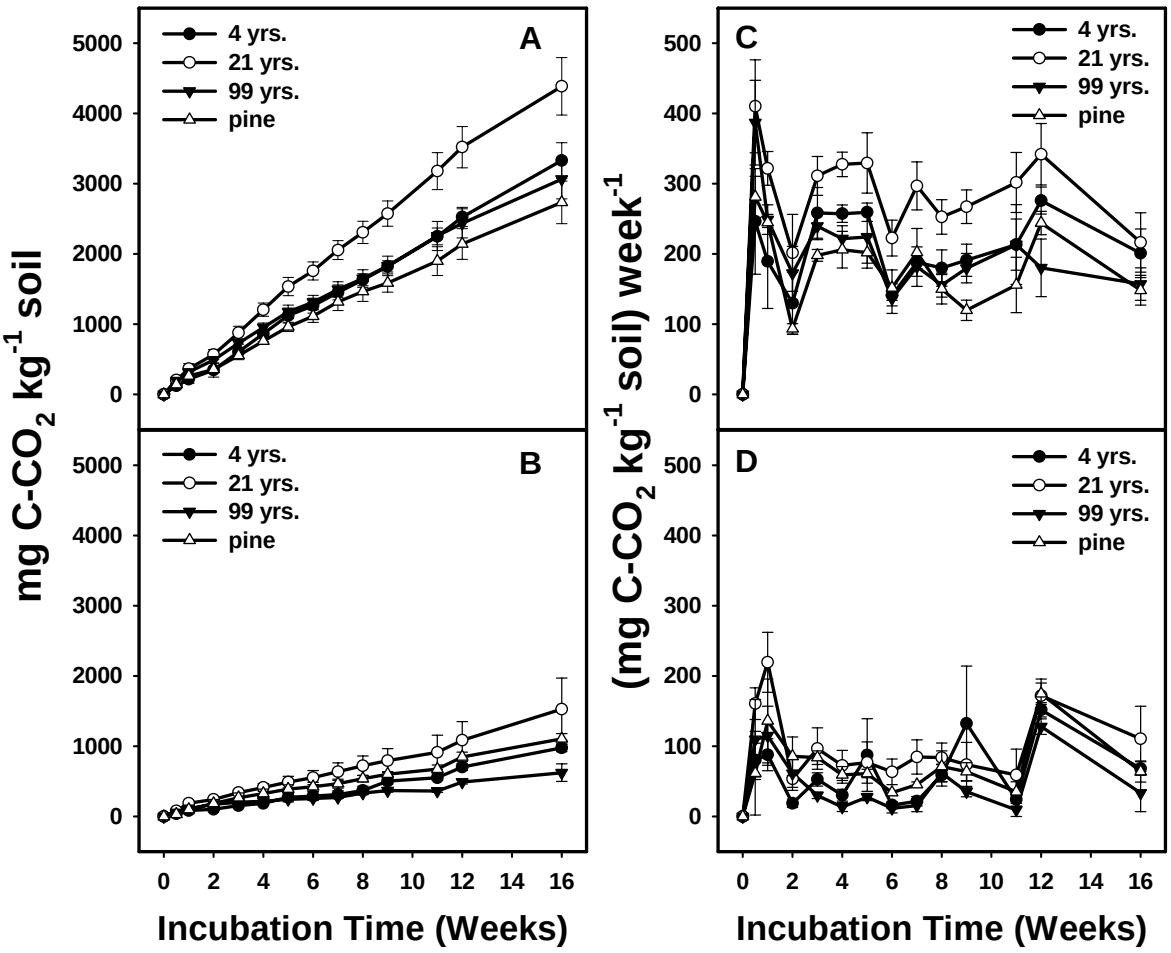


Figure 7. Cumulative CO_2 respired (A, B) and CO_2 respiration rate (C, D) during organic matter mineralization in soil samples from the 0-5 cm-depth (A, C) and 5-15 cm-depth (B, D) during laboratory incubations at 25 ± 2 °C. Bars represent standard errors (n=6).

SORPTION OF SIMAZINE AND *S*-METOLACHLOR TO SOILS FROM A CHRONOSEQUENCE OF TURFGRASS SYSTEMS

(Formatted for Submission to Weed Science)

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Pesticide sorption by soil is among the most sensitive input parameter in many pesticide-leaching models. For most pesticides, organic matter is the most important soil constituent influencing pesticide sorption. Increased fertility, irrigation, and mowing associated with highly maintained turfgrass areas results in constant deposition of organic material creating a soil system that can change drastically with time. These changes in soil characteristics could affect the environmental fate of pesticides applied to turfgrass systems of varying ages. Therefore, sorption characteristics of the herbicides simazine and *S*-metolachlor were determined on five soils from bermudagrass systems of increasing ages (1, 4, 10, 21, and 99 yrs.) and compared to adjacent native pine and bareground areas. Surface soil (0-5 cm) and

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subsurface soil (5-15 cm) from all sites were air-dried and passed through a 4-mm sieve for separation from plant material. Using a batch-equilibrium method, sorption isotherms were determined for each soil. Data were fit to the Freundlich equation and K_d and K_{oc} values were determined. Sorption of both herbicides was greatest on the surface soil from the oldest soil system and decreased with age of the bermudagrass soil system. Sorption decreased as soil depth increased. ^{14}C-simazine sorbed more to subsurface soil of the oldest system when compared to ^{14}C-*S*-metolachlor. Sorption and soil system age was directly related to organic matter content in the soil. These results indicate leaching potential and bioavailability of simazine and *S*-metolachlor may decrease as bermudagrass systems age.

Nomenclature: Simazine, [6-chloro-*N,N′*-diethyl-1,3,5-triazine-2,4-diamine], *S*-metolachlor, {2-chloro –*N*-(2-ethyl-6-methylphenyl)-*N*-[(1*S*)-2-methoxy-1-methyethyl]acetamide}, bermudagrass, *Cynodon dactylon* [(L.) Pers.]

Key words: Sorption, turfgrass, K_d, K_{oc}, soil, chronosequence, organic matter.

About two billion kilograms of pesticides are used each year in the United States, with agricultural usage accounting for approximately 77% (Aspelin and Grube 1999). Over 20 million hectares or approximately 15% of cropland area in the USA is managed as turfgrasses (Qian and Follett 2002). Turfgrasses are essential components of the urban landscape, providing both recreational and environmental benefits (Beard and Green 1994). Realistically, greater than 250 million kilograms of pesticides are used in turfgrass each year. Due to close proximity of turfgrass areas to the public, there is widespread concern that these areas are environmentally problematic due to intensive use of fertilizers, pesticides, and irrigation. Pesticide regulations are currently based on data from traditional row crop agriculture, and therefore may not be appropriate for turfgrass systems. Pesticide contamination via leaching and/or surface runoff has been the primary focus of environmental research in turfgrass systems with little attention given to soil sorption behavior (Cummings 2004; Gardner and Branham 2001; Haith and Rossi 2003; Raturi et al. 2003).

The physicochemical properties of a pesticide govern its behavior and ultimately its biological activity in turfgrass systems. Pesticide properties such as molecular size, ionizability, water solubility, lipophilicity, polarity, charge distribution, and volatility are all key properties, which determine the fate of pesticides in soil (Pignatello and Xing 1996; Senesi 1992; Weber 1972; Weber et al. 1993). In addition, soil physical and chemical properties such as bulk density, clay content, OM content, cation exchange capacity, and pH can affect pesticide fate (Hatzinger and Alexander 1995; Piatt and Brusseau 1998). Although sorption to mineral, non-organic soil components such as clay particles does occur (Ball and

Roberts 1991a, 1991b; Mader et al. 1997), it is thought that sorption to OM is the dominant process in the sequestration of most pesticides (Alexander 2000; Hatzinger and Alexander 1997; Nam et al. 1998; Weber et al. 1993). Sorption is probably the most important interaction between soil and pesticides because it controls the amount of pesticide in soil solution. Pesticide concentration in soil solution is an important factor in determining the ability to contaminate groundwater and surface water.

Weak base herbicides, such as simazine (pK_a = 1.6), become protonated as soil solution pH approaches their pK_a values (Weber et al. 1993) (Table 1). These pesticides can behave similar to cations such as K^+ or Ca^{2+} and become sorbed to clay particles and/or organic matter (OM) (Weber et al. 1969; Weber 1994). Sorption of *s*-triazines to OM is governed by hydrogen bonding and proton transfer between *s*-triazines and acid groups of humic substances especially in a hydrophobic environment where hydrogen bonds with water molecules are not dominant (Martin-Neto et al. 1994). Although simazine is moderately sorbed to soil, there are many reports of presence in groundwater, primarily due to long persistence (60-186 d) (Barbash et al. 2001; Senseman 2007).

Non-ionic pesticides, such as *S*-metolachlor (Table 1), can be sorbed to soil in numerous other mechanisms, including Van der Waals forces, ligand exchange, charge-transfer complexes, hydrophobic partitioning, covalent bonding, and sequestration or combinations of these reactions (Berry and Boyd 1985; Dec and Bollag 1997). Soil sorption of metolachlor has been correlated with high clay and/or OM contents, with low to moderate mobility in most soils (Kozak et al. 1983; Peter and Weber 1985; Rao et al. 1986; Wood et al. 1987). Metolachlor leaches readily in sandy soils, and has been detected in groundwater

probably due to intensive use in soybeans and corn (Braverman et al. 1986; Huang and Frink 1989; Maas et al. 1995).

Turfgrass soils generally have high levels of OM, and pesticides may be immobilized by sorption onto OM and not available for microbial degradation, plant uptake, and eventual leaching into groundwater. Pesticide sorption could be affected by a number of factors associated with the age of a turfgrass system. In newly created turfgrass systems, significant soil disturbance occur causing adjustments in soil physical and chemical properties due to construction and establishment. The prevailing disturbances may include partial replacement of surface soil with the subsoil or sand from an external source, soil compaction and an abrupt change in landscape cover and thus plant residues. Turfgrass systems are not tilled allowing the grass canopy to grow continuously, uninterrupted by crop removal. Frequent mowing results in leaf clippings being left on the turfgrass surface and allowed to decompose resulting in a highly managed ecosystem in which soil OM is likely to accumulate (Bandaranayake et al. 2003; Qian and Follett 2002).

A turfgrass chronosequence represents a practical system to evaluate temporal carbon transformations that regulate OM levels and therefore the potential for pesticide sorption and eventual downward mobility in turfgrass systems. Inclusion of adjacent natural lands from which turfgrass systems were constructed would facilitate a better assessment of ecological sustainability of the turfgrass system. We hypothesized that increasing OM as turfgrass systems age due to long-term management practices, including frequent irrigation, fertilization, mowing, and pesticide application would change sorption of simazine and *S*-metolachlor to soil. Taking into account the differences in OM and microbial activity, one

might think that pesticide fate in turfgrasses would be unlike agronomic systems. Information concerning these differences would allow for a better understanding on the mechanisms of pesticides behavior in turfgrass systems.

Our objectives were (i) to compare sorption of simazine and *S*-metolachlor to soils from a chronosequence of turfgrass systems, and (ii) to determine how soil depth influences simazine and *S*-metolachlor soil sorption in a turfgrass system. Soil sorption characteristics in turfgrass systems were then evaluated against those in adjacent natural ecosystems and bareground areas.

Materials and Methods

Turfgrass Sites: Four golf courses and a research experiment station were selected as study sites. In addition, soil was removed from adjacent native pine areas and a bareground area adjacent to the 10-year-old turfgrass system for comparison purposes. Each golf course was within a 20-kilometer radius of one another near or in the city of Wilmington, North Carolina, USA. The Sandhills Research Station near Jackson Springs, NC is approximately 240 kilometers to the northwest of Wilmington, NC. The turfgrass systems were established in 1905, 1983, 1994, 2000, and 2004 were 99, 21, 10, 4, and 1 year(s)-old, respectively when soil samples were taken in 2004. All sites were planted to common bermudagrass [*Cynodon dactylon* (L.) Pers.] or hybrid bermudagrass (*Cynodon dactylon* × *transvaalensis*), a warm-season perennial. The oldest site had been replanted to different bermudagrass varieties numerous times, but constant turfgrass cover was maintained from time of establishment on

all sites. In general, all golf course sites received annual applications of simazine in the fall for the control of winter annual grass and broadleaf weeds. Early records of the 99-year-old site were not available, but simazine was not applied prior to its introduction in 1956 (Cremlyn 1990). All sites were constructed on previously undeveloped land. Golf courses were built in a manner such that portions of the native pine forest were removed and planted to bermudagrass. Considerable soil disturbance usually occurs during golf course construction, especially on more recent courses. Since the soils in these regions are almost uniformly sandy, the disturbance during construction probably had little affect on soil texture.

Experimental Soils. Soils were sampled from three individual fairways from each golf course in September 2004 before fall applications of simazine. Fifteen intact cores (5 cm diameter × 15 cm length) were taken from each fairway. Five cores from each fairway were combined and represented a replication for a total of three replications per turfgrass system age. Soil cores were obtained in an identical manner from the adjacent native pine areas. Twenty cores were removed from the 10-year-old turfgrass system and adjacent bareground area. Intact soil cores were placed on ice and transported to the lab. The cores were then sectioned into 0–5 and 5–15 cm depths. Soil from each section was sieved (< 4 mm), and stored at 4 °C for later analysis after visible roots and plant residues were removed. Soils collected were: Baymeade sand (loamy, siliceous, semiactive, thermic Arenic Hapludults) (99 yrs.), Lakeland sand (thermic, coated Typic Quartzipsamments) (21 yrs.), Candor sand (sandy, siliceous, thermic Grossarenic Kandiudult) (10 yrs.), Kenansville sand (loamy,

siliceous, subactive, thermic Arenic Hapludults) (4 yrs.), and Leon sand (sandy, siliceous, thermic Aeric Alaquods) (l yr.). Particle size was determined using a hydrometer in air-dried, sieved soil samples suspended in a sodium metaphosphate solution (Gee and Orr 2002). Soil pH was determined using a glass electrode and reference buffers on a 1:1 soil to water mixture (Peech 1965). Effective CEC was measured using the summation of exchangeable cations procedure described by Mehlich (1984a). Percent OM was determined using a colorimetric Walkley-Black procedure (Nelson and Sommers 1982). Percent humic matter (HM) was quantified by photometric determination (Mehlich 1984b).

Additionally, surface soil from the 99-year-old turfgrass system was separated into three separate density fractions according to Meijboom et al. (1995). Briefly, five batches of 500 g of soil were wet sieved over two sieves (top sieve mesh size, 250 mm; bottom sieve, 150 mm). Soil was forced through the top sieve until the water passing through the sieve became clear. The material present on both sieves was saved, and separated from the mineral material by numerous decantations. The organic fraction recovered on both sieves (> 150 mm) is referred to as macroorganic matter. Further separation from the mineral fraction was achieved by swirling and decantation on a 150 mm sieve several times until no visible organic particles were present in the mineral fraction below the sieve. The organic material was fractionated in Ludox[1], an aqueous colloidal dispersion of silica particles. The particles are dispersed in an alkaline medium (0.2% NaOH, pH 9.1) which reacts with the silica surface to produce a negative charge. The tray containing the organic material was placed in the silica suspension with a density of 1.37 g cm^{-3} and was mixed several times. The floating fraction was collected and put in a similar tray, which was placed in Ludox with a density of

1.13 g cm^{-3}. This material was also separated into floating and settling fractions. In both Ludox suspensions mixing was repeated several times until the quantity of floatable material became negligible. Finally, three fractions were obtained: a light fraction (LF) with a density < 1.13 g cm^{-3}; an intermediate fraction (IF) with a density between 1.13-1.37 g cm^{-3} and a heavy fraction (HF) with a density > 1.37 g cm^{-3}. The three fractions were thoroughly washed with tap water followed by distilled water and freeze dried.

Herbicides. Technical grade simazine[2] (96% purity), ^{14}C-ring-labeled simazine[3] [98.7% purity, specific activity (1.8 MBq mg^{-1})], technical grade *S*-metolachlor[4] (99% purity), and ^{14}C-*S*-metolachlor[5] [97.6% purity, specific activity (MBq $mmol^{-1}$)] were donated by Syngenta Corporation, Greensboro, NC (Table 1) (Senseman 2007). Radiolabeled simazine and *S*-metolachlor stock solutions were prepared with technical grade herbicide in methanol.

Simazine and *S*-Metolachlor Soil Sorption. Amount of simazine or *S*-metolachlor removed from soil solution by the different soils was determined using a batch-equilibrium method. The herbicide solutions were prepared in 0.01 M $CaCl_2$ with simazine concentrations of 4.95, 9.92, 14.88, and 19.83 µM and *S*-metolachlor concentrations of 3.52, 7.05, 10.57, and 14.09 µM. Ring-labeled ^{14}C-simazine and ^{14}C-*S*-metolachlor were added to produce solutions that contained approximately 0.16 kBq of ^{14}C per milliliter. Technical grade simazine and *S*-metolachlor were added to achieve correct solution concentrations. A 10-ml aliquot of each solution was added to 2 g of soil from each soil and 250 µg of each macroorganic matter fraction in a 30-ml Teflon-lined centrifuge tube[6] and the tubes were

sealed with a Teflon-lined cap. Macroorganic matter sorption was only determined for simazine. In preliminary studies, about 96% of ^{14}C-simazine and 92% ^{14}C-*S*-metolachlor was sorbed in the first 8 h. The amount of ^{14}C-simazine and ^{14}C-*S*-metolachlor sorbed between 24 and 48 h was less than 2%. Therefore, a 24-h sorption time was used with the slurry mechanically shaken at about 180 excursions min^{-1} at 22 °C. After 24 h, the tubes were centrifuged for 10 min at 8,500 × *g*. Duplicate 1-ml aliquots of supernatant were removed and added to scintillation cocktail[7]. Activity of ^{14}C in solution was determined by liquid scintillation counting[8] for 10 min. ^{14}C-simazine and ^{14}C-*S*-metolachlor sorption on each soil was calculated to be the difference between the ^{14}C in the soil-free blank and amount of ^{14}C remaining in the supernatant. Sorption isotherms for each concentration–soil treatment were determined using a linear form of the Freundlich equation:

$$\log (x/m) = \log K_f + (1/n) \log C_e \quad [1]$$

where x/m is micromoles of herbicide sorbed per kilogram of soil, C_e is micromoles of herbicide per liter of supernatant solution after equilibration, and K_f and $1/n$ are empirical constants where K_f is the Freundlich coefficient (L kg^{-1}) and $1/n$ is a dimensionless parameter that accounts for sorption nonlinearity. The sorption distribution coefficients (K_d) were calculated as follows:

$$K_d = (x/m) / C_e \quad [2]$$

Distribution coefficients were determined at each concentration and averaged across all equilibrium concentrations to obtain a single estimate of K_d for each replication. The sorption distribution coefficient was normalized to the organic carbon (OC) content of the soil (K_{oc}):

$$K_{oc} = (K_d / \%OC) \times 100 \quad [3]$$

Percent organic carbon was calculated from OM using the equation, %OC = %OM / 1.724 (Comfort et al. 1994).

Data Analyses. The experiment was a completely randomized design with three replications per soil. The experiment was performed twice. Data were pooled and statistical evaluation of the sorption included comparison of slopes and intercepts of the regression lines and calculation of the intercept (log K_f) and slope ($1/n$). Nonlinear regression analysis was used to derive K_f and $1/n$ minimized the weighted residual sum of squares. Linear correlation analysis was conducted also to determine relationships between selected soil parameters and K_f values. Asymptotic errors were calculated and presented for all Freundlich sorption parameters. All nonlinear and linear analyses were performed using Sigmaplot 10 software[9]. K_d and K_{oc} were analyzed by analysis of variance (ANOVA) for a completely randomized design using SAS[10], and means separated by Fisher's Protected LSD at the 5% level. The relationship between the K_d, K_{oc}, K_f, and $1/n$ values for each herbicide and the physical and chemical properties of the soils were evaluated through correlation analysis. By comparing

Pearson correlation coefficients (r), those soil factors contributing most to the variation in sorption of the herbicides in the soils were identified. Further evaluation of the influence of the soil properties on herbicide sorption were performed by stepwise multiple regression analyses. The principle purpose of these statistical treatments was to derive a suitable regression model that would best predict the K_d value of the herbicides in soils.

Results and Discussion

Soil Properties. All soils had similar soil series descriptions, texture (sand), and cation exchange capacity (CEC) (Table 2). Turfgrass soil contained an average of 94% sand, 2% silt and 4% clay, very similar to the adjacent native pine soil that consisted of 92% sand, 4% silt and 4% clay and bareground soil (94% sand, 3% silt, and 3% clay). Soil OM increased as turfgrass soil systems matured and decreased with increasing soil depth (Table 2). Soil pH was lowest in the native pine area and oldest turfgrass soil system (Table 2).

Simazine Sorption. The Freundlich parameter coefficients for the ^{14}C-simazine sorption isotherms of Figure 1 are given in Table 3. The Freundlich coefficients, K_f, ranged from 0.23 to 9.09 among the soil locations and depths. The range of $1/n$ (0.75 to 1.20) values for simazine sorption indicated that the pool of unoccupied sites available for sorption decreased as the solution concentration increased. Slope ($1/n$) and intercept (K_f) comparisons indicate that the order of sorption in surface soil (0-5 cm) by soil location was 99 > pine > 21 > 10 > bare > 4 > 1. Soil from both depths of the 99-year-old turfgrass system and native pines had

higher capacity for ^{14}C-simazine sorption compared to all other soils. Overall, ^{14}C-simazine sorption K_f and K_d values in this study were slightly higher than the values reported by others (Garcia-Valcarcel and Tadeo 1999; Gerritse et al. 1996; Regitano et al. 2006). ^{14}C-simazine sorption was probably greater due to higher levels of OM in turfgrass surface soils. The ^{14}C-simazine K_d values were generally smaller than the K_f in all soils due to nonlinearity in sorption (Table 3). Except for two soils (pine and 99-yrs. subsurface soil), K_{oc} values were similar among all soils. Typically a very narrow range of K_{oc} among soils with varying levels of organic matter indicated that organic matter is a major factor controlling the sorption process. ^{14}C-simazine sorption distribution coefficients (K_d) were most related (r = 0.74) to OM levels followed by pH (r = -0.59) (Table 4). These results are similar to those reported for atrazine, where OM content played a significant role in sorption (Novak et al., 1997). Similar K_{oc} values among soil and high correlation of K_d values to OM indicate that ^{14}C-simazine became readily incorporated into OM polymer structures associated with turfgrass soils. Although pH values were fairly similar for all soils, K_f and K_d values were highest in the pine and 99-year-old turfgrass system where pH values were lowest. Increased H^+ concentration associated with low pH leads to a higher percentage of protonated simazine and higher sorption to negatively charged soil colloids.

^{14}C-simazine sorbed readily to all macroorganic matter density fractions with K_f values ranging from 32.7 to 40.2 (Table 5). Light macroorganic matter primarily consisted of non-degraded leaf and stem material, IF consisted of partially degraded plant material and HF consisted of completely degraded organic material complexed with soil mineral particles. These data confirm that simazine is sorptive to all density fractions of OM. Evaluating

simazine sorption by macroorganic matter fractions on a per volume basis would have probably revealed that heavy macroorganic matter is the primary fraction of OM for sorbing simazine.

_S_-Metolachlor Sorption. Sorption of ^{14}C-*S*-metolachlor to soils followed a similar trend to ^{14}C-simazine with K_f values ranging from 0.54 to 7.90 among all locations and depths (Table 6). The more narrow range of $1/n$ (0.88 to 1.24) values for ^{14}C-*S*-metolachlor sorption indicated that the pool of unoccupied sites available for sorption remained relatively stable as the solution concentration increased. Sorption also increased as *S*-metolachlor concentration increased for all soils within the concentration range evaluated (Figure 2). Slope ($1/n$) and intercept (K_f) comparisons indicate that the order of sorption in surface soil (0-5 cm) by soil location was 99 > 21 > 10 > 4 > bare > 1. Increased soil depth resulted in a decrease in OM levels and K_f values. Soil from the 99-year-old turfgrass system had the highest capacity for ^{14}C-*S*-metolachlor sorption compared to all other soils. In general, ^{14}C-*S*-metolachlor K_d values were similar to the K_f values in all soils due to linearity in sorption (Table 6). Again, except for the subsurface soil from the 99-year-old turfgrass system, a very narrow range of K_{oc} among soils was detected, indicating that OM is a major factor controlling the sorption process (Table 6). Correlation analysis revealed that ^{14}C-*S*-metolachlor sorption distribution coefficients (K_d) were directly related ($r = 0.95$) to OM levels (Table 4). Unlike simazine, *S*-metolachlor is non-ionizable; therefore pH had no effect on soil sorption.

Nonlinear regression with a two-parameter exponential rise to max model revealed a strong relationship between years since bermudagrass establishment and both K_f and OM

(Figure 3). A rapid initial incline levels off at approximately 20 to 30 years after establishment. These results are supported by previous research showing that OM accumulates in turfgrass systems with time since establishment increases (Qian and Follett 2002; Shi et al. 2006). Rapid initial OM accumulation slows as equilibrium is established. Higher populations of soil microorganisms associated with older turfgrass systems breakdown OM quickly, resulting in little accumulation.

Simple linear regression analysis of the 14 soils indicated that OM (r = 0.74), CEC (r = 0.88), and pH (r = -0.59) were the major contributors to the variation in K_d values for simazine and OM (r = 0.95) and CEC (r = 0.99) only for *S*-metolachlor (Table 4). Multiple regression analysis was performed to determine the potential contribution to the model from multiple soil properties (Table 7). Increasing combinations of soil properties improved the r^2 value for simazine only. Organic matter was the major contributor in both models, with pH and CEC added to the simazine model (r^2 = 0.92) and OM only incorporated into the *S*-metolachlor model (r^2 = 0.92) (Table 7). This high correlation of simazine and *S*-metolachlor sorption to OM was expected, especially for soils with similar textural classification. Soils with more diverse textural classification need to be evaluated to establish reliable relationships between simazine and *S*-metolachlor and soil properties associated with turfgrass soil systems.

Simazine and *S*-metolachlor sorption was greatest on the surface soil from the oldest soil system and decreased with age and increased soil depth (Table 3, 6; Figure 1, 2). Sorption and soil system age was directly related to OM levels in the soil (Figure 3). Similar to degradation experiments, results indicate leaching potential and bioavailability of simazine

may decrease as turfgrass systems age (Hixson et al. previous research). Overall, the higher the OM content, the greater was the soil's sorptive capacity for simazine and *S*-metolachlor. Greater sorption occurred in the surface soil of all turfgrass soil systems except in the 1-year-old system where K_f and K_d values were similar at both depths. Although soil sorption alone does not determine the leaching potential of a pesticide, it is typically the most important input for soil leaching models (Carsel et al. 1984; Davis et al. 1990; Weber 2003). Thus, increased sorption by established turfgrass systems could be a major factor in reduced leaching of simazine and *S*-metolachlor in these areas. Although pH would not affect sorption and leaching of *S*-metolachlor, high soil pH would decrease simazine sorption to soil and possibly increase leaching potential. Low OM and coarse textured soils with moderate to high pH and shallow depth to groundwater are most susceptible to water contamination by simazine and *S*-metolachlor. Recently established bermudagrass systems such as newly constructed golf courses and recently harvested sod farms should be cautious when applying these herbicides. Frequently, coarse-textured topsoil is used during turfgrass establishment and topdressing as part of a typical maintenance regime. This could contribute to significant changes in native soil properties causing increased opportunity for leaching in newly established bermudagrass systems. Therefore, much caution should be used when applying simazine and *S*-metolachlor to turfgrass systems with coarse textured soils with less than 1.5% OM.

Sources of Materials

[1] Ludox® TMA colloidal silica, 34 wt. % suspension in water, E.I. du Pont de Nemours & Co., Inc., 1007 Market Street, Wilmington, DE, 19899.

[2] Simazine, Syngenta Corporation, 2200 Concord Pike, P.O. Box 8353, Wilmington, DE 19803.

[3] ^{14}C-simazine, Syngenta Corporation, 2200 Concord Pike, P.O. Box 8353, Wilmington, DE 19803.

[4] *S*-metolachlor, Syngenta Corporation, 2200 Concord Pike, P.O. Box 8353, Wilmington, DE 19803.

[5] ^{14}C-*S*-metolachlor, Syngenta Corporation, 2200 Concord Pike, P.O. Box 8353, Wilmington, DE 19803.

[6] Nalgene® Oak Ridge FEP Teflon Centrifuge Tubes, 30-ml, Nalge Nunc International, 75 Panorama Creek Drive, Rochester, NY, 14625.

[7] Scintiverse® SX18-4 Universal Liquid Scintillation Cocktail, Fisher Scientific, 1 Regeant Road, Fair , NJ 07410.

[8] Liquid scintillation counter, Tri-Carb 2100TR, Packard Instrument Co., 2200 Warrenville Road, Downers Grove, IL 60515.

[9] Sigmaplot 10, Systat Software Inc., 1735 Technology Drive, Suite 430, San Jose, CA 95110.

[10] SAS, Statistical Analysis Systems, 2003, Release 9.1, Statistical Analysis Systems Institute, Cary, NC 27513.

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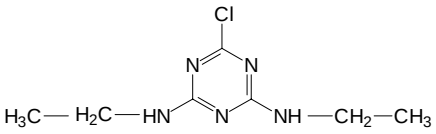
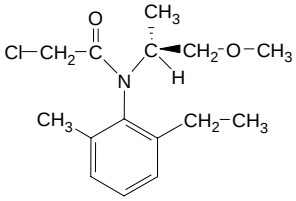
Table 1. Herbicide physicochemical properties (20-25 °C).[a]

Property	Simazine	*S*-Metolachlor
Chemical family[b]	*s*-triazine	Acetamide
Structure		
Reactivity[b]	Weak base	Nonionizable
Ionizability (pK_a)[b]	1.62	Nonionizable
Aqueous solubility (mg L^{-1})[b]	3.5 (20 °C)	488
Vapor pressure (Pa)[b]	8.1×10^{-7} (20 °C)	1.73×10^{-3} (20 °C)
Longevity (DT_{50}, days)	55-186[b]	51[c]
Soil retention (K_d, mL g^{-1})[b]	0.48-4.31	0.1-2.1
Leaching potential[d]	56	63

[a] Abbreviations: DT, disappearance time, K_d, herbicide-partition coefficient.

[b] Senseman 2007

[c] Miller et al. 1997

[d] Pesticide leaching potential (PLP) (Warren and Weber 1994; Weber, 2005).

Table 2. Characteristics of soils from two depths (0-5 and 5-15 cm) at five different aged bermudagrass systems, adjacent native pine forest, and bareground area.[a]

Location	Soil Series	OM[b]	OC[c]	HM[d]	Sand[e]	Clay[e]	CEC[f]	pH[g]
		%					cmol kg^{-1}	1:1
		0-5 cm depth						
Bareground	Candor	1.2	0.58	-	94	2	2.5	5.8
Native pines	Mixed[h]	3.5	2.18	2.6	92	2	6.0	4.6
1-yr turf	Leon	0.7	0.30	-	96	2	1.5	6.2
4-yr turf	Kenansville	1.8	1.66	0.4	96	2	3.6	6.3
10-yr turf	Candor	3.0	1.88	-	94	2	5.9	6.2
21-yr turf	Lakeland	4.1	2.46	1.5	96	2	5.2	6.0
99-yr turf	Baymeade	4.5	3.90	2.7	92	2	7.8	5.4
		5-15 cm depth						
Bareground	Candor	1.0	0.54	-	92	4	1.9	5.0
Native pines	Mixed[h]	2.6	1.43	1.1	94	2	5.8	4.7
1-yr turf	Leon	0.6	0.30	-	98	2	1.2	5.8
4-yr turf	Kenansville	0.4	0.10	0.3	96	2	1.9	6.2
10-yr turf	Candor	0.8	0.67	-	92	4	3.0	6.0
21-yr turf	Lakeland	1.3	0.90	0.6	94	2	2.0	6.3
99-yr turf	Baymeade	1.7	0.96	1.1	94	2	4.8	5.8

[a] Abbreviations: OM, organic matter; OC, organic carbon; HM, humic matter; CEC, cation exchange capacity.

[b] Organic matter was determined using the Walkley-Black procedure (Nelson and Sommers 1982).

Table 2. (continued)

[c] Organic carbon was estimated using the equation: %OC = (%OM / 1.724) (Comfort et al. 1994).

[d] Humic matter was determined by photometric determination (Mehlich 1984b).

[e] Particle analysis was determined using the hydrometer method (Gee and Orr 2002).

[f] Cation-exchange capacity was determined using the summation of exchangeable cations procedure (Mehlich 1984a).

[g] pH was determined using a 1:1 soil:distilled water ration (Peech 1965).

[h] Soil was removed from native pine areas adjacent to each turfgrass system and mixed.

Table 3. Freundlich sorption isotherm parameters (K_f and $1/n$ values), coefficients of determination (r^2) and distribution (K_d), and organic carbon normalized distribution coefficients (K_{oc}) of simazine sorption on the soils.[a]

	Freundlich sorption parameter[b]			Distribution coefficients[c]	
	K_f	$1/n$	R^2	K_d	K_{oc}
Location	$g^{1-1/n}L^{1/n}kg^{-1}$	Dimensionless		L kg^{-1}	L kg^{-1}
		0-5 cm depth			
Bareground	1.97 (0.073)	0.80 (0.075)	0.98	1.30fg	187f
Native pines	5.31 (0.041)	0.90 (0.051)	0.99	4.52c	223e
1-yr turf	0.69 (0.235)	0.79 (0.229)	0.86	0.49h	120i
4-yr turf	1.91 (0.147)	0.75 (0.150)	0.93	1.10g	126hi
10-yr turf	3.77 (0.036)	0.83 (0.041)	0.99	2.74e	157fgh
21-yr turf	4.30 (0.061)	0.88 (0.072)	0.99	3.56d	150ghi
99-yr turf	7.23 (0.005)	0.88 (0.007)	0.99	6.18ab	254de
		5-15 cm depth			
Bareground	2.30 (0.081)	0.82 (0.086)	0.98	1.60fg	274d
Native pines	9.09 (0.031)	0.76 (0.042)	0.99	6.40a	424b
1-yr turf	0.79 (0.161)	0.82 (0.158)	0.93	0.58h	164fg
4-yr turf	0.23 (0.102)	1.20 (0.099)	0.99	0.41h	177fg
10-yr turf	2.37 (0.049)	0.78 (0.052)	0.99	1.50fg	323c
21-yr turf	2.78 (0.061)	0.76 (0.065)	0.99	1.70f	225e
99-yr turf	8.31 (0.006)	0.77 (0.009)	0.99	5.84c	592a

Table 3. (continued)

[a] Abbreviations: K_f, Freundlich herbicide-partition coefficient; K_d, herbicide-partition coefficient; K_{oc}, organic carbon partition coefficient

[b] Values in parentheses are asymptotic standard errors.

[c] Means within each column followed by the same letter are not different according to Fisher's Protected LSD at P = 0.05.

Table 4. Pearson correlation coefficients (r) for K_f, $1/n$, K_{oc}, and K_d values compared to important soil properties determining sorption of simazine and *S*-metolachlor.[a,b]

Properties	OM	CEC	pH
$K_{f\,sim}$	0.66**	0.82***	-0.56**
$K_{d\,sim}$	0.74***	0.88***	-0.59**
$K_{oc\,sim}$	0.0007	0.24	-0.38
$1/n_{\,sim}$	-0.02	-0.03	0.05
$K_{f\,met}$	0.96***	0.99***	-0.14
$K_{d\,met}$	0.95***	0.99***	-0.18
$K_{oc\,met}$	0.39	0.59**	0.04
$1/n_{\,met}$	-0.53*	-0.56*	0.38

[a] Abbreviations: OM, organic matter; OC, organic carbon; CEC, cation exchange capacity; sim, simazine; met, *S*-metolachlor; K_f, Freundlich herbicide-partition coefficient; K_d, herbicide-partition coefficient; K_{oc}, organic carbon partition coefficient.

[b] Significance at *10%, **5%, ***1% levels of probability, respectively.

Table 5. Freundlich sorption isotherm parameters (K_f and $1/n$ values), coefficients of determination (r^2) and distribution (K_d) of simazine sorption on macroorganic matter fractions from the 99-year-old bermudagrass system.[a,b]

	Freundlich sorption parameter [b]			
	K_f	$1/n$	R^2	K_d[c]
Macroorganic matter fraction [d]	$g^{1-1/n}L^{1/n}kg^{-1}$	Dimensionless		L kg^{-1}
HF	32.7 (0.02)	0.895 (0.02)	0.99	26.4b
IF	40.2 (0.02)	0.873 (0.03)	0.99	31.5a
LF	37.0 (0.02)	0.925 (0.02)	0.99	32.1a

[a] Abbreviations: HF, heavy fraction; IF, intermediate fraction; LF, light fraction; K_f, Freundlich herbicide-partition coefficient; K_d, herbicide-partition coefficient.

[b] Values in parentheses are asymptotic standard errors.

[c] Means within the column followed by the same letter are not different according to Fisher's Protected LSD at P = 0.05.

Table 6. Freundlich sorption isotherm parameters (K_f and $1/n$ values), coefficients of determination (r^2) and distribution (K_d), and organic carbon normalized distribution coefficients (K_{oc}) of *S*-metolachlor sorption on the soils.[a]

	Freundlich sorption parameter[b]			Distribution coefficients[c]	
	K_f	$1/n$	R^2	K_d	K_{oc}
Location	$g^{1-1/n}L^{1/n}kg^{-1}$	Dimensionless		L kg^{-1}	L kg^{-1}
		0-5 cm depth			
Bareground	1.04 (0.030)	0.94 (0.099)	0.99	1.08fg	156e
1-yr turf	0.68 (0.019)	1.24 (0.068)	0.99	0.63fg	156e
4-yr turf	3.29 (0.023)	0.99 (0.056)	0.99	3.36d	386b
10-yr turf	4.37 (0.014)	0.94 (0.030)	0.98	4.64c	267c
21-yr turf	6.43 (0.035)	0.96 (0.066)	0.99	6.74b	283c
99-yr turf	7.90 (0.068)	0.88 (0.123)	0.96	9.32a	357b
		5-15 cm depth			
Bareground	1.14 (0.032)	0.97 (0.104)	0.99	1.17fg	202d
1-yr turf	0.67 (0.014)	1.02 (0.049)	0.99	0.67fg	193de
4-yr turf	0.54 (0.033)	1.24 (0.122)	0.98	0.51g	220d
10-yr turf	1.24 (0.003)	0.93 (0.009)	0.98	1.29f	278c
21-yr turf	2.17 (0.028)	0.96 (0.080)	0.99	2.23e	296c
99-yr turf	4.68 (0.023)	0.91 (0.047)	0.99	5.12c	519a

[a] Abbreviations: HF, heavy fraction; IF, intermediate fraction; LF, light fraction; K_f, Freundlich herbicide-partition coefficient; K_d, herbicide-partition coefficient.

Table 6. (continued)

[b] Values in parentheses are asymptotic standard errors.

[c] Means within the column followed by the same letter are not different according to Fisher's

Table 7. Regression equations for the distribution coefficients of simazine and *S*-metolachlor (K_d) as a function of significant predictive soil parameters.[a]

R^2	Linear regression equation
0.56	$K_{d\ sim}$ = 0.36 + 1.07 OM (%)
0.84	$K_{d\ sim}$ = -1.25 – 1.41 OM (%) + 1.73 CEC
0.92	$K_{d\ sim}$ = 7.06 - 1.53 OM (%) + 1.78 CEC – 1.39 pH
0.92	$K_{d\ met}$ = -0.40 + 1.97 OM (%)

[a] Abbreviations: sim, simazine; met, *S*-metolachlor; K_d, herbicide-partition coefficient.

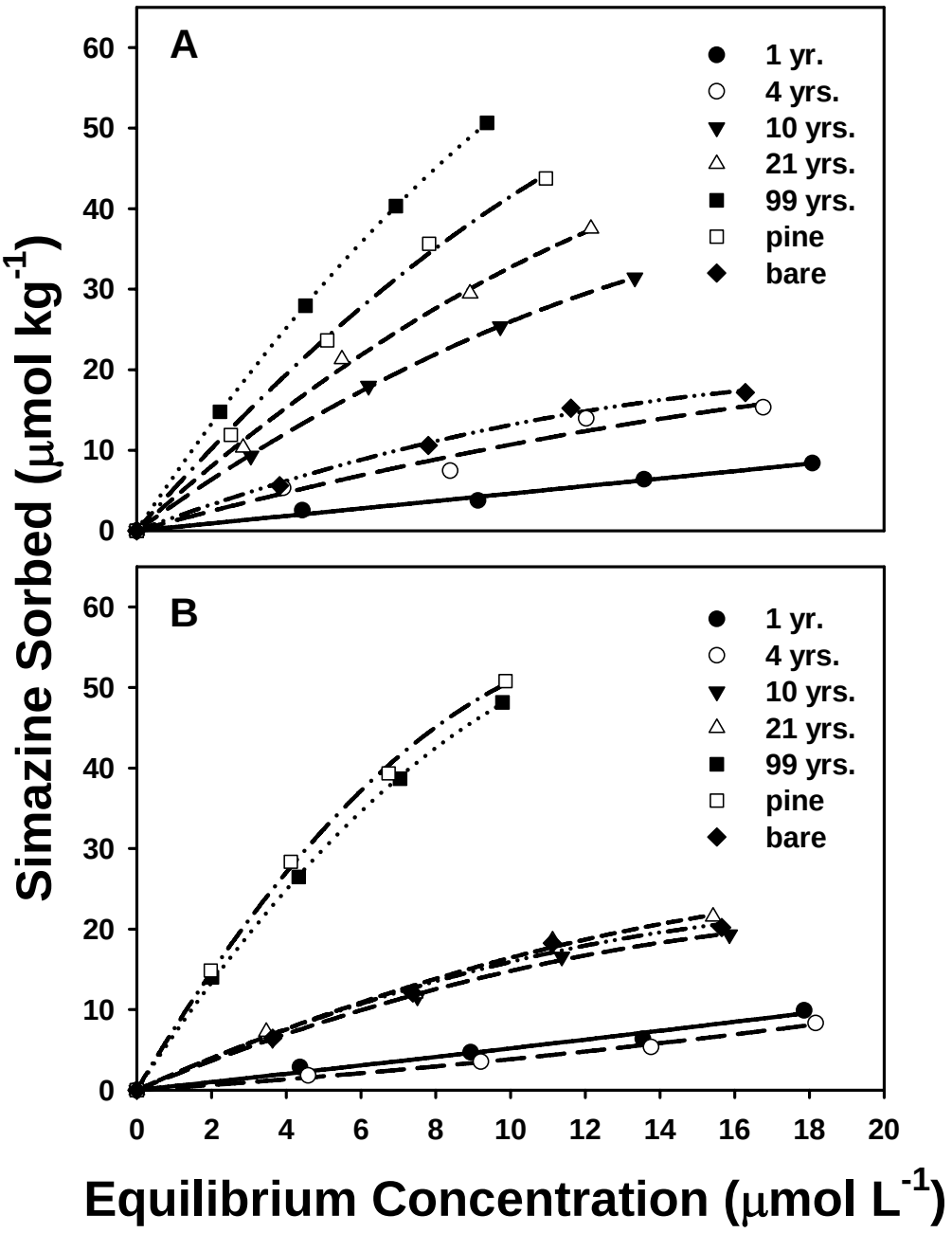


Figure 1. Freundlich isotherms fitted using nonlinear regression that describe simazine sorption in A) surface soil (0-5 cm) and B) subsurface soil (5-15 cm) from a chronosequence of bermudagrass soil systems, adjacent native pine, and bareground areas.

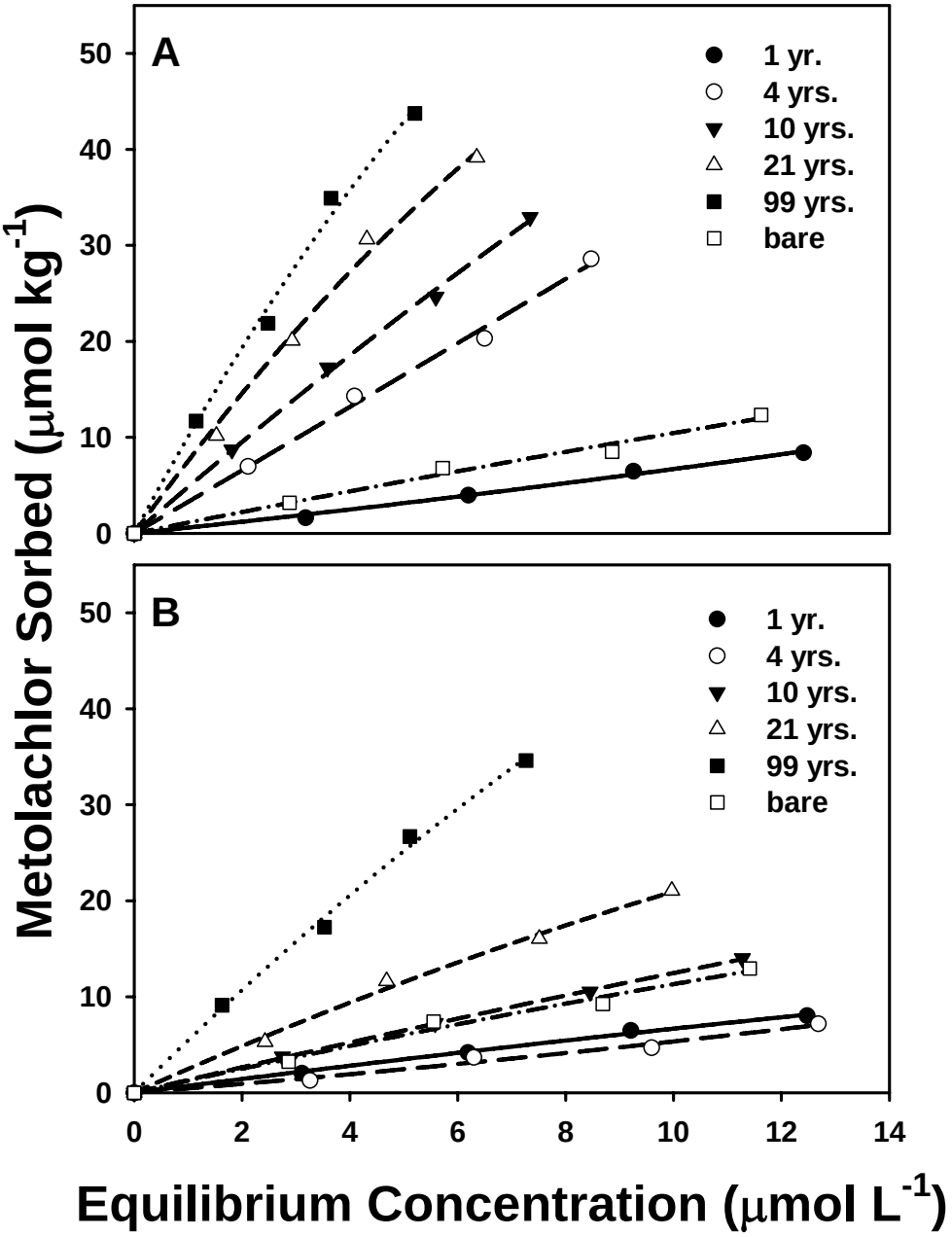


Figure 2. Freundlich isotherms fitted using nonlinear regression that describe S-metolachlor sorption in A) surface soil (0-5 cm) and B) subsurface soil (5-15 cm) from a chronosequence of bermudagrass soil systems, adjacent native pine, and bareground areas.

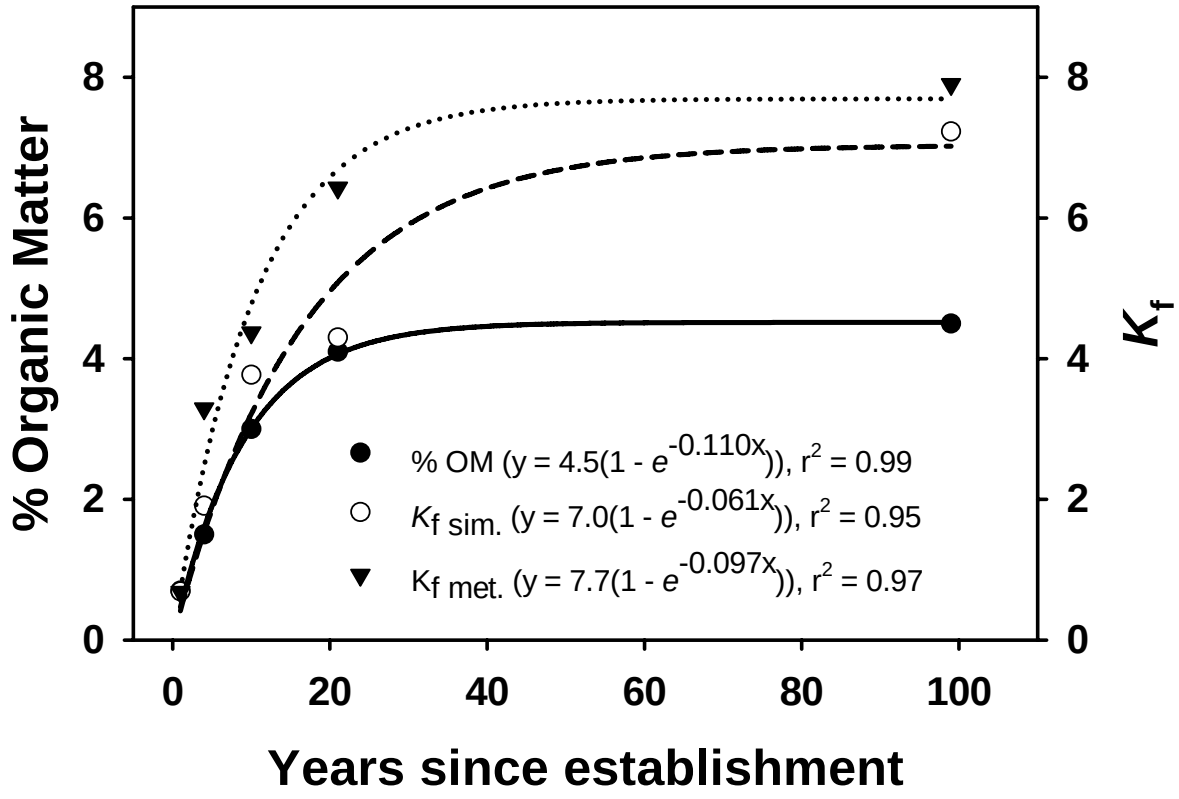


Figure 3. Relationship between percent organic matter, years since establishment, and K_f values generated for simazine and *S*-metolachlor. Nonlinear regression equations were derived by fitting a two-parameter exponential rise to max model to the data. Closed circles represent the percent organic matter, open circles represent the simazine K_f values, and closed triangles represent the *S*-metolachlor K_f values.

SOIL PROPERTIES INFLUENCE EFFICACY OF SAFLUFENACIL

(Formatted For Submission to Weed Science)

Adam C. Hixson, Kyle E. Keller, Jerome B. Weber, Stevan Z. Knezevic, and Fred H. Yelverton*

Saflufenacil, a new herbicide discovered by BASF, is targeted for contact and residual broadleaf weed control in select crop and non-crop areas. The extent of residual bioactivity may depend on varying soil properties. Greenhouse and laboratory experiments were conducted on 29 soils obtained from different agricultural areas of the United States to represent a wide range of soil properties. Varying rates of saflufenacil were applied preplant incorporated to each soil and then seeded with canola (*Brassica napus* L.). Fourteen days after treatment, visual ratings, fresh, and dry weights were taken and then subjected to nonlinear regression analyses to obtain effective saflufenacil doses for 50, 80, and 90% fresh weight inhibition (ED_{50}, ED_{80}, and ED_{90}). Linear correlation analyses were then performed on ED values and selected soil parameters. Saflufenacil bioactivity (ED_{90}) was highly

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correlated to organic matter (r = 0.85) and humic matter (r = 0.81) and less correlated to cation exchange capacity (r = 0.49). Saflufenacil bioactivity (ED_{50}) was negatively correlated to sand content (r = -0.32). Stepwise regression analysis indicated that organic matter, humic matter, and sand content combined are the best predictors (r^2 = 0.77) for estimating the activity of saflufenacil as related to soil properties. Therefore, saflufenacil rate adjustments for PRE and PPI applications should be made based on organic matter content and soil texture for optimal crop safety and weed control.

Nomenclature: Saflufenacil, [*N*′-[2-chloro-4-fluoro-5-(3-methyl-2,6-dioxo-4-(trifluoromethyl)-3,6-dihydro-1(2*H*)-pyrimidinyl)benzoyl]-*N*-isopropyl-*N*-methylsulfamide], canola, *Brassica napus* L.

Key words: Herbicide bioactivity, organic matter, soil properties.

Soil-applied herbicide use has recently increased as a result of herbicide resistant weeds and numerous escapes (Johnson and Gibson 2006; Ellis and Griffin 2002). A new herbicide, saflufenacil [*N*′-[2-chloro-4-fluoro-5-(3-methyl-2,6-dioxo-4-(trifluoromethyl)-3,6-dihydro-1(2*H*)-pyrimidinyl)benzoyl]-*N*-isopropyl-*N*-methylsulfamide] (Figure 1) has recently been introduced to be applied preemergence (PRE), preplant incorporated (PPI), and/or postemergence (POST) for broadleaf weed control in many crops and non-cropland areas. Saflufenacil is a moderately acidic, highly aqueous soluble herbicide with a pK_a value of 4.41 and aqueous solubility of 30 mg L^{-1} at pH 5 and 2100 mg L^{-1} at pH 7 (BASF Agricultural Products 2008).

Saflufenacil inhibits protoporphyrinogen oxidase in the chlorophyll biosynthetic pathway, and has potential for use in several crops. It controls many weeds by inhibiting protoporphyrinogen oxidase to induce massive accumulation of porphyrins and to enhance peroxidation of membrane lipids, which leads to irreversible damage of the membrane function and structure of susceptible plants (BASF Agricultural Products 2008; Duke et al. 1991). Currently, the highest use rate of saflufenacil from a market-share perspective is in field corn (*Zea mays* L.), providing season long control of troublesome and resistant broadleaf weeds such as morningglories (*Ipomoea* spp.), tall waterhemp [*Amaranthus tuberculatus* (Moq.) Sauer], giant ragweed (*Ambrosia trifida* L.), common cocklebur (*Xanthium strumarium* L.) and horseweed [*Conyza canadensis* (L.) Cronq.]. It also has potential for use in soybean [*Glycine max* (L.) Merr.] weed management, despite the possibility for saflufenacil to injure soybeans based on varietal difference in sensitivity. There is also interest for saflufenacil to be used in cereal crops, aquatic environments, trees,

nuts, vines, and rights-of-way. Understanding the behavior of saflufenacil in soil will lead to a better ability to predict rates needed for sufficient weed control and tolerance of desirable crops.

Herbicide performance may be influenced by the complex dynamic soil system. Herbicide availability in soil for uptake by plants, and thus its efficacy and subsequent performance, depends on the soil sorption capacity and the strength of affinity between the herbicide molecule and exchange sites on soil particle surfaces (Bailey and White 1970; Calvert 1980; Harper 1994; Peter and Weber 1985; Weber 1970). Many investigators have studied the effects of organic matter (OM), humic matter (HM), clay, pH, specific surface area, water holding capacity, and cation exchange capacity (CEC) on herbicide activity (Corbin et al.1971; Weber et al. 1993; Wolcott 1970; Blumhorst et al. 1990; Harrison et al. 1976;). Among these soil properties, OM was consistently the factor with the most significant affect on herbicide activity (Parochetti 1973; Rahman and Matthews 1979; Sheets et al. 1962; Stevenson 1972; Weber et al. 1987). Herbicide bioactivity has also been inversely correlated with HM and soil clay mineral content (Blumhorst et al. 1990; Harper 1994; Peter and Weber 1985; Weber 1970). Soil pH indirectly affects sorption of ionizable herbicides through its effect on the properties of particle surfaces and the herbicide (Corbin et al. 1971). Cation exchange capacity is the sum of positive charges of sorbed cations that a soil can sorb, and is directly related to OM and clay mineral content. Therefore, CEC can often be inversely correlated with herbicide bioactivity (Kerr et al. 2004).

Soil bioactivity of other acidic herbicides such as 2,4-D, oryzalin, chlorsulfuron, metsulfuron, and sulfentrazone were inversely related to OM and directly related to soil pH

(Anderson 1985; Anderson and Barrett 1985; Grey et al. 1997; Jorgensen and Hamner 1948; Kerr et al., 2004; Weber et al., 1974). Acidic herbicides are repelled by clays under neutral conditions but sorbed through physical bonding mechanisms under acidic conditions when the compounds are in the molecular form (Bailey and White 1970; Frissel and Bolt 1962;; Weber et al. 1993). For this reason, increasing soil pH causes more acidic herbicide anions to remain in soil solution and available for uptake by plants. With a pK_a value less than five, saflufenacil will be primarily in the anionic form in almost all agricultural soils, probably resulting in small pH effect on soil bioactivity.

Soil series and properties vary widely across growing regions in the United States causing herbicide rates to vary as well. Relating application rates for soil-applied compounds to soil parameters must be determined before their release for public use. The objectives of this study were (i) to examine the relationship between the bioactivity of saflufenacil and selected soil parameters and (ii) to develop a model which would allow one to calculate herbicide rate recommendations based on soil tests.

Materials and Methods

Experimental Soils. Bulk samples from the top 15 cm of 27 soils and one subsoil from different agricultural areas of the United States were collected. In addition, one soil was amended with calcium oxide (CaO) to increase pH. Soil where herbicides had been applied recently was avoided. The 29 soils used contained a broad range of OM, HM, texture, CEC, and pH (Table 1).

Soils included were: Arapahoe silt loam and sandy loam (coarse-loamy, mixed, semiactive, nonacid, thermic Typic Humaquept); Barnes loam (fine-loamy, mixed, superactive, frigid Calcic Hapludolls); Bosket silt loam (fine-loamy, mixed, active, thermic Mollic Hapludalf); three Candor loamy sands (sandy, siliceous, thermic Grossarenic Kandiudult); Dark Brown Chernozem (Typic Boroll) clay; Dothan loamy sand and sand (fine-loamy, kaolinitic, thermic Plinthic Kandiudults); Drummer silt loam, silty clay loam, and loam (fine-silty, mixed, superactive, mesic Typic Endoaquoll); two Dundee silt loams (fine-silty, mixed, active, thermic Typic Endoaqualf); Elliott silt loam (fine, illitic, mesic Aquic Argiudolls); Greenville sandy clay loam (fine, kaolinitic, thermic Rhodic Kandiudult); Grenada silt loam (fine-silty, mixed, active, thermic Oxyaquic Fraglossudalfs); three Hastings silt loams (fine, smectitic, mesic Udic Argiustolls); Loring silt loam (fine-silty, mixed, active, thermic Oxyaquic Fragiudalf); Manter sandy loam (fine, smectitic, mesic Aridic Argiustolls); Motark silt loam (coarse-silty, mixed, superactive, nonacid, mesic Oxyaquic Udifluvents); Oshtemo sandy loam (coarse-loamy, mixed, active, mesic Typic Hapludalf); Roxana silty clay loam (coarse-silty, mixed, superactive, nonacid, thermic Typic Udifluvents); Sharkey clay (very-fine, smectitic, thermic Chromic Epiaquert); Tunica clay loam (clayey over loamy, smectitic over mixed, superactive, nonacid, thermic Vertic Epia); Webster clay loam (fine-loamy, mixed, superactive, mesic Typic Endoaquolls).

Soils were characterized using standard soil analyses (Black 1965a, 1965b). Particle size was determined using a hydrometer in air-dried, sieved soil samples suspended in a sodium metaphosphate solution (Gee and Orr 2002). Percent OM was determined using a colorimetric Walkley-Black procedure (Nelson and Sommers 1982). Percent HM was

quantified by photometric determination (Mehlich 1984a). Soil pH was determined using a glass electrode and reference buffers on a 1:1 soil to water mixture (Peech 1965). Effective CEC was measured using the summation of exchangeable cations procedure described by Mehlich (1984b).

Bioactivity Determination. The experiment was conducted in a growth chamber and greenhouse with three or four replications depending on soil availability. Ten selected soils were repeated to verify repeatability of experimental conditions. Saflufenacil EC[1] and enough deionized water to bring screened, air-dried soil up to three to seven percent moisture content was added to 300 or 400 g of soil in one-quart sealed plastic bags[2]. Soil and herbicide solution was allowed to equilibrate for 24 hours. Soil was thoroughly mixed in the bag and passed through a 2-mm sieve three times to insure even distribution of the herbicide solution. Plastic cups[3] (150-ml) were filled with equal dry weights (100 g) of herbicide treated soil. Herbicide rates were established during preliminary experiments. They ranged from 0.25 to 40 g ai ha^{-1} of saflufenacil. Canola (*Brassica napus* L.) was chosen to determine bioactivity because of its extreme sensitivity to saflufenacil. Planting depth ranged from 0.6 to 1 cm depending on soil type.

Soil cups were placed in a growth chamber[4] on a 25/15 ºC temperature cycle with a 14/10 h light/dark cycle. Light was provided by overhead fluorescent bulbs (400 µmol m^{-2} s^{-1}) set on a 14-h photoperiod. Humidity was maintained at 80% to avoid rapid drying of soils during plant germination. Following emergence, plants were placed in a greenhouse with average day/night temperatures of 32/24 ºC. Natural daylight was supplemented with

300 μmol m^{-2} s^{-1} illumination at canopy level provided by high-pressure sodium lamps for a 14-h photoperiod. Soil cups were watered daily after removal from the growth chamber to maintain a moist soil environment for optimal growth on each soil type. Visual percent control, aboveground and belowground plant weights (fresh and dry) were recorded 14 days after treatment as indices of plant growth, with total plant fresh weight being chosen as the best bioassay measurement.

Data Analyses. Saflufenacil ED_{50}, ED_{80}, and ED_{90}'s (effective saflufenacil dose required to inhibit total plant fresh weight by 50, 80, or 90%) were derived through curve fitting using the program 'R' (R Development Core Team 2006; Knezevic et al. 2007; Ritz and Streibig 2005). Using a three-parameter log logistic {Y = d / (1 + exp b(log(x) – log(e)))}, three-parameter Weibull {Y = d exp(- exp(b(log(x) – e)))}, or Brian-Cousens [Y = c + {(d + fx – c) / (1 + exp(b(log(x) – log(e))))}] model, a regression equation was determined which related plant response to herbicide concentration (Brian and Cousens 1989; Streibig et al. 1993; Seefeldt et al. 1995; Schabenberger et al. 1999). The equations were utilized where the coefficient of determination (r^2) was equal to or greater than 0.90.

The relationship between the ED_{50}, ED_{80}, and ED_{90} values and the physical and chemical properties of the soils were evaluated through correlation analysis. By comparing Pearson correlation coefficients (r) generated using SAS[5], those soil factors contributing most to the variation in the phytotoxic behavior of the herbicide in the soil were identified. Further evaluation of the influence of the soil properties on phytotoxicity was made through linear and multiple stepwise regression analyses. The principle purpose of these statistical

treatments was to derive a suitable regression model that would best predict the phytotoxic behavior of saflufenacil in the soil.

Results and Discussion

The variable soils and range of saflufenacil provided a unique study system for examining the associations between soil properties and herbicide efficacy (Table 1). There were high correlations among soil properties, with OM, HM, and CEC being the most related to each other indicated by having the highest Pearson correlation coefficients (Table 2). As expected CEC was inversely related to sand content (r = -0.55) and positively related to clay content (r = 0.73) and OM (r = 0.64). Organic matter and HM were also highly correlated (r = 0.83), indicating a close relationship between these soil properties.

Saflufenacil soil bioactivity was measured and correlated at three levels, ED_{50}, ED_{80}, and ED_{90} to insure consistency and accuracy of data, and determine the additional saflufenacil needed to increase efficacy on individual soils (Table 1). In general, saflufenacil rates required for 50, 80, and 90% canola inhibition generally increased as OM and HM contents of soils increased and sand content decreased (Table 1 and 3). Correlation values were highest for OM (r = 0.85) and HM (r = 0.81) when ED_{90} values were compared. Correlation analysis with ED_{50} and ED_{80} values resulted in lower correlation coefficients for OM and HM due to less difference between ED values among soils. Although correlations also were observed between plant response and sand content, these were usually smaller (Table 3). No clear associations were observed between plant response and soil pH;

however, this is likely the result of OM overshadowing the effects of soil pH. As saflufenacil becomes predominantly anionic in soil solution pH above its pK_a (4.41), it is repelled by negatively charged soil particles resulting in greater herbicide concentration in soil solution. When all other soil properties are held constant and soil pH is adjusted, ED_{90} values differed greatly. Using CaO, soil pH in the Candor loamy sand was raised from 4.9 to 6.5. This resulted in higher saflufenacil soil bioactivity as indicated by ED_{90} values decreasing from 9.7 to 4.9 g ai ha^{-1} (Table 1).

Because of the relationships between ED_{50}, ED_{80}, and ED_{90} values and several of the soil properties and the intercorrelations among the soil properties, it was logical to perform multiple regression analyses involving all soil properties into one equation [y = f(OM + HM + CEC + pH + sand + clay)]. This analysis did account for variability over OM alone (R^2 = 0.69), but including other selected soil properties improved fit, so the two best-fit equations using ED_{90} values were selected to be used for calculating herbicide rates (Table 4, Figure 2). The best predictive model with an R^2 = 0.77, incorporated OM, HM, and sand into the equation (Table 4). Residuals were also examined for any particular patterns, but none were apparent, probably because OM and HM were highly related to one another and CEC and pH were capacity and reactivity measurements, respectively, which were related to the two soil constituents.

Predicted rates for 90% canola fresh weight inhibition based on either percent HM or OM for all soils used in this study were very similar (Table 4). Using the model with the highest R^2, Saflufenacil predicted rates ranged from 4.7 to 34.6 g ai ha^{-1} and were in agreement with projected labeled rates, which range from 25 to 125 g ai ha^{-1} based on soil

texture and OM content (data not shown) (BASF Agricultural Products 2008). Rate adjustments based on these soil properties is necessary to achieve sufficient efficacy without causing significant crop injury. Herbicide rates calculated with equations based on soil parameters were in the range of recommended field rates, but were generally substantially lower, except for soils high in OM (> 5%). Canola is extremely sensitive to saflufenacil, and therefore, resulted in low rate estimates for bioactivity in all soils. Variation in sensitivity of other crops and weeds to saflufenacil would probably change rate estimates, but bioactivity relationship to soil properties would remain similar.

Several reasons may explain the correlation between saflufenacil ED values and soil properties. Plant available herbicide concentration may have varied across the soils as a function of soil properties previously discussed. Sorption of saflufenacil increased with increasing OM and HM (Hixson et al. 2008, unpublished data). Thus, soils with higher OM and HM have a higher affinity for saflufenacil, and therefore, less herbicide is available for plant uptake. In addition, the plant-available herbicide concentration may have increased with soil particle size. Results of the gravimetric water content analyses indicated cups with coarse textured soils had approximately one-half the water content of fine-textured soils (data not shown). All else being equal, reducing water content by half would double the concentration of herbicide in soil water solution. For this reason, potential for saflufenacil activity in plants may be further influenced by soil texture. Highest saflufenacil bioactivity occurred in coarse textured, low OM (< 1.5%) soils, and lowest bioavailability occurred in high OM (> 4%) soils regardless of texture. Therefore, application rates for saflufenacil should be adjusted corresponding to both OM content and soil textural class. The predictive

equations presented here need to be tested at a variety of field locations, and depending on crop and weed species sensitivity some refinement will be required.

Calculated rates were derived under controlled conditions in the growth chamber and greenhouse where conditions were optimal for plant growth and herbicide activity. Results from experiments in climate controlled situations can be difficult to extrapolate to field conditions. These experiments were conducted to establish a confident relationship between soil parameters and bioactivity of saflufenacil. Under field conditions, projected labeled rates are based to some extent on maximizing long term residual and economical weed control. Herbicide losses, which may lead to weed control failure, would be affected to the greatest degree on coarse-textured soils with low OM. Use of the herbicide rate equations would provide considerable savings in most cases when using saflufenacil, and still provide acceptable weed control and reduce the herbicide load to the environment. The equations need to be further tested under field conditions at a variety of locations, and some additional adjustments may be needed. Future research combined with research presented herein could be utilized to create a correction factor relating soil properties to the amount of saflufenacil in contact with the plant.

Sources of Materials

[1] Saflufenacil, BASF Corporation, Agricultural Products Division, 26 Davis Drive, Research Triangle Park, NC 27609.

[2] Ziploc® plastic bags, quart size, S.C. Johnson & Son, Inc., 1525 Howe Street, Racine, WI 53403.

[3] Dixie® clear plastic PETE cups, 5 oz. size, Georgia-Pacific Corporation, 133 Peachtree Street, N.E., Atlanta, GA 30303.

[4] Conviron® reach-in growth chamber, Controlled Environments Limited, 590 Berry Street, Winnipeg, Manitoba Canada, R3H 0R9.

[5] SAS, Statistical Analysis Systems, 2003, Release 9.1, Statistical Analysis Systems Institute, Cary, NC 27513.

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Table 1. Soil properties of 0-15-cm-deep soil samples from each site.[a]

Series	State/Province	Tex.[i]	OM[b]	HM[c]	Sand[d]	Silt[d]	Clay[d]	CEC[e]	BD[f]	pH[g]	ED_{50}[h]	ED_{80}[h]	ED_{90}[h]
			%					$cmol\ kg^{-1}$	$g\ cm^{-3}$	1:1	$g\ ai\ ha^{-1}$		
Arapahoe	NC	SiL	4.6	2.85	30	58	12	15.0	0.92	4.9	12.8 (1.2)	19.6 (1.8)	25.1 (3.3)
Arapahoe	NC	SL	8.3	7.55	66	22	12	16.1	0.98	5.4	11.2 (2.3)	22.5 (4.6)	33.7 (6.9)
Barnes	ND	L	3.1	2.54	40	38	22	17.1	1.18	5.6	11.5 (0.6)	15.2 (0.8)	17.8 (0.9)
Bosket	MS	SiL	1.1	0.52	31	57	12	6.7	1.26	6.0	5.5 (0.4)	9.4 (0.6)	12.8 (0.8)
Candor	NC	LS	2.2	1.93	80	12	8	5.2	1.41	4.9	5.4 (0.2)	7.8 (0.3)	9.7 (0.4)
Candor	NC	LS	2.2	1.35	80	12	8	7.3	1.47	6.5	3.1 (0.2)	4.1 (0.4)	4.9 (0.7)
Candor	NC	LS	0.9	0.40	86	6	8	2.4	1.47	4.7	3.2 (0.2)	4.7 (0.4)	5.9 (0.5)
Chernozem	SK[j]	C	3.3	0.14	24	24	52	27.4	1.10	7.6	6.9 (0.3)	9.7 (0.5)	11.9 (0.6)
Dothan	GA	LS	1.1	1.11	81	13	6	2.8	1.57	6.7	1.1 (0.1)	2.3 (0.3)	3.4 (0.4)
Dothan	GA	S	1.0	0.50	88	4	8	2.7	1.56	5.8	4.3 (0.5)	5.1 (0.6)	5.7 (0.6)
Drummer	IL	SiL	3.1	2.75	20	54	26	18.3	1.20	5.9	17.3 (1.2)	21.8 (1.5)	25.0 (1.7)
Drummer	IL	SiCL	5.3	3.64	13	59	28	24.9	1.21	6.5	18.7 (1.3)	23.5 (1.7)	26.9 (1.9)
Drummer	IL	L	3.9	0.77	36	44	20	22.7	1.17	6.4	6.5 (0.2)	7.9 (0.3)	8.9 (0.3)
Dundee	MS	SiL	1.0	0.35	36	56	8	10.2	1.28	5.6	4.9 (0.5)	7.6 (0.8)	9.8 (1.1)
Dundee	LA	SiL	1.5	0.99	30	58	12	14.2	1.15	5.1	6.8 (0.7)	9.4 (1.2)	11.3 (2.0)
Elliott	IL	SiL	4.5	3.77	20	58	22	14.8	1.12	5.6	8.8 (1.0)	14.8 (1.6)	20.0 (2.2)
Greenville	GA	SCL	1.3	0.35	60	12	28	3.1	1.29	6.4	3.3 (0.4)	5.2 (0.6)	6.8 (0.7)

Table 1. (continued)

Series	State/Province	Tex. [h]	OM [b]	HM [c]	Sand [d]	Silt [d]	Clay [d]	CEC [e]	BD [f]	pH [g]	ED_{50}	ED_{80}	ED_{90}
			%					$cmol\ kg^{-1}$	$g\ cm^{-3}$	1:1	$g\ ai\ ha^{-1}$		
Grenada	TN	SiL	2.0	0.35	6	70	24	14.2	1.28	6.1	4.4 (0.4)	6.2 (0.6)	7.7 (0.7)
Hastings	NE	SiL	3.0	0.78	16	62	22	13.3	1.10	7.5	9.3 (0.7)	14.3 (1.0)	18.5 (1.3)
Hastings	NE	SiL	3.0	3.60	10	66	24	18.6	1.13	5.2	6.4 (0.5)	9.5 (0.8)	11.9 (1.0)
Hastings	NE	SiL	3.3	2.17	10	66	24	15.2	1.12	6.0	5.6 (0.4)	8.9 (0.6)	11.7 (0.7)
Loring	TN	SiL	1.3	0.26	24	64	12	6.9	1.19	5.5	4.6 (0.4)	6.5 (0.6)	8.0 (0.7)
Manter	KS	SL	1.8	0.33	77	13	10	6.7	1.48	7.4	4.3 (0.3)	6.9 (0.4)	9.0 (0.5)
Motark	MO	SiL	1.6	0.33	16	68	16	10.8	1.23	7.5	7.9 (0.3)	9.4 (0.4)	10.4 (0.4)
Oshtemo	MI	SL	1.6	0.79	72	20	8	3.3	1.54	5.8	1.6 (0.2)	4.1 (0.5)	7.1 (0.9)
Roxana	AR	SiCL	1.5	0.64	6	66	28	13.7	1.26	6.3	4.3 (0.2)	5.5 (0.3)	6.2 (0.3
Sharkey	MS	C	2.1	0.49	9	29	62	29.4	1.20	6.8	5.4 (0.3)	8.6 (0.4)	11.3 (0.6)
Tunica	MS	CL	1.4	0.40	34	32	34	19.7	1.24	6.7	4.9 (0.1)	5.9 (0.2)	6.6 (0.2)
Webster	MN	CL	4.5	2.35	28	44	28	22.3	1.06	5.8	6.4 (0.6)	12.0 (1.2)	17.3 (1.7)

[a] Abbreviations: OM, organic matter; HM, humic matter; CEC, cation exchange capacity; BD, bulk density; ED, effective dose; C, clay; L, loam; S, sand; Si, silt.

[b] Organic matter was determined using the Walkley-Black procedure (Nelson and Sommers 1982).

[c] Humic matter was determined by photometric determination (Mehlich 1984b).

Table 1. (continued)

[d] Particle analysis was determined using the hydrometer method (Gee and Orr 2002).

[e] Cation-exchange capacity was determined using the summation of exchangeable cations procedure (Mehlich 1984a).

[f] pH was determined using a 1:1 soil:distilled water ratio (Peech 1965).

[g] Bulk density was determined by weighing one cm^3 of disturbed soil (g cm^{-3}).

[h] Values in parentheses are standard error.

[i] Soil texture

[j] Saskatchewan, Canada.

Table 2. Pearson correlation coefficients (*r*) among soil properties.[a,b]

Properties	Silt	Clay	OM	HM	CEC	pH
Sand	-0.93***	-0.56**	-0.22	-0.06	-0.55**	-0.15
Silt		0.23	0.13	0.08	0.33*	-0.02
Clay			0.29	-0.03	0.73***	0.43**
OM				0.83***	0.64***	-0.06
HM					0.31	-0.31
CEC						0.26

[a] Abbreviations: OM, organic matter; HM, humic matter; CEC, cation exchange capacity

[b] Significance at *10%, **5%, ***1% levels of probability, respectively.

Table 3. Pearson correlation coefficients (*r*) between saflufenacil rates required for 50, 80, and 90% canola growth inhibition (ED_{50}, ED_{80}, and ED_{90}) values on selected soil properties.[a,b]

Soil Property	ED_{50}	ED_{80}	ED_{90}
Sand	-0.33*	-0.29	-0.25
Silt	0.28	0.26	0.23
Clay	0.22	0.17	0.13
OM	0.64***	0.79***	0.85***
HM	0.59***	0.74***	0.81***
CEC	0.55**	0.53***	0.49***
pH	-0.04	-0.12	-0.16

[a] Abbreviations: OM, organic matter; HM, humic matter; CEC, cation exchange capacity; ED, effective dose

[b] Significance at *10%, **5%, ***1% levels of probability, respectively.

Table 4. Herbicide rate equations for 90% canola growth inhibition and coefficients of determination (R^2) based on organic matter (OM), sand, and clay content of soils.[a]

R^2	Rate equation for 90% growth inhibition
0.66	ED_{90} = 6.96 + 3.7 HM (%)
0.73	ED_{90} = 2.47 + 3.8 OM (%)
0.75	ED_{90} = 3.46 + 2.65 OM (%) + 1.40 HM (%)
0.77	ED_{90} = 5.56 + 2.30 OM (%) + 1.68 HM (%) – 0.04 sand (%)

[a] Abbreviations: ED, effective dose; OM, organic matter; HM, humic matter

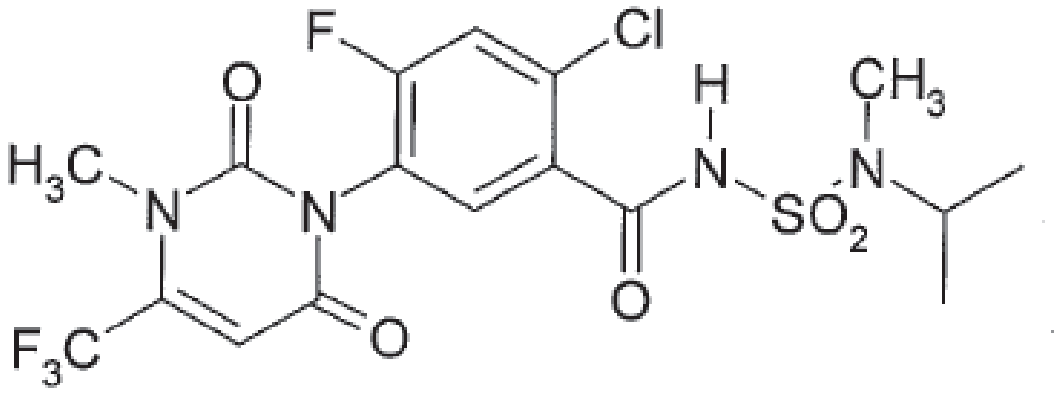

Figure 1. Chemical structure of saflufenacil.

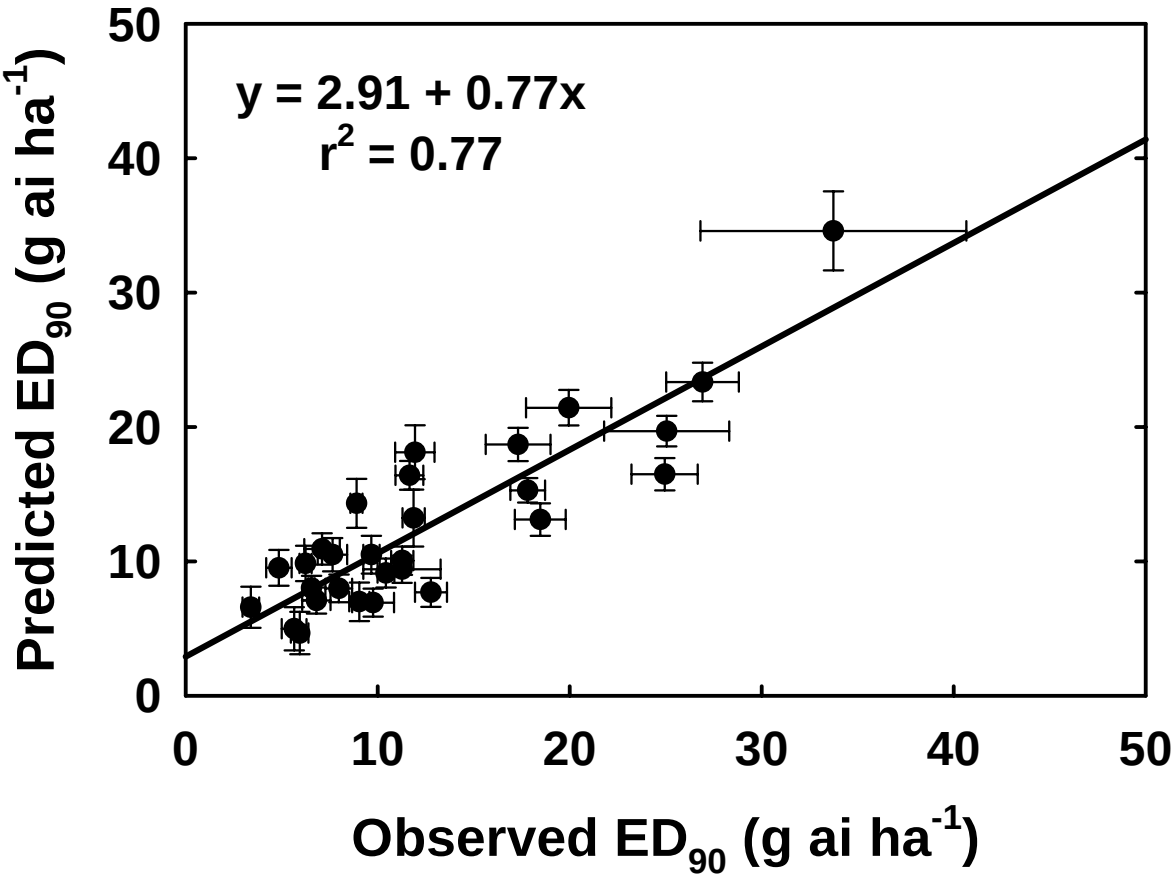

Figure 2. Plot of observed rates of saflufenacil needed to achieve 90% canola fresh weight inhibition compared to rates predicted by the highest ranking model created [ED_{90} = 5.56 + 2.30 OM (%) + 1.68 HM (%) – 0.04 sand (%)].

WASH-OFF OF SAFLUFENACIL AND OTHER HERBICIDES FROM CROP RESIDUES

(Formatted for submission to Agronomy Journal)

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Abbreviations: TPW, theoretical percent wash-off; WG, wettable granule; SC, suspension concentrate.

ABSTRACT: At the time of preemergence herbicide application, a combination of crop residue, weeds, and/or cover crops can nearly cover the soil surface in no-till and reduced till cropping systems and certain orchard/grove management systems. A high percentage of an applied herbicide can be intercepted, depending on crop residue and vegetation type and percent coverage. Herbicides are usually washed from residues by rainfall, but the quantity reaching the soil surface is dependent upon amount and timing. The amount of herbicide that washes from crop residue is also dependent on the type of residue and the physicochemical properties of the herbicide. Therefore, wash-off characteristics of saflufenacil, mesotrione, isoxaflutole, oxyfluorfen and flumioxazin from sweet almond, sweet orange, wheat, soybean, and corn under simulated rainfall (32, 64, and 128 mm) on two soils (Candor loamy sand and Drummer loam) were determined. A bioassay greenhouse experiment was performed in which percent growth inhibition of canola was used to determine ability of herbicides to wash-off crop residues. A laboratory experiment was also performed to provide an analytical evaluation of saflufenacil wash-off from the same crop residues and simulated rainfalls. In the Candor loamy sand, saflufenacil WG and saflufenacil SC easily washed off all crop residues with a majority (≈ 80%) of the two formulations washed off with the first 32 mm of simulated rainfall. The laboratory experiment results support this finding. Relationships between herbicides were similar on the Drummer loam, but wash-off was more related to increasing rainfall amounts. In general, sweet almond = sweet orange > wheat = soybean > corn in wash-off ability across all herbicides. Among herbicides, saflufenacil > mesotrione > isoxaflutole > oxyfluorfen > flumioxazin in wash-off ability across all crop residues. Wash-

off appears to be positively correlated with the water solubility of the herbicide. From these results, crop residues could impede the ability of some preemergence herbicides to reach soil.

Ideally, preemergence herbicide applications would be applied in a manner such that 100 percent always comes into direct contact with the soil surface. With the increasing adoption of no-till and reduced till cropping systems, crop residues remaining on the soil surface from year to year have increased resulting in reduced amounts of herbicide actually reaching the soil surface. Several studies on best management practices have shown distinct advantages of minimum or no-tillage systems (Banks and Robinson 1982; Dao 1991, 1995). Plant residue left on the soil surface reduces soil erosion as well as nutrient and pesticide loss in runoff, conserves soil moisture, and may also offer other benefits such as improved physical properties of soil, increased soil organic carbon (Blevins and Frye 1993), and enhanced microbial populations and soil enzyme activities (Wagner et al. 1995). Plant residues suppress weed germination and emergence of many weeds (Liebl et al. 1992; Teasdale et al. 1991; Teasdale and Daughtry 1993) by altering the light, temperature, and moisture conditions under the mulch (Teasdale and Mohler 1993). Small grain and legume residues have been shown to release allelochemicals that suppress germination and growth of weed species (Putnam 1988; White et al. 1989).

Positive effects of plant residue on weed suppression, however, are typically insufficient for adequate weed control. Therefore, many no-till and reduced till growers apply preemergence and postemergence herbicides to achieve acceptable weed control. As much as 80% of an applied herbicide can be intercepted, depending on crop residue and vegetation type and percent coverage (Isensee et al. 1998; Teasdale and Daughtry 1993). Since a portion of applied herbicide is intercepted by the residue (Banks and Robinson 1982; 1986), this fraction must be washed off the residue before it can contact the soil where it is

effective. Herbicides are usually washed from residues where the quantity reaching the soil surface is dependent upon the amount and timing of the rainfall and/or irrigation. The amount of herbicide that washes from plant residue is also dependent on the type of residue. Herbicide wash-off is generally greater from dead tissue resulting from a burndown treatment than living tissue (Isensee et al. 1998; Teasdale and Daughtry 1993). A large portion of preemergence herbicide is intercepted by the weed or cover crop residues, and the extent of herbicide washed from residues into soil by precipitation depends on many factors, e.g. formulation, herbicide chemical properties, plant species, plant uptake and retention to plant foliage (Reddy et al. 1995a; Reddy and Locke 1996).

Plant residues often form nearly impenetrable mats covering a large proportion of the soil surface area and have a strong affinity for retaining herbicides (Banks and Robinson 1986; Ghadiri et al. 1984; Reddy et al. 1995b; Reddy and Locke 1996). Depending on how strongly the intercepted herbicide is retained by the residue, wash-off may be slow. An advantage to herbicide interception by crop residues is the continued slow-release and increased efficiency of these herbicides leading to a potential reduction in postemergence chemical inputs. The gradual herbicide desorption from the straw mulch may provide extended control of second flushes of weed emergence and growth (Dao 1991). Research on corn and wheat has shown the crop residue is capable of greater retention of applied chemicals when compared with the soil surface layer (Boyd et al. 1990; Dao 1995). Herbicide binding can be weak or strong depending on the type and degree of decomposition of cover crop residue. Increased herbicide retention by plant residue not only reduces the amount reaching the soil (affecting weed control) but also prolongs herbicide persistence.

Saflufenacil, a new herbicide, has recently been introduced to be applied preemergence (PRE) and/or postemergence (POST) for broadleaf weed control in many crops and non-cropland areas. Saflufenacil is a moderately acidic (pK_a = 4.41), highly aqueous soluble herbicide (K_s = 2100 mg L^{-1} at pH 7) (Table 1). It controls many weeds by inhibiting protoporphyrinogen oxidase to induce massive accumulation of porphyrins and to enhance peroxidation of membrane lipids, which leads to irreversible damage of the membrane function and structure of susceptible plants (BASF Agricultural Products 2008; Duke et al. 1991).

The objective of this study was to evaluate the influence of crop residue type and rainfall amount on wash-off and efficacy of saflufenacil and other herbicides with varying physiochemical properties. Two separate experiments were performed (i) Bioassay greenhouse experiment involving two soils, five crop residues, and five herbicides and (ii) Laboratory experiment with saflufenacil where wash-off water samples were analyzed after differing amounts of rainfall were applied to treated crop residues. Information produced would be essential for determining proper use pattern and expected efficacy of saflufenacil in no-till and reduced tillage cropping systems and orchard/grove management systems where tree clippings and shredded mulch remain on the soil surface.

MATERIALS AND METHODS

Greenhouse Experiment

Experimental Soils. The soils used in this study were Candor loamy sand (sandy, siliceous, thermic Grossarenic Kandiudult) and a Drummer loam (fine-silty, mixed, superactive, mesic Typic Endoaquoll). Particle size was determined by the hydrometer method (Gee and Orr 2002). Soil pH was determined using a glass electrode and reference buffers on a 1:1 soil to water mixture (Peech 1965). Effective cation-exchange capacity (CEC) was measured using the summation of exchangeable cations procedure described by Mehlich (1984). Percent soil organic matter (OM) was determined using a colorimetric Walkley-Black procedure (Nelson and Sommers 1982).

Soils were air-dried and passed through a 4-mm sieve. The sieved soils were then added to 10-cm square pots to which ten canola seeds per pot were planted 7.5 mm deep. Canola, a sensitive species to all the herbicides used in this study, was used as a bioassay indicator to determine ability of herbicides to wash-off crop residues.

Crop Residues. Wheat, field corn, soybean, sweet almond, and sweet orange residues were collected from the field following the growing season and air-dried for at least two months. Once dry, all residues were shredded or cut to a size small enough to fit on the soil surface of the seeded 10-cm square pots. Residue amount per pot was determined by 100% visual coverage and repeated on subsequent pots by weight. Residue amounts were equivalent to: wheat = 3,390 kg ha^{-1}; soybean = 6,297 kg ha^{-1}; corn = 9,202 kg ha^{-1}; sweet almond = 43,592

kg ha^{-1}; sweet orange = 14,531 kg ha^{-1}. Bare soil pots were also used as a treatment comparison.

Herbicides. Two separate bioassay greenhouse experiments were performed. In the first experiment, two saflufenacil formulations (water dispersible granule, WG; suspension concentrate, SC) at 6 g ai ha^{-1}, mesotrione as CALLISTO® at 20 g ai ha^{-1} and oxyfluorfen as GOAL® at 0.9 kg ai ha^{-1} were compared in the Candor loamy sand (Table 1). A subsequent experiment compared these four herbicides plus flumioxazin as VALOR® at 25 g ai ha^{-1} and isoxaflutole[5] as BALANCE PRO® at 25 g ai ha^{-1} in the Drummer loam (Table 1). Herbicides were applied to all the pots using a single nozzle research track sprayer equipped with an 8003-E even flat-fan nozzle at 276 kPa with a spray volume of 374 L ha^{-1}. Herbicide rates were determined by preliminary experiments in which preemergence applications were made to bare soil. The rate of each herbicide that provided approximately 80% growth inhibition of canola at 12 days after treatment was chosen.

Bioassay Wash-off. After the herbicides were applied to the crop residues, simulated rainfall at 32, 64 and 128 mm was applied using the single nozzle research track sprayer equipped with an 8003-E even flat-fan nozzle. The simulated rainfall was applied approximately two hours following herbicide application when herbicide droplets were not visible on the crop residues. After the simulated rainfall was applied, the crop residues were allowed to dry. The air-dried crop residues were then removed from the pots. All the pots were then moved to the greenhouse and watered overhead as needed to maintain plant growth. The greenhouse

was set with day/night temperatures of 27/22 °C and ambient relative humidity. Supplemental lighting (80 μmol m^{-2} s^{-1}) provided a 14-h photoperiod. A modified Hoagland's nutrient solution was applied one day following germination and seven days later. To make comparisons between crop residues, herbicides, and rainfall amounts, visual percent growth inhibition of canola at 12 days after treatment was compared to bare soil treatments.

Data Analyses. The two greenhouse experiments consisted of a factorial design with five (residues) × four (herbicides) × three (simulated rainfalls) for the Candor loamy sand and five (residues) × six (herbicides) × three (simulated rainfalls) for the Drummer loam with three single-pot replicates for each treatment. The Candor loamy sand experiment was performed twice and four of the six herbicides were repeated for a third time on the Drummer loam soil. Data for each experiment were transformed to theoretical percent wash-off (TPW) relative to bare soil treatments using equation:

$$TPW = \left[\left(\frac{\%\ canola\ \ inhibition\ with\ crop\ residue}{\%\ canola\ \ inhibition\ on\ bare\ soil}\right)\right] \times 100 \qquad [1]$$

The bare soil treatment was not included in the analysis because transforming the data to TPW relative to the bare soil treatment would set the bare soil treatment to 100%. Higher values indicate more wash-off from crop residues as there is a greater difference between crop residue and bare soil treatments.

Data were tested for homogeneity of variance by plotting residuals. An arc-sin square root transformation did not improve homogeneity, so non-transformed data were used in analysis and presentation for clarity. Analyses of variance (ANOVA) were performed using a General Linear Models procedure (Proc GLM) of SAS, and sums of squares were partitioned to evaluate the effect of crop residue, simulated rainfall, herbicide, and greenhouse trials using error partitioning appropriate to a factorial treatment analysis. Study repetition was considered a random variable, and main effects and interactions were tested by the appropriate mean square associated with the random variable. Means were separated with the appropriate Fisher's protected LSD test at P = 0.05.

Laboratory Experiment

Analytical Wash-off. A laboratory experiment was performed with the SC formulation of saflufenacil. All crop residues were prepared as previously explained and enough of each residue was placed on 13-cm-diam. Büchner funnels to achieve 100% visual coverage. Similar to the greenhouse experiment, saflufenacil and simulated rainfall were applied using the same single nozzle research track sprayer. Büchner funnels were suspended above 250-ml Erlenmeyer flasks using a wooden frame. Saflufenacil was applied such that 113 µg of saflufenacil was sprayed onto each crop residue. Following a two hour drying period, 32, 64, and 127 mm of simulated rainfall was applied. Wash-off water samples were collected for each rainfall increment and immediately transferred to 20-ml scintillation vials and refrigerated at 4 °C until analysis. Before analysis, particulate material was filtered out using an Acrodisc syringe filter fitted with a 45 µm PTFE membrane.

Saflufenacil concentrations in the water samples were detected by HPLC-MS/MS. Parent saflufenacil was quantified using a Perkin Elmer series 200 micro pumps + Perkin Elmer 200 Series Auto Sampler HPLC system coupled to a PE Sciex API 3000 Mass Spectrometer MS/MS system with Electrospray, positive ionization, source temperature: 400 °C. The analytical column for the HPLC was a Betasil C18 (100 mm x 2.0 mm, 5μm). The sample injection volume was 20 μL. The mobile phases were as follows: A, Water with 0.1% formic acid and 4 mM ammonium formate, and B, Methanol with 0.1% formic acid and 4 mM ammonium formate. The HPLC method used a five minute gradient with the flow rate of 300 μL min^{-1}. The MS/MS transition used for integrations was 501.0/459.0. Quantitation of saflufenacil was achieved using external standard calibration curves.

Data Analyses. The laboratory experiment consisted of a factorial design with five crop residues × three simulated rainfall amounts. Treatments were replicated twice and the entire experiment was repeated. Data were transformed to percent of applied by comparing to saflufenacil concentration in stock solution. Data were tested for homogeneity of variance by plotting residuals. Statistical analyses were performed using SAS and graphs were generated using SigmaPlot 10. Analysis of variance (ANOVA) was performed using a General Linear Models procedure (Proc GLM) of SAS, and sums of squares were partitioned to evaluate the effect of crop residue and simulated rainfall using error partitioning appropriate to a factorial treatment analysis. Standard errors were calculated and presented in bar graphs.

RESULTS AND DISCUSSION

Greenhouse Experiments

Analysis of variance revealed no significant treatment by trial interaction and error variances were homogeneous; consequently, data were combined over time for analysis and presentation. Herbicide, crop residue, and simulated rainfall main effects were strongly significant in all experiments, but herbicide × simulated rainfall and herbicide × crop residue interactions were present. Therefore data are presented for these interactions. Means were separated with the appropriate Fisher's protected LSD test at P = 0.05.

Candor loamy sand Bioassay. Soil particle size analysis and the Walkley-Black procedure revealed that the Candor loamy sand consisted of 80% sand, 12% silt, 8% clay and 2.2% OM. Other soil properties measured were soil pH (6.5) and CEC (7.3 cmol kg^{-1}). Averaged across residue types, the majority of both saflufenacil formulations and mesotrione washed off from all residues with 32 mm of simulated rainfall (Table 2). Crop residues significantly reduced wash-off of oxyfluorfen at all simulated rainfall amounts with TPW ranging from 20 to 28%. As reflected by higher TPW, increasing rainfall resulted in more wash-off of mesotrione and saflufenacil WG (Table 2). The little difference in TPW among rainfall amounts for saflufenacil and mesotrione are probably due to the herbicides leaching below the seed zone from the higher amounts of rainfall. This occurrence resulted in TPW being similar to those at lower rainfall amounts. Mesotrione and saflufenacil leaching below the seed zone was indicated by lower percent growth inhibition after 128 mm of rainfall (Table

3). For example, percent growth inhibition in bare soil significantly decreased from 90 to 52% for saflufenacil SC when simulated rainfall amount increased from 32 to 128 mm (Table 3). This deviation from the targeted 80% growth inhibition in bare soil could have been caused by the high water solubility of both herbicides combined with the coarse textured soil.

Averaged across simulated rainfalls, corn reduced wash-off greater than all other residues for saflufenacil (Table 4). Again, oxyfluorfen had the lowest TPW for all crop residues tested. Higher wash-off for all herbicides was associated with the sweet almond residue, with significant differences occurring for mesotrione and oxyfluorfen. Higher wash-off was probably due to the physical composition of the residue. With more branches and waxy leaf material associated with the sweet almond residue there is less opportunity for sorption of water and herbicides. In addition, 100% visual coverage was difficult to achieve with the sweet almond residue allowing openings for the original spray solution to make contact with the soil surface before simulated rainfall occurred. Although similar weights of each crop residue were used for each replicated treatment, the heterogeneity (stems, leaves, seed pods, cobs, etc.) of all five crop residues caused data to be variable. This heterogeneity, coupled with leaching of the highly water soluble herbicides, may have led to the lack of difference among simulated rainfall treatments (Table 2). Therefore, a second experiment was performed with a fine textured, high organic matter soil (Drummer loam) to prevent variability due to herbicide leaching below the seed zone.

Drummer loam Bioassay. Soil analyses showed that the Drummer loam consisted of 36% sand, 44% silt, 20% clay, and 3.9% OM with a soil pH = 6.4, and a CEC = 22.7 cmol kg^{-1}.

Averaged across residue types, both saflufenacil formulations easily washed off the residues by the simulated rainfall (Table 5). Even with the lowest simulated rainfall amount (32 mm), saflufenacil SC and WG washed off significantly more compared to the other herbicides. At this lowest simulated rainfall, mesotrione > isoxaflutole = oxyfluorfen > flumioxazin in the theoretical amounts washed off the residues. Initially, flumioxazin did not wash off as well with 2 TPW after 32 mm of simulated rainfall, but was similar to oxyfluorfen with higher rainfall amounts. The VALOR® label suggests reduced efficacy when applications are intercepted by plant residues, and is verified by our research. In general, increased simulated rainfall resulted in greater herbicide wash-off, but rarely demonstrated a consistent statistical difference between single increments in rainfall amounts. Isoxaflutole, mesotrione, flumioxazin and both saflufenacil formulations had a significant change in TPW when rainfall increased from 32 to 128 mm (Table 5). Isoxaflutole was the only herbicide to demonstrate increased wash-off with each rainfall amount.

Among crop residues, wash-off appears to be positively correlated with the water solubility of the herbicide (Table 1). Again, corn consistently reduced herbicide wash-off greater than most other residues for both saflufenacil formulations and mesotrione (Table 6). Oxyfluorfen and flumioxazin had the lowest TPW for all crop residues tested except sweet almond. Similar to the Candor loamy sand experiment, consistently higher TPW for all herbicides was associated with sweet almond residue. In general, saflufenacil wash-off from crop residues as greatest to least: sweet almond = sweet orange > wheat > corn = soybean. Waxy surfaces associated with sweet almond, sweet orange and wheat residues seem to contribute to more wash-off of saflufenacil. From these results, depending on herbicide

properties, crop residues remaining on the soil surface from conservation tillage or orchard/grove management practices, could significantly impede the ability of preemergence herbicides to reach soil and targeted weeds.

Analytical Saflufenacil Wash-Off

A follow-up experiment was performed using crop residues and saflufenacil SC to support results from the bioassay experiments. Again, analyses of variance revealed no significant treatment by trial interaction and error variances were homogeneous; consequently, data were combined over time for analysis and presentation. Crop residue and simulated rainfall main effects were strongly significant in all experiments. Means were separated with the appropriate Fisher's protected LSD test at $P = 0.05$.

Averaged across residue types, increasing simulated rainfall increased the amount of saflufenacil and total water recovered when compared to the no residue treatments (Fig. 1). Approximately 51% of the applied saflufenacil was washed-off residues with the first 32 mm of simulated rainfall. Increasing the simulated rainfall resulted in higher amounts of saflufenacil washed off with 69 and 79% of the applied at 64 and 128 mm rainfall (Fig. 1).

The amount of water absorbed by the residues measured as a percentage of the no residue treatment showed differences between rainfall amounts. A majority of the water the residue absorbed occurred with the first 32 mm of rainfall. Sixty-four percent of the water applied to the residues leached through the residues with 32 mm of rainfall. In other words, 36% of the water applied was absorbed by the residues. As expected, as more rainfall was applied, less water absorption occurred because the residues were near or already saturated.

Water absorption by the residues may help to explain the inconsistent results found in the first bioassay study with the coarse loamy sand. With the residues impeding a portion of the water from coming in contact with the soil, there was less opportunity for leaching through the soil compared to the no residue treatments.

Across all rainfall amounts, the percent of saflufenacil washed off the residues was similar (Fig. 2). Only soybean and almond were significantly different in the level of saflufenacil washed off (52% vs. 70%, respectively). Wheat, corn, citrus and almond were all equal in the amount of saflufenacil washed off. Percent of simulated rainfall collected followed a similar pattern to saflufenacil. Soybean and corn residues absorbed more water than the other three residues, allowing less water to pass through the residues (Fig. 2). Less water and less saflufenacil washing off corn and soybean residues was reflected in the bioassay experiments, as these residues resulted in the greatest reduction in TPW. All residues retained at least 15% of the water applied with corn and soybean retaining greater that 30% of the water (Fig. 2). As a result of the reduced levels of water coming off the crop residues, there was less opportunity for leaching in the greenhouse experiments. This occurrence led to increased growth inhibition of canola by saflufenacil at higher rainfall events compared to no residue (bare soil) treatments in the Candor loamy sand. Analytical data agreed with bioassay data when crop residues and simulated rainfall amount were compared. These data verified the assumption that greater saflufenacil wash-off was occurring in the sweet almond and sweet orange and less with the wheat, soybean, and corn residues.

CONCLUSIONS

From these results, projecting the amount of rainfall needed to wash off all saflufenacil from crop residues in difficult. Assuming irreversible binding to crop residues is low, 100% wash-off from corn, soybean, and wheat residue can be achieved with 190 to 200 mm of rainfall (Fig. 3). Low rainfall amounts washed greater than 50% of saflufenacil applied from almond and citrus residues, but increasing rainfall amount did not result in a large increase in wash-off. Therefore, extending linear relationship for these residues to 100% of applied revealed the rainfall amount needed was approximated 220 mm for almond and 280 mm for citrus (Fig. 3). Realistically, there will be some irreversible binding of saflufenacil to all crop residues leading to a maximum wash-off of less than 100% of applied.

Results from these studies suggest that herbicide performance under no-till or reduced till crop production or orchard/grove management systems may be significantly affected by the type of crop residue on the surface at time of application and by subsequent rainfall events (Ghadiri et al. 1984; Dao 1991, 1995). Our results suggest that saflufenacil > mesotrione > isoxaflutole > oxyfluorfen > flumioxazin in the ease of wash-off, particularly when rainfall or irrigation amounts are limiting. In row-crop production systems, it appears that soybean, wheat and corn residues are all equal in the degree for which saflufenacil was washed off. Whereas in orchard/grove management systems, equal amounts of saflufenacil were washed off citrus and almond residues. Regardless of the crop residue type, the majority of saflufenacil washed off occurred with the first 32 mm of rainfall or irrigation.

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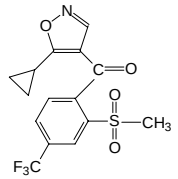
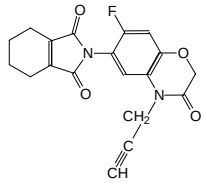
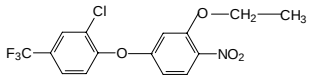
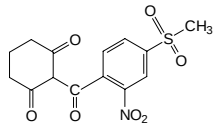
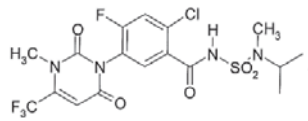
Table 1. Herbicide physiochemical properties (20-25 ºC) and rates applied to crop residues.†

Herbicide	Chemical Family	Structure	pK_a‡	K_s‡	VP‡	K_{oc}‡	Rate§
				mg L^{-1}	Pa	mL g^{-1}	g ai ha^{-1}
Isoxaflutole	**isoxazole**		**nonionizable**	**6.2**	**1.0×10^{-6}**	**93-131**	**25**
Flumioxazin	**N-phenylphtalimide**		**nonionizable**	**1.8**	**3.2×10^{-3}**	**116-200¶**	**40**
Oxyfluorfen	**diphenyl ether**		**nonionizable**	**0.1**	**2.7×10^{-4}**	**5,585-32,381**	**900**
Mesotrione	**triketone**		**3.1**	**15,000 @ pH 6.9**	**5.7×10^{-6}**	**14-390**	**25**
Saflufenacil	**pyrimidinedione**		**4.4 [e]**	**2100 @ pH 7#**	**2.0×10^{-14}#**	**4-92††**	**6**

† Abbreviations: K_s, aqueous solubility; VP, vapor pressure; K_{oc}, organic carbon partition coefficient.

‡ Senseman 2007.

Table 1. (continued)

§ Rate applied to crop residue and bare soil treatments.

¶ Ferrel et al. 2005.

BASF Agricultural Products 2008.

†† Hixson et al. 2008, unpublished data.

Table 2. Theoretical percent wash-off (TPW) measured by difference between bare soil treatments and crop residue treatments for herbicide and simulated rainfall combinations averaged across crop residue treatments in the Candor loamy sand experiment.†, ‡

	Simulated rainfall (mm)		
Herbicide	32	64	128
	TPW		
saflufenacil SC	80	76	82
saflufenacil WG	79	86	88
mesotrione	75	86	85
oxyfluorfen	20	27	28
LSD	9		

† Abbreviations: TPW, theoretical percent wash-off; SC, suspension concentrate; WG, wettable granule

‡ Means within table followed by the same letter are not different according to Fisher's Protected LSD at P = 0.05.

Table 3. Visual percent growth inhibition of canola for bare soil herbicide treatments on Candor loamy sand and Drummer loam.†

	Candor loamy sand‡			Drummer loam‡		
	Simulated rainfall (mm)					
Herbicide	32	64	128	32	64	128
	% growth inhibition					
saflufenacil SC	90	86	52	97	97	62
saflufenacil WG	93	88	60	82	93	82
mesotrione	77	76	72	75	83	77
oxyfluorfen	74	75	76	83	85	92
flumioxazin	-	-	-	87	85	92
isoxaflutole	-	-	-	75	53	62
LSD	11			12		

† Abbreviations: SC, suspension concentrate; WG, wettable granule

‡ Means within soil series followed by the same letter are not different according to Fisher's Protected LSD at P = 0.05.

Table 4. Theoretical percent wash-off (TPW) measured by difference between bare soil treatments and crop residue treatments for herbicide and crop residue combinations averaged across simulated rainfall treatments in the Candor loamy sand experiment.†, ‡

Herbicide	Crop Residue				
	Wheat	Soybean	Sweet orange	Sweet almond	Corn
	TPW				
saflufenacil SC	82	80	84	83	67
saflufenacil WG	87	83	91	91	71
mesotrione	87	79	80	90	76
oxyfluorfen	24	26	20	38	17
LSD	11				

† Abbreviations: TPW, theoretical percent wash-off; SC, suspension concentrate; WG, wettable granule

‡ Means within table followed by the same letter are not different according to Fisher's Protected LSD at P = 0.05.

Table 5. Theoretical percent wash-off (TPW) between visual plant inhibition for bare soil treatments and crop residue treatments for herbicide and simulated rainfall combinations averaged across crop residue treatments in the Drummer loam experiment.†, ‡

	Simulated rainfall (mm)		
Herbicide	32	64	128
	TPW		
saflufenacil SC	61	70	84
saflufenacil WG	62	58	81
mesotrione	37	72	73
isoxaflutole	24	43	72
oxyfluorfen	25	25	23
flumioxazin	2	26	22
LSD	11		

† Abbreviations: TPW, theoretical percent wash-off; SC, suspension concentrate; WG, wettable granule

‡ Means within table followed by the same letter are not different according to Fisher's Protected LSD at P = 0.05.

Table 6. Theoretical percent wash-off (TPW) between visual plant inhibition for bare soil treatments and crop residue treatments for herbicide and crop residue combinations averaged across simulated rainfall treatments in the Drummer loam experiment.†, ‡

	Crop Residue				
Herbicide	Wheat	Soybean	Sweet orange	Sweet almond	Corn
	TPW				
saflufenacil SC	71	54	94	100	39
saflufenacil WG	84	32	84	95	40
mesotrione	56	75	55	75	42
isoxaflutole	52	37	58	59	25
oxyfluorfen	14	17	24	65	2
flumioxazin	15	3	14	44	6
LSD	14				

† Abbreviations: TPW, theoretical percent wash-off; SC, suspension concentrate; WG, wettable granule

‡ Means within table followed by the same letter are not different according to Fisher's Protected LSD at P = 0.05.

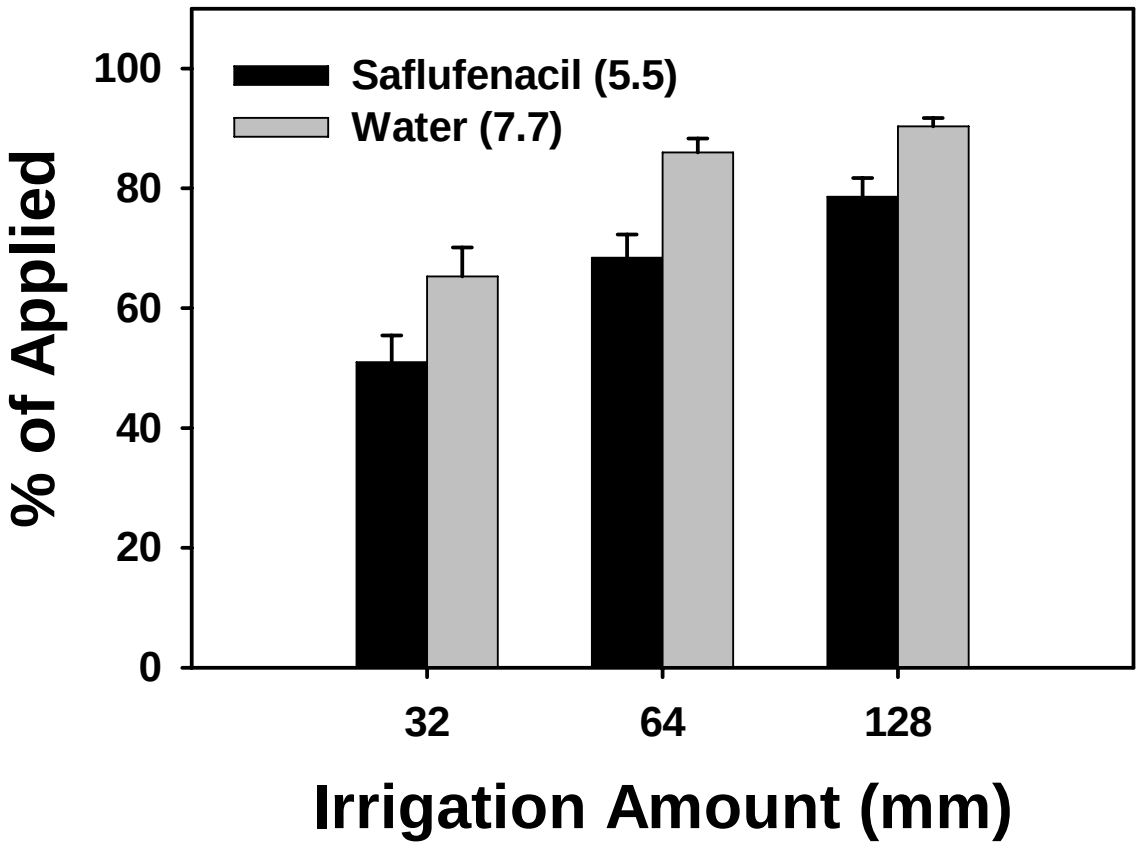


Fig. 1. Amount of saflufenacil SC and water, measured as percent of applied that washed off the crop residues at each simulated rainfall level. Fisher's protected LSD values are in parentheses following labels. Bars represent standard error (n=4).

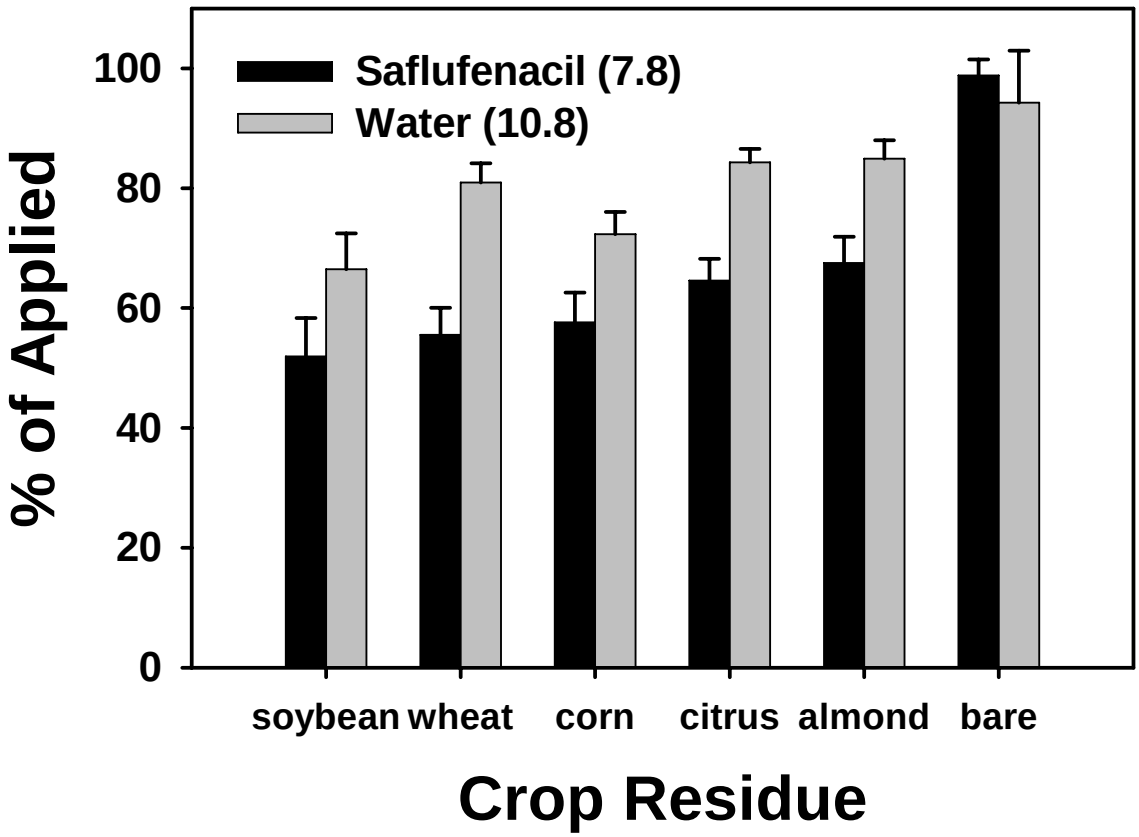


Fig. 2. Amount of saflufenacil SC and water, measured as percent of applied that washed off the crop residues averaged across all simulated rainfall amounts. Fisher's protected LSD values are in parentheses following labels. Bars represent standard error (n=4).

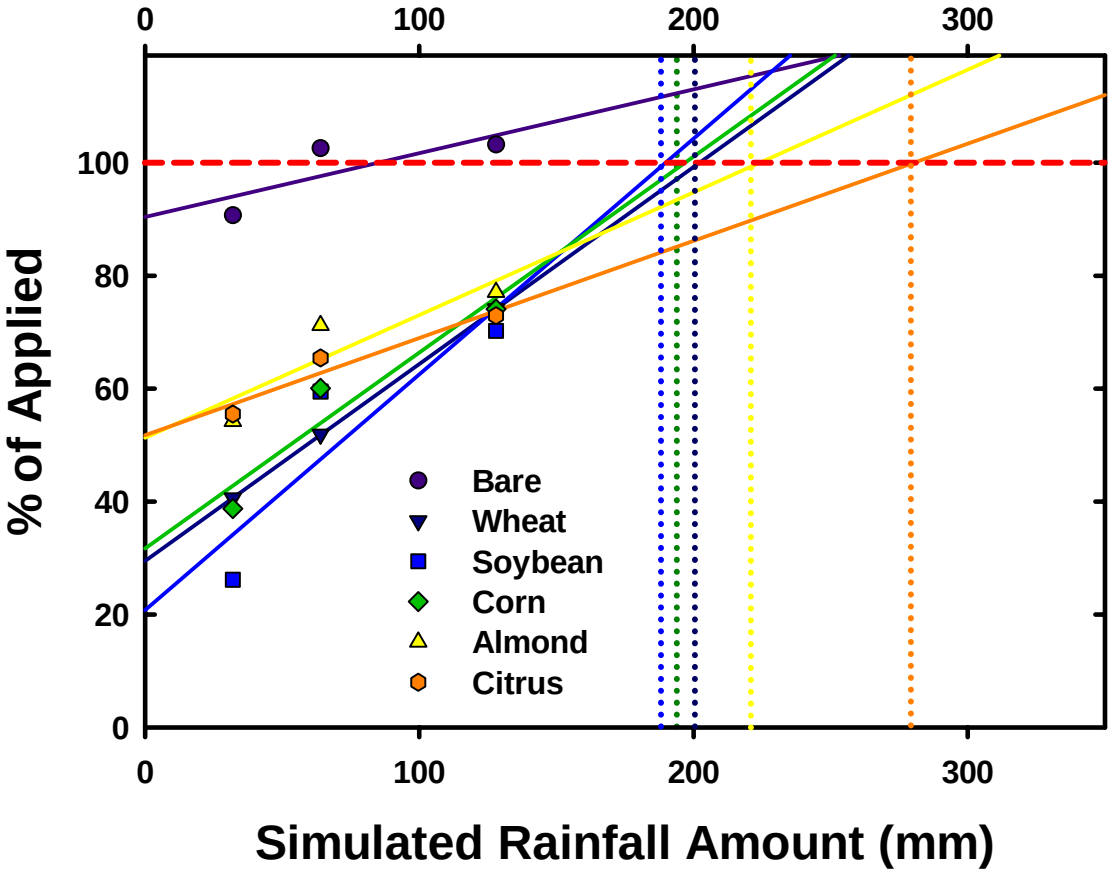


Fig. 3. Linear regression used to predict amount of rainfall needed to wash off 100% of saflufenacil SC from crop residues. Vertical lines indicate predicted amount of simulated rainfall amount needed to wash off 100% of saflufenacil. Data points are means of four replications.

SAFLUFENACIL SORPTION, DESORPTION, AND MOBILITY IN SOIL

(Formatted for submission to Weed Science)

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Understanding herbicide mobility and sorption/desorption in soils is necessary to prevent groundwater contamination and ascertain efficacy and tolerance of crops and weeds planted at various soil depths. Using hand-packed soil columns and bioassay procedures, we compared the mobility distribution of saflufenacil to five herbicides in Candor loamy sand and to atrazine in six soils. Saflufenacil sorption and desorption isotherms were constructed for nine soils using batch equilibration. In the Candor loamy sand, saflufenacil was the most mobile herbicide, followed by mesotrione > atrazine = isoxaflutole > flumioxazin = oxyfluorfen. Saflufenacil mobility was greatest in Dundee silt loam > Candor loamy sand II (pH 6.5) = Candor loamy sand III (0.9% organic matter, subsoil) > Candor loamy sand I (pH 4.9) = Drummer loam = Arapahoe sandy loam. Saflufenacil sorption (K_f and K_d) on nine soils showed strong correlation to organic matter and humic matter contents. Percent

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saflufenacil desorbed correlated inversely with clay content indicating that increasing clay content in soils lowered desorption.

Nomenclature: Saflufenacil; atrazine; flumioxazin; isoxaflutole; mesotrione; oxyfluorfen; canola, *Brassica napus* L.

Key words: Leaching, mobility, sorption, desorption, K_d, soil column, herbicide

Saflufenacil, a new herbicide for use in several crops, is a moderately acidic, highly aqueous soluble herbicide used to control broadleaf weeds when applied pre- or postemergence (BASF Agricultural Products 2008) (Table 1). Saflufenacil controls many weeds by inhibiting protoporphyrinogen oxidase to induce massive accumulation of porphyrins and to enhance peroxidation of membrane lipids, which leads to irreversible damage of the membrane function and structure of susceptible plants (BASF Agricultural Products 2008; Duke et al. 1991). Currently, the highest use rate of saflufenacil from a market-share perspective is corn (*Zea mays* L.), providing season long control of troublesome and resistant broadleaf weeds such as tall waterhemp [*Amaranthus tuberculatus* (Moq.) Sauer], giant ragweed (*Ambrosia trifida* L.), and horseweed [*Conyza canadensis* (L.) Cronq.]. It also has potential for use in soybean [*Glycine max* (L.) Merr.] weed management, despite the possibility for saflufenacil to injure soybeans and varietal difference in sensitivity. There is also interest for saflufenacil to be used in cereal crops, aquatic environments, fruit and nut trees and rights-of-way. As weed resistance to glyphosate and acetolactate synthase (ALS) inhibiting herbicides spread, there will be an increasing need for alternative mode of action herbicides (Heap 2008).

Soil applied herbicides can be sorbed to soil colloids and organic matter (OM). Sorption to soil determines the bioavailability of herbicides, and one of the main factors controlling soil solution concentration (Walker 1980). Herbicide sorption may be affected by OM, clay content, and pH (Calvert 1980; Loux and Reese 1992; Mueller et al. 1992; Reddy and Locke 1998). Therefore, herbicide application rates sometimes vary according to soil type and are generally lower for soils with low clay content or OM (Blumhorst et al. 1990;

Carringer et al. 1975; Peter and Weber 1985; Walker 1980). Herbicide bioavailability and soil mobility can change with some types of ionic chemicals under varying soil pH because of the ability of these herbicides to be charged or neutral (Keller et al. 1998; Loux and Reese 1992; Schneiders et al. 1993).

With a pK_a of 4.41, soil pH will probably have little affect on binding of saflufenacil, as a majority of agriculturally productive soils do not have pH levels this low. Saflufenacil has a water solubility of 30 mg L^{-1} at pH 5.0, and 2100 mg L^{-1} at pH 7 and a vapor pressure of 2.0×10^{-14} Pa at 25 °C (BASF Agricultural Products 2008) (Table 1). Since saflufenacil is a new herbicide, comparisons to current herbicides of varying physicochemical properties are necessary for reference purposes. The historically researched and reported herbicide, atrazine, is typically included as a reference compound when evaluating a new herbicide in soil behavioral studies. Atrazine is a weakly basic, low aqueous soluble herbicide used to control broadleaf and grass weeds when applied pre- or postemergence in corn and grain sorghum [*Sorghum bicolor* (L.) Moench] (Senseman 2007) (Table 1). Its retention in soil has been attributed to binding to OM (Novak et al. 1997; Talbert and Fletchall 1965; Weber et al. 1969), clay minerals (Frissel 1961; Gunther and Gunther 1970; Weber 1966, 1970) and by being pH-dependent (McGlamery and Slife 1966; Weber 1966, 1970). Atrazine and its metabolites have been reported to leach in coarse-textured, low OM soils (Jayachandran et al. 1994; Rogers 1968; Schiavon 1988).

Herbicide mobility is both an agronomic and environmental concern. Agronomically, herbicides that readily move through the soil profile can result in reduced weed control. Herbicides that are highly mobile in soil may be a potential groundwater contaminant due to

vertical movement through the soil profile. Mobility has been studied using soil columns numerous times (Fleming et al. 1992; Keller et al. 1998; Ohmes and Mueller 2007). Herbicide mobility is highly influenced by both soil and herbicide properties (Grey et al. 1997; Peter and Weber 1985). Coarse textured soils, such as sands or loamy sands, may have increased flow of percolating water which can affect the residence time the herbicide has to sorb to soil colloids and/or OM.

Objectives of this research were (i) to evaluate the sorption and desorption of saflufenacil using a batch-slurry technique, (ii) to assess saflufenacil mobility in six soils under unsaturated conditions in hand-packed columns, and (iii) compare saflufenacil mobility to four commercially available herbicides under unsaturated conditions in hand-packed columns. The purpose of this research is to provide information concerning how soil mobility and sorption can affect weed control and crop tolerance. From an environmental perspective, this research can used to predict which soils are more likely susceptible to leaching and eventual groundwater contaminations.

Materials and Methods

Herbicides. For the sorption/desorption study, technical grade (99% purity) and ^{14}C-labeled (99.5% purity, specific activity (4.26 MBq mg^{-1})) saflufenacil[7] were donated by BASF Corporation, Research Triangle Park, NC, and used without further purification. Herbicide stock solutions were prepared in acetonitrile (ACS grade, 99.9%) and used within one hour

of preparation. Appropriate volumes of ^{14}C- and technical grade stock solutions were diluted with 0.01 M $CaCl_2$.

For the mobility study, six herbicides with rates used and their properties are shown in Table 1. Saflufenacil [1] was a 480 g L^{-1} suspension concentrate. Atrazine[2] consisted of AATREX NINE-O® (90% atrazine wettable granule) whereas flumioxazin[3] was as CHATEAU® (51% wettable dispersible granule). Oxyfluorfen[4] treatments consisted of GOAL® 2XL (240 g L^{-1}) while mestrione[5] treatments consisted of CALLISTO® 4SC (480 g L^{-1}, suspension concentrate). Isoxaflutole[6] treatments consisted of BALANCE PRO® 4EC (480 g L^{-1}, emulsifiable concentrate).

Experimental Soils. Seven soils were collected from the 0-15 cm depth and one subsoil (15-30 cm; Candor III) from seven locations in four states and one Canadian province (Table 2). In addition, one soil (Candor II) was amended with calcium oxide (CaO) to increase pH (Table 2). Soils where herbicides had been applied recently were avoided. Soils included were: Drummer loam (fine-silty, mixed, superactive, mesic Typic Endoaquoll); Arapahoe sandy loam (coarse-loamy, mixed, semiactive, nonacid, thermic Typic Humaquept); three Candor loamy sands (sandy, siliceous, thermic Grossarenic Kandiudult); Dark Brown Chernozem (Typic Boroll) clay; Dundee silt loam (fine-silty, mixed, active, thermic Typic Endoaqualf); Elliott silt loam (fine, illitic, mesic Aquic Argiudolls); Sharkey clay (very-fine, smectitic, thermic Chromic Epiaquert). All soils were air-dried and passed through a 4-mm sieve before use. Particle size was determined using the hydrometer method (Gee and Orr 2002). Percent OM was determined using a colorimetric Walkley-Black procedure (Nelson

and Sommers 1982). Percent humic matter was quantified by photometric determination (Mehlich 1984a). Soil pH was determined using a glass electrode and reference buffers on a 1:1 soil to water mixture (Peech 1965). Effective cation exchange capacity (CEC) was measured using the summation of exchangeable cations procedure described by Mehlich (1984b).

Soil Mobility. Prior to filling with soil, polyvinyl chloride (PVC) columns (7.5 cm i.d. and 30 cm in length), were bisected lengthwise using a table-saw to allow for the creation of column halves. The matching column halves were joined using duct tape and large hose-clamps. Using two rubber bands, four layers of cheese cloth[8] were attached to the bottom of each column to prevent soil loss. Columns were packed by adding small amounts of soil to each column while it was agitated and gently packed with a 2-cm-diam. wooden dowel. Soil was added to within one centimeter from top of the column. Each herbicide and related rate (Table 1) in 6 mL of water contained in a pipette was applied in a cross-hatch pattern to the soil surface. Rates used were higher than those used for field applications to obtain a clear response from the bioassay species used. Glass fiber filter paper[9] was placed on the soil surface to minimize surface disturbance during simulated rainfall. A simulated rainfall apparatus was constructed to apply rainfall at rate of 1.25 cm hr^{-1}. Briefly, the simulated rainfall apparatus consisted of 1.5 L cylindrical containers mounted 60 cm above 13-cm-diam. Büchner funnels[10] (Figure 1). Soil columns were placed directly on the Büchner funnels, and simulated rainfall was applied through 25-gauge needles[11] at rate in which unsaturated flow occurred without surface pooling. One pore volume of water was applied to

each column. Depending on the pore volume of each soil, rainfall events lasted from 2.5 to 5 hours. A pore volume was determined by continual subirrigation of the soil column to where the soil surface became near saturated. This was achieved by placing the hand-packed column in a secondary container of the same height as the column. Water was continually introduced to the outside of the column but yet contained in the secondary container. Water was continually added until it reached the height of the soil surface of the column. Once the soil surface was near saturated, the soil column was then allowed to free drain for 24 hours. Pore volume was then determined by weighing the wet column vs. the dry column (Table 2).

Two separate soil mobility experiments were performed to determine saflufenacil movement through the hand-packed columns. In one experiment, saflufenacil and five other herbicides were compared in the Candor I loamy sand (Table 2). For the second experiment, the Drummer loam, Arapahoe sandy loam, three Candor loamy sands and the Dundee silt loam were used and packed to the bulk densities shown in Table 2. For these soils, only saflufenacil and atrazine were compared.

Herbicide Distribution Analysis. A bioassay was used to determine herbicide concentrations in the soil columns. Canola (*Brassica napus* L.) was an ideal bioassay species because of its sensitivity to all herbicides used. Concurrently, mobility and standard curve experiments were conducted in the growth chamber and greenhouse. Standard curve data were obtained by adding known quantities of herbicide to the same soil used in the columns. Canola response to increasing herbicide concentrations was noted. In making the standard curves, specific herbicide concentrations and deionized water were added to 300 g of the

sieved, air-dried soil. Each herbicide rate and soil was contained in plastic bags[12] to create a 3 to 7 percent soil moisture. The soil and herbicide solution was allowed to equilibrate for 24 hours. Soil was thoroughly mixed in the bag and passed through a 2-mm sieve three times to insure even distribution of the herbicide solution. Clear plastic cups[13] at a 150 mL volume were filled with equal weights (100 g) of herbicide treated soil for a total of three replications per bag. Herbicide rates were established during preliminary experiments. They ranged from 1 to 30 g ai/ha for saflufenacil. Planting depth for the canola ranged from 0.6 to 1 cm depending on soil type.

Standard curve cups were placed in a growth chamber[14] on a 25/15 °C temperature cycle with a 14/10 hour light/dark cycle. Fluorescent lights provided 400 µmol m^{-2} s^{-1} illumination at canopy level for a 14-h photoperiod. Humidity was maintained at 80% to avoid rapid drying of soils during plant germination. Following germination, plants were placed in a greenhouse with average day/night temperatures of 30/25 ºC. Natural daylight was supplemented with 300 µmol m^{-2} s^{-1} illumination at canopy level provided by high-pressure sodium lamps for a 14-h photoperiod. Cups were watered daily after removal from the growth chamber to maintain a moist soil environment for optimal growth on each soil type. Aboveground portions of plants were harvested 17 days after planting and fresh and dry weights were recorded. The curve fitting program 'R' (R Development Core Team 2006; Knezevic et al. 2007; Ritz and Streibig 2005) utilized a three-parameter log logistic model $\{Y = d / (1 + \exp b(\log(x) - \log(e)))\}$ to produce a regression equation which related plant response to herbicide concentration for each soil. The equations were utilized where the coefficient of determination (R^2) was equal to or greater than 0.90.

The depth to which the herbicides moved in the columns was determined by bioassay and a mobility index (MI) to be described later. The duct tape and hose-clamps were removed from each column. Starting at the bottom of the column, the columns were split in half by pulling a wire upward between the halves. The paired halves were placed horizontally in plastic trays and seeded in furrows with canola. The furrows were pressed closed. The split column halves were placed in a growth chamber and treated similar to standard curve cups. Following germination, column halves were placed in the greenhouse and irrigated with a mist sprayer as needed. Plant growth was evaluated 17 days after planting for all compounds and soils. At plant harvest, visual ratings were recorded for twelve 2.5 cm depth increments and shoots were clipped at the soil surface for each depth increment. Fresh and dry weights were recorded and percent reduction was determined by comparing weights to nontreated plant weights. Visual percent growth inhibition and aboveground plant weights (fresh and dry) were recorded as indices of plant growth, with fresh weight being chosen as the optimal bioassay measurement.

Saflufenacil Sorption/Desorption. A batch equilibrium technique was used to determine sorption of saflufenacil to soil. Saflufenacil solutions were formulated by dissolving technical grade saflufenacil and ^{14}C- saflufenacil in acetonitrile. The saflufenacil – acetonitrile solutions were diluted with 0.01 M $CaCl_2$ to create < 1% acetonitrile 0.01 M $CaCl_2$ solutions containing, 0.01, 0.02, 1.0, 2.0, 5.0, and 10.0 µM saflufenacil. These solution concentrations encompass the saflufenacil use rate range for the soils after adjustment for soil texture and OM content when uniformly incorporated to 7.5 cm. Blank

controls also were equilibrated with each soil type so that background levels of saflufenacil could be confirmed. Deionized water was used for all solutions. Soil, 10 g (dry-weight basis), was added to 30-ml Teflon-lined centrifuge tubes[15]. Saflufenacil solutions were combined with each soil type (1:1) and equilibrated on a horizontal shaker (140 cycles min^{-1}) for 24 h at room temperature (27 °C). The study was conducted as a completely randomized design with four replications for each saflufenacil concentration and soil combination. Preliminary studies indicated that saflufenacil sorption was completed within 24 h. After equilibration, samples were centrifuged at 4,700 × *g* for 20 min.

Desorption was determined immediately after sorption using the same samples. Following removal of 80 to 90% of the supernatant, herbicide-free 0.01 M $CaCl_2$ solution was added to the soil pellet. The pellet was resuspended by vortexing. The samples were reequilibrated for 24 h and centrifuged as described above. One additional 24-h desorption cycle was conducted for all concentrations, and three additional 24-h desorption cycles were conducted for the 10 µM concentration for a total of four.

Duplicate 1-ml aliquots of supernatant were counted for radioactivity using liquid scintillation counting[16]. An external standard calibration was used to correct for sample quenching. Preliminary experiments showed that saflufenacil sorption to centrifuge tubes were negligible (data not shown). Sorption and desorption coefficients were calculated using the linearized form of the Freundlich equation

$$\log (x/m) = \log K_f + (1/n) \log C_e \qquad [1]$$

where x/m is μmol of test substance per kilogram of soil, C_e is μmol of test substance per liter of supernatant after equilibration, and K_f and $1/n$ are empirical constants where K_f is the Freundlich coefficient (L kg^{-1}) and $1/n$ is a dimensionless parameter that accounts for sorption nonlinearity. Hereafter, $K_{f,s}$ and $1/n_s$ indicate sorption, whereas $K_{f,d}$ and $1/n_d$ refer to desorption. The sorption distribution coefficients (K_d) were calculated as follows:

$$K_d = (x/m) / C_e \quad [2]$$

Distribution coefficients were determined at each concentration and averaged across all equilibrium concentrations to obtain a single estimate of K_d. The sorption coefficient was normalized to the organic carbon (OC) content of the soil (K_{oc}), and hysteresis (ω) was quantified as described by Ma et al., 1993:

$$K_{oc} = (K_d / \%OC) \times 100 \quad [3]$$

$$\omega = [(1/n_s) / (1/n_d) - 1] \times 100 \quad [4]$$

Percent organic carbon was calculated from OM using the equation, %OC = %OM / 1.724 (Comfort et al. 1994).

Data Analyses. The mobility experiments used a completely randomized block design with two replications for each soil and herbicide combination plus untreated controls and both

experiments were conducted twice. Data for each experiment were transformed to percent growth inhibition relative to the nontreated check. The nontreated check was not included in the analysis because transforming the data to percent growth inhibition relative to the nontreated check would set the nontreated check to 0%. Percent growth inhibition values were then related to standard curve data to generate percent of herbicide applied at each 2.5-cm depth increment in the soil columns. Analysis of variance (ANOVA) performed using SAS[17] revealed no significant treatment by experiment interaction and error variances were homogeneous; consequently, data were combined over time for analysis and presentation. Mobility data are present in horizontal bar format based on percentage of herbicide applied by depth with error bars on each column (Figures 3, 4). For each lysimeter, a mobility index (MI = $\sum D \times F$, where D = depth in cm and F = fraction of chemical present) was calculated from the distribution of total chemical detected in the soil profile, normalized to 100% recovered for comparisons, as described by Weber et al. (1999). A higher MI indicated more herbicide movement through the soil column. Mobility index data were subjected to ANOVA, and means were separated with the appropriate Fisher's protected LSD test at the 5% significance level. In addition, relative pesticide leaching potential (PLP) and soil leaching potential (SLP) were calculated using a simple decision-aid model (Warren and Weber, 1994; Weber, 2005) (Tables 1, 2).

The sorption/desorption experiment used a completely randomized design with two replications per soil, and the entire experiment was repeated. Nonlinear regression analysis were used to derive $K_{f,s}$ and $K_{f,d}$, and $1/n_s$ and $1/n_d$ minimized the weighted residual sum of squares. Asymptotic errors were calculated and presented for all Freundlich sorption and

desorption parameters. All nonlinear and linear analysis was performed using Sigmaplot 10 software[18]. K_d, K_{oc}, and ω were analyzed by analysis of variance (ANOVA) for a completely randomized design using SAS, and means separated by Fisher's Protected LSD at the 5% level. The relationship between the K_d, K_{oc}, K_f, and $1/n$ values for each herbicide and the physical and chemical properties of the soils were evaluated through correlation analysis. By comparing Pearson correlation coefficients (r), those soil factors contributing most to the variation in sorption of the herbicides in the soils were identified.

Results and Discussion

Soil Mobility. Differences in bulk densities resulted in different pore volumes for each soil (Table 2). Consistency of wetting front was determined for each soil to insure absence of wall and/or macropore preferential flow (Figure 2). Results were repeatable among replications and runs, and standard errors were small. There were clear differences between the soils and herbicides, indicating that our test system had sufficient sensitivity to discern differences. Air-dried soil was used to best evaluate chromatographic movement of the herbicides through the soil profiles. With the addition of one pore volume, a mobility index (MI) could be calculated (Weber et al. 1999) and were used to determine differences among treatments.

Multiple Soils Mobility: Saflufenacil was detected at every depth increment in every soil except the 27.5-cm depth increment in the Arapahoe sandy loam and the Candor loamy sand

I (Figure 3). Saflufenacil and atrazine movement was lowest in the Arapahoe sandy loam, resulting in the lowest MI's for both herbicides (Figure 3, Table 2). Highest concentration of saflufenacil was at the midpoint of the column whereas atrazine did not move out of the top depth increment. High OM content associated with this soil resulted in high rapid sorption, reducing the movement of saflufenacil and atrazine through the soil column. Although high OM content sorbed much of the herbicides, saflufenacil was able to move throughout most of the column because the coarse soil texture allowed for rapid infiltration of water.

Herbicide movement was highest in the Dundee silt loam with MI's of 21.1 and 7.5 for saflufenacil and atrazine, respectively (Figure 3, Table 2). Approximately 67% of saflufenacil was in the bottom three depth increments of the Dundee silt loam column. Low OM content and high pore volume contributed to the increased movement through the soil column. There is potential for reduced control of surface seeded weeds in similar soils.

Saflufenacil and atrazine movement through Drummer loam was similar to Arapahoe sandy loam with the highest concentration of saflufenacil in the 12.5 and 15-cm-depth increments, respectively (Figure 3, Table 2). Saflufenacil was detected by the bioassay in every section of the soil column, indicating slightly more movement than in the Arapahoe sandy loam. Medium to high OM content with 20% clay content slowed water movement and allowed more time for the soil colloids to interact with the herbicides in the Drummer loam. Even though saflufenacil sorption was low (Table 3), movement in the soil profile could have been reduced due to the increased amount of exposure to soil colloids. In addition, when equal amounts of simulated rainfall were added to each soil, the wetting front

in the Drummer loam moved the least (Figure 2). This indicates slower water movement through the soil profile.

Herbicide movement through Candor loamy sand I, II, and III differed considerably. To facilitate comparison of soil pH differences, Candor loamy sand I at pH 4.9 was limed to pH 6.5, creating Candor loamy sand II (Table 2). In addition, the subsoil (Candor loamy sand III) was used to compare differences in mobility between soils with similar texture and pH, but different amount of OM. Higher pH caused more saflufenacil to be in the anionic form; therefore saflufenacil was more evenly distributed throughout the bottom half of the Candor loamy sand II column (Figure 3). Lower soil pH resulted in a higher percentage of saflufenacil in the molecular form which resulted in a higher affinity for the OM present in Candor loamy sand I and III. But, since less OM was present in the subsoil (Candor loamy sand III) mobility was higher, as indicated by the difference in MI's (Figure 3, Table 2). Although correlation analysis does not indicate a relationship between MI and soil pH, this information shows the importance of both soil pH and OM content (Table 3). Correlation coefficients (r) indicate a strong relationship between MI for both herbicides and OM and HM (Table 3). Due to the strong relationship between OM and HM, and HM and K_d, it is reasonable to assume that HM is the major soil parameter determining mobility and sorption of saflufenacil in soil. Overall, saflufenacil and atrazine mobility was greatest in Dundee silt loam > Candor loamy sand III = Candor loamy sand II > Candor loamy sand I = Drummer > Arapahoe (data not shown). With a one-time rainfall event, excluding persistence differences, saflufenacil was more mobile in soil than atrazine.

Multiple Herbicides Mobility: Herbicide soil mobility comparisons revealed saflufenacil mobility measured by MI was higher than atrazine, flumioxazin, isoxaflutole, mesotrione, and oxyfluorfen in the Candor loamy sand I (Figure 4). Saflufenacil had a MI = 12.7 and was detected at all soil depths with the highest concentration occurring at the 15-cm-depth (Figure 4). All oxyfluorfen and > 95% of flumioxazin remained in the 2.5-cm-depth increment (Figure 4). Atrazine and isoxaflutole had similar soil mobility with MI's = 3.0 and 2.8, respectively (Figure 4). Atrazine moved to the 10-cm-depth and isoxaflutole moved to the 12.5-cm-depth increment. Order of soil mobility in Candor loamy sand I from greatest to least is: saflufenacil > mesotrione > atrazine = isoxaflutole > oxyfluorfen = flumioxazin. Herbicide mobility of the anionic and nonionizables molecules was closely related to aqueous solubility with the highest MI's associated with the herbicides with the highest aqueous solubility (Table 1 and 2).

The amount of time a herbicide has to adsorb to clay particles and OM may be an important factor in a herbicide's leaching potential, depending on adsorption kinetics. In these packed-soil columns, water velocity varied with texture. More rapid water movement was observed in the three Candor loamy sand soils than in the other soils evaluated. More rapid movement would disfavor saflufenacil sorption to soil particles and could contribute to greater movement. Most herbicides have rapid initial sorption followed by a slower sorption with equilibrium achieved after 24 to 48 hours. We feel since one pore volume was added to the soil columns in 8 to 10 h that only rapid herbicide sorption was occurring.

Saflufenacil movement through the soil columns was substantially different from soil to soil. The test system used represented a 'worst case' scenario with high rainfall intensity

and volume. In soils with higher OM, some saflufenacil remained in the top soil section, and water conditions of the type used to leach the soil columns would only occur with an intense rainfall event lasting a few hours. In addition, evaporation of water between rainfall events could carry herbicide back to the surface or to be further sorbed (Weber et al., 1999). Therefore, it is unlikely that saflufenacil would leach significantly enough in high OM soils to reduce weed control, although under some conditions it is possible (rapid water infiltration on soils with coarse texture). A small amount of leaching could lead to increased efficacy on large seeded broadleaf weeds. Saflufenacil is most efficacious when the seed and root are exposed; therefore higher concentrations in the seed zone could lead to better large seeded broadleaf weed control. These large seeded broadleaf weeds include some of the most troublesome weeds including giant ragweed, velvetleaf, and morningglory. In addition, crop tolerance could be influenced by saflufenacil movement in the soil profile. Extended root exposure could result in leaf chlorosis and stunting of some crops, such as soybeans. Therefore, if significant rainfall occurred and saflufenacil moved into the root zone of young soybean plants, injury is more likely to occur. This information could be significant when making decisions concerning weed control and crop selection on certain soils. Soil mobility of saflufenacil could cause problems with weed control and crop tolerance when applied to coarse textured soils with very low OM levels (< 1.0 %). In addition, intense rainfall events (> 7.5 cm) could be problematic for medium and fine textured soils with very low OM levels. Although these data revealed the possibility of saflufenacil to have high soil mobility, these experiments do not take into account degradation rates, rainfall amounts, and delayed soil sorption.

Sorption. Saflufenacil sorption (reported as a $K_{f,s}$ value) differed among the nine soils (Table 4). Sorption values ranged from a high of 2.34 for the Arapahoe loamy sand to a low of 0.04 for the Sharkey clay. Within the range of concentration evaluated in this experiment, the Freundlich equation adequately described saflufenacil sorption to all soils ($r^2 \geq 0.95$). The average $1/n$ values for all soils were ≤ 1.06 but ≥ 0.94. Therefore, adsorption data were assumed to be approximately linear over the concentration range evaluated. The Freundlich sorption constant, $1/n_s$, is a measure of sorption nonlinearity. When $1/n_s$ approaches 1, sorption is linearly proportional to the equilibrium solution concentration and a distribution coefficient (K_d) is more appropriate for making comparisons among treatments. Thus, K_d values were estimated and compared between soils.

Although Drummer loam had more OM than the Candor loamy sands (Table 2), the $K_{f,s}$ values were smaller compared to the Candor loamy sands (Table 4), possibly due to higher clay content and lower humic matter (Table 2). $K_{f,s}$ values decreased as clay content increased and humic matter decreased (Tables 2 and 4). Because saflufenacil is a weak acid with a pK_a of 4.4, saflufenacil exists primarily in anionic form from 5 to 7.5 pH. This causes a repulsion of the anionic molecules by negatively charged colloidal surfaces, causing less sorption in soils with more negatively charged clay particles. $K_{f,s}$ values did not show a relationship with pH because all soils tested had a pH greater than the pK_a causing a majority of the saflufenacil molecules to be in the anionic form.

The saflufenacil K_d values were similar to the $K_{f,s}$ values in all soils due to the linearity in sorption (Table 4). The K_{oc} values (K_d values normalized to organic carbon

content of soil) ranged from 4 to 92. Usually, a very narrow range of K_{oc} among soil with varying levels of OM indicates the OM is a major factor controlling the sorption process. Organic carbon values used to generate K_{oc} values were calculated from measured OM values, therefore K_{oc} values are indicative of the role of OM in saflufenacil sorption. The wider range of K_{oc} values observed for saflufenacil (Table 4) indicates that other soil properties in addition to OM, influence saflufenacil sorption. Acidic herbicide anions and molecules sorb to OM polymers and as these polymers become more weathered, HM content increases. Correlation analysis revealed that $K_{f,s}$ and K_d values were highly correlated with HM (r = 0.90 and 0.89). Sorption (K_d) was highly correlated to HM (r = 0.90) and less so to OM (r = 0.72) (Table 3). This relationship is expected as HM is usually highly sorptive to organic compounds (Shea 1989; Strek and Weber, 1982). As indicated by low correlation between MI and K_{oc} values, use of K_{oc} values may be an incorrect predictor of mobility in many soils. Since OC values were calculated from OM content, K_{oc} values were not representative of the humic matter levels of the soils. Even though a low OM level indicates a low humic matter level, moderate to high OM does not necessarily mean a soil has a high humic matter level (Table 2). Sorption values ($K_{f,s}$, K_d, and K_{oc}) were not related to pH, but when all other soil properties were held constant and pH was adjusted (Candor loamy sand I vs. II) all values changed significantly. Higher pH associated with Candor loamy sand II resulted in less sorption than its more acidic counterpart.

Simple regression analysis of nine soils indicated that organic matter and humic matter gave equations with r^2 values greater than 0.52 for saflufenacil sorption ($K_{f,s}$) (Table 5). Multiple regression analysis was performed to study the potential contribution to the

model from all soil properties studied. Although combination of two soil properties improved the r^2 for $K_{f,s}$, more soils would establish reliable relationships between saflufenacil sorption and soil properties (Table 5).

Desorption. Desorption isotherms relate the amount of saflufenacil retained by the soil matrix to saflufenacil concentration in the solution at each desorption cycle (Table 6 and Figure 5). The latter represents the amount of saflufenacil that was desorbed from soil and is susceptible to transformation and transport in soil. High $K_{f,d}$ values are indicative of strong binding or very slow release of saflufenacil to the soil matrix. As expected, moderate to high $K_{f,d}$ values were detected in the Arapahoe sandy loam and Candor loamy sand due to low initial desorption (Table 6). Amount of ^{14}C- saflufenacil desorbed in four desorptions was highest in Candor loamy sand II, III, and Dundee silt loam (~75% of sorbed saflufenacil) (Table 6). Low OM coupled with higher pH in the Candor loamy sand II caused weaker sorption to soil particles. Desorption was lowest in the Sharkey and Chernozem clays suggesting the small amounts of saflufenacil were sorbed very strongly or entrapped in interlayers and pores of soil particles (Table 6). Similar results were found in sorption/desorption studies with another acidic herbicide, dicamba (Carringer et al. 1975). Overall, the amount desorbed by 0.01 M $CaCl_2$ was highest in the first step followed by the second, third, and fourth step (Table 6).

Desorption of saflufenacil from all soils with 0.01 M $CaCl_2$ was hysteretic as indicated by higher $K_{f,d}$ values for desorption compared to sorption and higher $1/n_s$ values for sorption compared to desorption (Tables 4 and 6). Desorption hysteresis indicates

irreversibility of the sorption mechanism (Clay and Koskinen 1990; Locke, 1992; Ma et al., 1993). The Freundlich $1/n$ value describes nonlinearity in the desorption isotherm and can be used as an index of desorption intensity (Pignatello and Huang, 1991). In this experiment, the $1/n_d$ values are smaller than the $1/n_s$ values for all soils, indicating hysteresis. The degree of hysteresis was quantified using eq. 4. The ω values for saflufenacil ranged from 23 to 861 (Table 4). Higher ω values indicate a slower rate of desorption. Soils with higher clay content (Table 2) had slower desorption than coarser textured soils as indicated by high negative correlation with percent saflufenacil desorbed (r = -0.97) (Table 3). These finer textured soils sorbed less saflufenacil, but the herbicide was highly resistant to desorption. Once a herbicide has been attenuated by a clay particle, accessibility by soil solution is limited. A definitive explanation for hysteresis does not exist in the literature but may include nonattainment of equilibrium, precipitate formation, changes in desorption solution composition, degradation, volatilization, and irreversible binding (Calvert, 1980; Ma et al. 1993).

The results of this study show that saflufenacil sorption was affected by OM and HM levels. The low application rates and high potential for sorption to OM may limit the bioavailability in high OM soils (> 5%). Increased residence time under field conditions could also increase the potential for season-long weed control and persistence in these soils. Saflufenacil movement was somewhat limited in Arapahoe sandy loam due to high OM, but other soils exhibited moderate to substantial movement. Some saflufenacil remained in the top depth increment of all soils, and one-time rainfall amounts applied in these studies rarely occur in nature. Thus, intense rainfall events occurring on low OM, coarse textured soils

soon after saflufenacil application could reduce weed control and affect crop tolerance of sensitive plants. It is unlikely that enough leaching would occur on medium to fine textured soils with moderate to high OM to cause reductions in weed control. In fact, a small amount of leaching could actually help weed control by moving saflufenacil into the large seeded weed zone. This could be the cause of numerous anecdotal reports that saflufenacil is very effective on troublesome broadleaf weeds including, tall waterhemp [*Amaranthus tuberculatus* (Moq.) Sauer], giant ragweed (*Ambrosia trifida* L.), morningglory (*Ipomoea* spp.), cocklebur (*Xanthium strumarium*), and velvetleaf (*Abutilon theophrasti*).

Sources of Materials

[1] Saflufenacil, BASF Corporation, Agricultural Products Division, 26 Davis Drive, Research Triangle Park, NC 27609.

[2] Atrazine, Syngenta Corporation, 2200 Concord Pike, P.O. Box 8353, Wilmington, DE 19803.

[3] Flumioxazin, Valent U.S.A. Corporation, P.O. Box 8025, Walnut Creek, CA 94596

[4] Oxyfluorfen, Dow AgroSciences LLC, 9330 Zionsville Road, Indianapolis, IN 46268.

[5] Mesotrione, Syngenta Corporation, 2200 Concord Pike, P.O. Box 8353, Wilmington, DE 19803.

[6] Isoxaflutole, Bayer CropScience LP, 2 T.W. Alexander Drive, P.O. Box 12014, Research Triangle Park, NC 27709

[7] ^{14}C-Saflufenacil, BASF Corporation, Agricultural Products Division, 26 Davis Drive, Research Triangle Park, NC 27609.

[8] 100% Cotton cheesecloth, Nation/Ruskin Inc., Montgomeryville, PA 18936.

[9] Whatman® Glass Fiber Filter Paper 60 mm, Whatman International Ltd., Whatman Holst Leonards Road, Allington, Maidstone, Kent ME160LS, U.K.

[10] Coors® porcelain Büchner funnel with fixed perforated plate, 114 mm-diam., CoorsTek, Inc., North Table Mountain, 16000 Table Mountain Parkway, Golden, CO 80403.

[11] Becton Dickinson Brand Single-Use Needles, 25 gauge, 7/8 inch, Becton Dickinson and Company, 1 Becton Drive, Franklin Lakes, NJ 07417-1884.

[12] Ziploc® plastic bags, quart size, S.C. Johnson & Son, Inc., 1525 Howe Street, Racine, WI 53403.

[13] Dixie® clear plastic PETE cups, 5 oz. size, Georgia-Pacific Corporation, 133 Peachtree Street, N.E., Atlanta, GA 30303.

[14] Conviron® reach-in growth chamber, Controlled Environments Limited, 590 Berry Street, Winnipeg, Manitoba Canada, R3H 0R9.

[15] Nalgene® Oak Ridge FEP Teflon Centrifuge Tubes, 30-ml, Nalge Nunc International, 75 Panorama Creek Drive, Rochester, NY, 14625.

[16] Liquid scintillation counter, Tri-Carb 2100TR, Packard Instrument Co., 2200 Warrenville Road, Downers Grove, IL 60515.

[17] SAS, Statistical Analysis Systems, 2003, Release 9.1, Statistical Analysis Systems Institute, Cary, NC 27513.

[18] Sigmaplot 10, Systat Software Inc., 1735 Technology Drive, Suite 430, San Jose, CA 95110.

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Table 1. Herbicide physiochemical properties (20-25 °C) and rates applied to soil columns.[a]

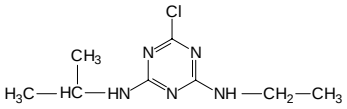
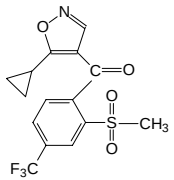
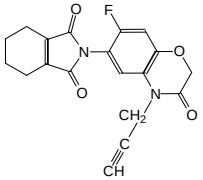
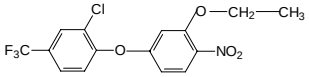
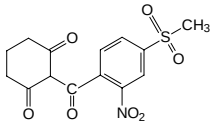
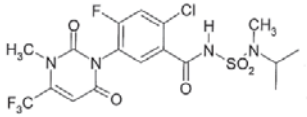
Herbicide	Chemical Family	Structure	pK_a[b]	K_s[b]	VP[b]	K_d[b]	PLP[c]	Rate[d]
				mg L^{-1}	Pa	L kg^{-1}		g ai ha^{-1}
Atrazine	**triazine**		**1.7**	**33**	**4.0×10^{-5}**	**0.2-2.5**	**64**	**3,000**
Isoxaflutole	**isoxazole**		**nonionizable**	**6.2**	**1.0×10^{-6}**	**1.2-4.0[f]**	**21**	**300**
Flumioxazin	**N-phenylphtalimide**		**nonionizable**	**1.8**	**3.2×10^{-3}**	**0.7-8.8[f]**	**33**	**400**
Oxyfluorfen	**diphenyl ether**		**nonionizable**	**0.1**	**2.7×10^{-4}**	**30.3-228.6**	**13**	**20,000**
Mesotrione	**triketone**		**3.1**	**15,000 @ pH 6.9**	**5.7×10^{-6}**	**0.1-5.0[g]**	**29**	**300**

Table 1. (continued)

Herbicide	Chemical Family	Structure	pK_a[b]	K_s[b]	VP[b]	K_d[b]	PLP[c]	Rate[d]
				mg L^{-1}	Pa	L kg^{-1}		g ai ha^{-1}
Saflufenacil	**pyrimidinedione**		**4.4** [h]	**2100 @ pH 7** [i]	**2.0×10^{-14}** [h]	**0.1-2.4**	**39**	**120**

[a] Abbreviations: K_s, water solubility; K_d, herbicide-partition coefficient; VP, vapor pressure; PLP, pesticide leaching potential.

[b] Senseman 2007

[c] Warren and Weber 1994; Weber 2005

[d] Rate applied to crop residue and bare soil treatments.

[e] Taylor-Lovell et al. 2000

[f] Ferrel et al. 2005

[g] Dyson et al. 2002

[h] BASF Agricultural Products 2008

Table 2. Physical and chemical properties, soil leaching potential, and mobility indices for saflufenacil and atrazine in all experimental soils.[a]

State	Series	Texture	pH[b]	OM[c]	HM[d]	Sand[e]	Silt[e]	Clay[e]	CEC[f]	Bulk density	Pore Volume[g]	SLP[h]	$MI_{Saflufenacil}$[i]	$MI_{Atrazine}$[i]
				%					cmol kg^{-1}	g cm^{-3}	ml			
NC	Arapahoe	SL	5.3	8.3	7.55	70	24	6	12.1	1.08	574	67	12.2d	1.3c
NC	Candor I	LS	4.9	2.2	1.93	80	12	8	5.2	1.40	330	123	13.2cd	2.4bc
NC	Candor II	LS	6.5	2.2	1.35	80	12	8	7.8	1.40	330	138	17.0b	2.7b
NC	Candor III	LS	4.7	0.9	0.40	86	6	8	2.4	1.45	342	163	15.3bc	7.1a
SK	Chernozem	C	7.5	3.7	0.14	26	28	46	27.2	-	-	96	-	-
IL	Drummer	L	6.4	3.9	0.77	36	44	20	22.7	1.27	502	114	12.6d	2.2bc
MS	Dundee	SiL	5.6	1.0	0.35	36	56	8	10.2	1.35	562	145	21.1a	7.2a
NE	Elliott	SiL	5.6	4.5	3.77	20	58	22	14.8	-	-	75	-	-
MS	Sharkey	C	6.8	2.4	0.49	9	29	62	23.1	-	-	84	-	-

[a] Abbreviations: OM, organic matter; HM, humic matter; CEC, cation exchange capacity; SLP, soil leaching potential; MI, mobility index; L, loam; S, sand; Si, silt; C, clay.

[b] pH was determined using a 1:1 soil:distilled water ration (Peech 1965).

[c] Organic matter was determined using the Walkley-Black procedure (Nelson and Sommers 1982).

[d] Humic matter was determined by photometric determination (Mehlich 1984b).

[e] Particle analysis was determined using the hydrometer method (Gee and Orr 2002).

Table 2. (continued)

[f] Cation-exchange capacity was determined using the summation of exchangeable cations procedure (Mehlich 1984a).

[g] Pore volumes were determined by subirrigating soil columns and weighing following a 24 h draining period.

[h] SLP determined by inputting soil parameter into a model created by Warren and Weber (1994).

[i] Mobility indices (MI's) of atrazine and saflufenacil leaching were calculated by MI = $\sum D \times F$, where D = mean depth, F = fraction of herbicide present (Weber et al., 1999). Indices followed by a different letter are different based upon Fisher's Protected LSD at the 5% level.

Table 3. Pearson correlation coefficients (*r*) for soil parameters, mobility indices, hysteresis, sorption, and desorption values.[a]

Property/Measurement	Sand	Clay	CEC	OM	HM	pH	$MI_{Saflufenacil}$[b]	$MI_{Atrazine}$[b]
$MI_{saflufenacil}$[b]	-0.26	-0.26	-0.19	-0.56***	-0.44**	0.10	-	0.66***
$MI_{atrazine}$[b]	-0.11	0.18	-0.67*	-0.70***	-0.55***	-0.37*	0.66***	-
K_d	0.45	-0.37	-0.22	0.72**	0.90***	-0.51	-0.48**	-0.49**
K_{oc}	0.79**	-0.60*	-0.74**	-0.07	0.25	-0.85***	-0.23	0.20
$K_{f,s}$	0.45	-0.37	-0.22	0.72**	0.89***	-0.51	-0.48**	-0.49**
$K_{f,d}$	0.54	-0.45	-0.34	0.66*	0.86***	-0.61*	-0.54***	-0.49**
$1/n_s$	-0.48	0.58*	0.34	-0.08	-0.02	0.35	0.60***	0.31
$1/n_d$	0.49	-0.57	-0.51	0.52	0.83***	-0.76**	-0.67*	-0.34
Ω	-0.64*	0.90***	0.82***	-0.12	-0.48	0.87***	0.13	0.06
% saflufenacil sorbed	0.61*	-0.54	-0.46	0.56	0.81***	-0.70**	-0.50**	-0.43**
% saflufenacil desorbed	0.71**	-0.97***	-0.92***	-0.21	0.12	-0.76**	0.60***	0.62***

[a] Abbreviations: MI, mobility index; CEC, cation exchange capacity; OM, organic matter; HM, humic matter; $K_{f,s}$, Freundlich herbicide-partition sorption coefficient; $K_{f,d}$, Freundlich herbicide-partition desorption coefficient; K_d, herbicide-partition coefficient; K_{oc}, organic carbon partition coefficient; ω, hysteresis.

Table 3. (continued)

[b] Correlation analysis performed on the six soils used in mobility experiments.

Table 4. Sorption parameter coefficients for saflufenacil sorption in soils.[a]

	Freundlich sorption parameter[b]			Distribution coefficients[c]		
	$K_{f,s}$	$1/n_s$	R^2	K_d	K_{oc}	ω^c
Soil	$\mu mol^{1-1/n}L^{1/n}kg^{-1}$	Dimensionless		L kg^{-1}	L kg^{-1}	
Sharkey clay	0.04 (0.083)	1.06 (0.116)	0.95	0.06g	4.35g	744b
Chernozem clay	0.07 (0.022)	0.99 (0.030)	0.99	0.07fg	3.46g	861a
Drummer loam	0.15 (0.010)	0.88 (0.014)	0.99	0.16ef	6.94fg	334c
Dundee silt loam	0.15 (0.015)	1.00 (0.021)	0.99	0.15ef	26.6d	176de
Candor loamy sand II	0.20 (0.013)	0.98 (0.017)	0.99	0.20e	15.8e	180d
Elliott silt loam	0.30 (0.009)	0.99 (0.013)	0.99	0.30d	11.5ef	107def
Candor loamy sand III	0.47 (0.004)	0.94 (0.005)	0.99	0.48c	92.0a	120def
Candor loamy sand I	0.96 (0.012)	0.94 (0.016)	0.99	1.01b	79.4b	74ef
Arapahoe sandy loam	2.34 (0.009)	0.97 (0.010)	0.99	2.42a	61.4c	23f

[a] Abbreviations: $K_{f,s}$, Freundlich herbicide-partition sorption coefficient; K_d, herbicide-partition coefficient; K_{oc}, organic carbon partition coefficient; ω, hysteresis.

[b] Values in parentheses are asymptotic standard errors.

[c] Means within column followed by the same letter are not different according to Fisher's Protected LSD at P = 0.05.

Table 5. Regression equations for the distribution coefficients of saflufenacil (K_d) as a function of significant predictive soil parameters.[a]

R^2	Linear regression equation
0.52	K_d = -0.25 + 0.24 OM (%)
0.81	K_d = 2.28 + 0.25 OM (%) – 0.43 pH
0.77	K_d = 0.02 + 0.28 HM (%)
0.86	K_d = -0.33 + 0.26 HM (%) +0.008 sand (%)

[a] Abbreviations: K_d, herbicide-partition coefficient; OM, organic matter; HM, humic matter

Table 6. Desorption parameter coefficients for saflufenacil desorption in soils.[a,b]

	Freundlich desorption parameter[c]			Desorbed saflufenacil by equilibration cycle[d]					
	$K_{f,d}$	$1/n_d$	r^2	Amt. Sorbed[e,f]	I (24 h)[f]	II (48 h)[f]	III (72 h)[f]	IV (96 h)[f]	Total[f,g]
Soil	$\mu mol^{1-1/n}L^{1/n}kg^{-1}$	Dimensionless		%					
Sharkey clay	0.35 (0.038)	0.17 (0.057)	0.76	6.5f	6.4e	0d	2.0d	2.6b	11.0c
Chernozem clay	0.38 (0.026)	0.11 (0.040)	0.73	6.4f	8.4e	4.6c	6.3bcd	3.4b	22.6c
Drummer loam	0.52 (0.041)	0.18 (0.061)	0.74	12.2ef	42.8b	5.4c	3.3cd	2.0b	53.6b
Dundee silt loam	0.43 (0.052)	0.33 (0.079)	0.86	15.0e	56.2a	9.6b	6.6abcd	2.6b	75.1a
Candor loamy sand II	0.66 (0.051)	0.28 (0.076)	0.82	19.2de	46.2ab	16.3a	8.2abc	3.9b	74.9a
Elliott silt loam	0.83 (0.024)	0.48 (0.045)	0.97	23.7d	30.6cd	15.5a	11.5ab	5.5b	63.0ab
Candor loamy sand III	1.05 (0.048)	0.38 (0.086)	0.86	31.7c	43.5b	17.7a	9.6ab	4.3b	75.1a
Candor loamy sand I	1.54 (0.032)	0.57 (0.079)	0.94	47.0b	32.4c	18.0a	11.1ab	11.1a	72.6a
Arapahoe sandy loam	2.62 (0.023)	0.77 (0.086)	0.96	70.2a	22.4d	14.5a	12.4a	7.5ab	56.9b

[a] Abbreviations: $K_{f,d}$, Freundlich herbicide-partition desorption coefficient.

[b] Desorption was determined using the highest saflufenacil concentration (10 µM)

[c] Values in parentheses are asymptotic standard errors.

[d] Represented as percentage of the amount sorbed for each 24-h desorption cycle.

[e] Percentage of total applied saflufenacil sorbed after the 24-h equilibration cycle.

Table 6. (continued)

[f] Means within column followed by the same letter are not different according to Fisher's Protected LSD at P = 0.05.

[g] Summation of the four desorption cycles.

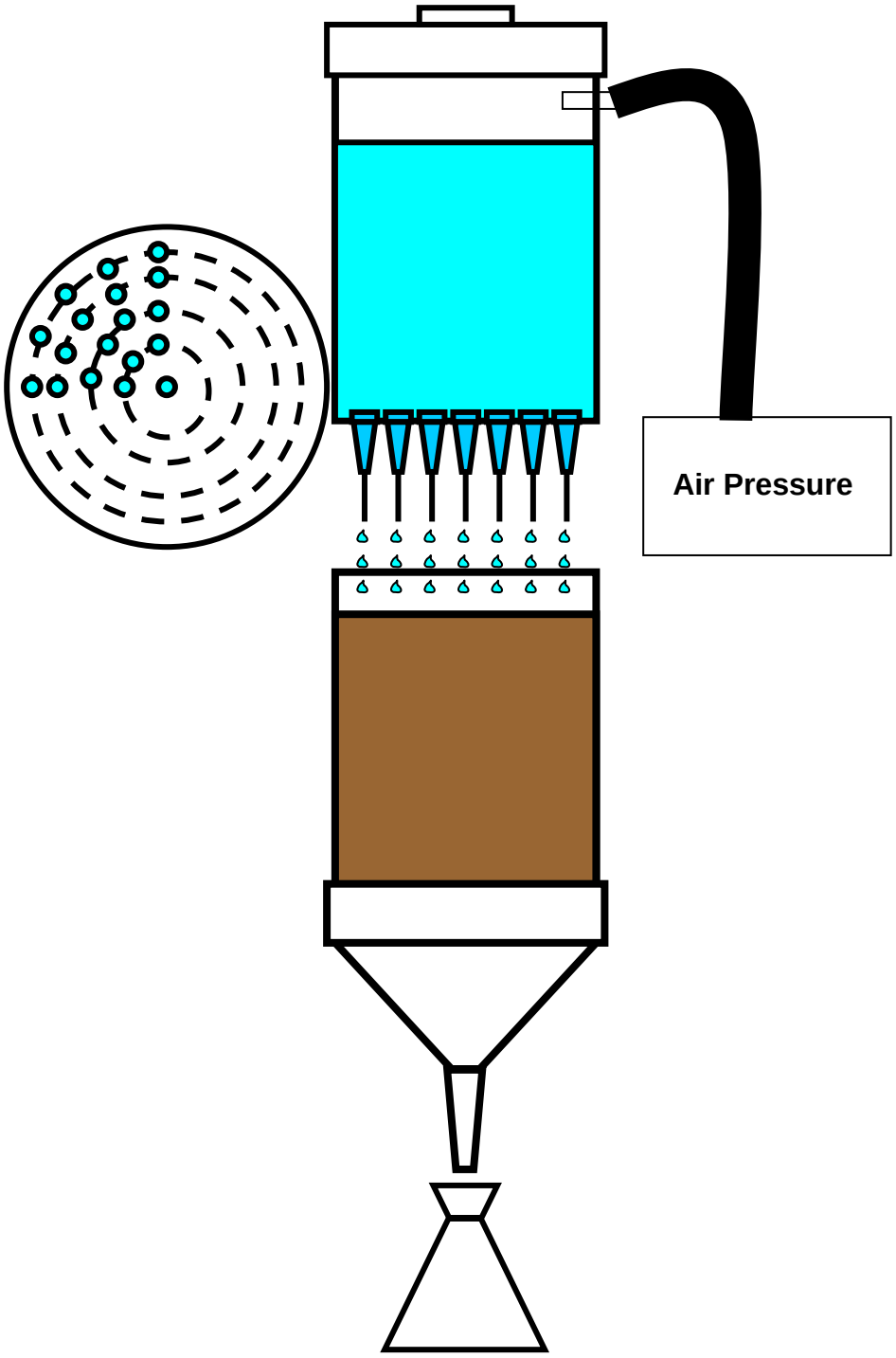


Figure 1. Apparatus constructed for applying simulated rainfall to soil columns.

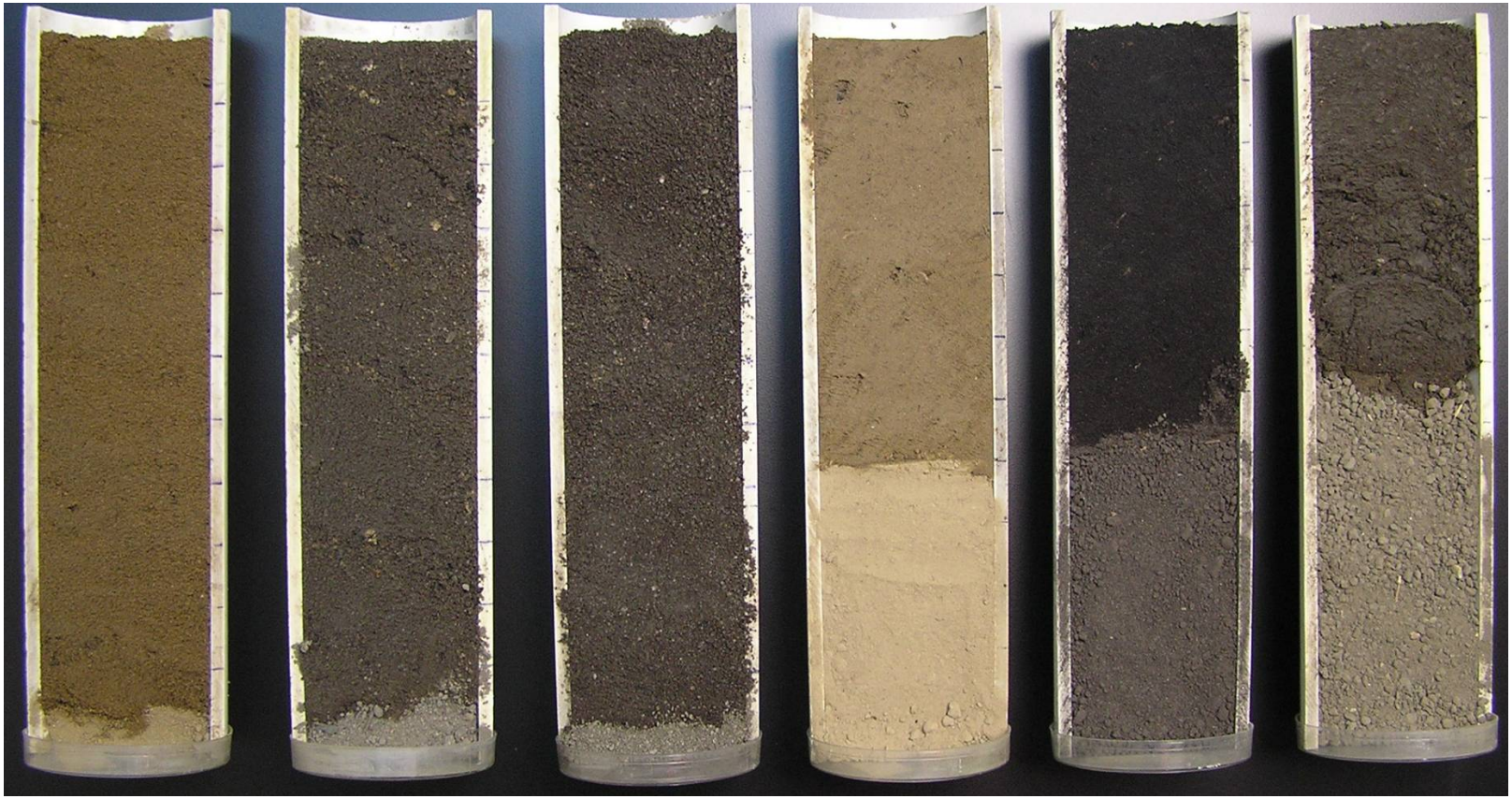


Figure 2. Wetting fronts in soil columns after 2.5 cm of rainfall. From left to right: Candor loamy sand III, Candor loamy sand II, Candor loamy sand I, Dundee silt loam, Arapahoe sandy loam, and Drummer loam.

Figure 3. Mobility of saflufenacil through columns packed with surface soil. Mobility index (MI) for each compound and soil combination, with greater mobility index values indicating more movement through each soil. Mobility Index (MI) = $\sum D \times F$, where D = mean depth, F = fraction of herbicide present (Weber et al., 1999). Error bars represent standard errors (n=4).

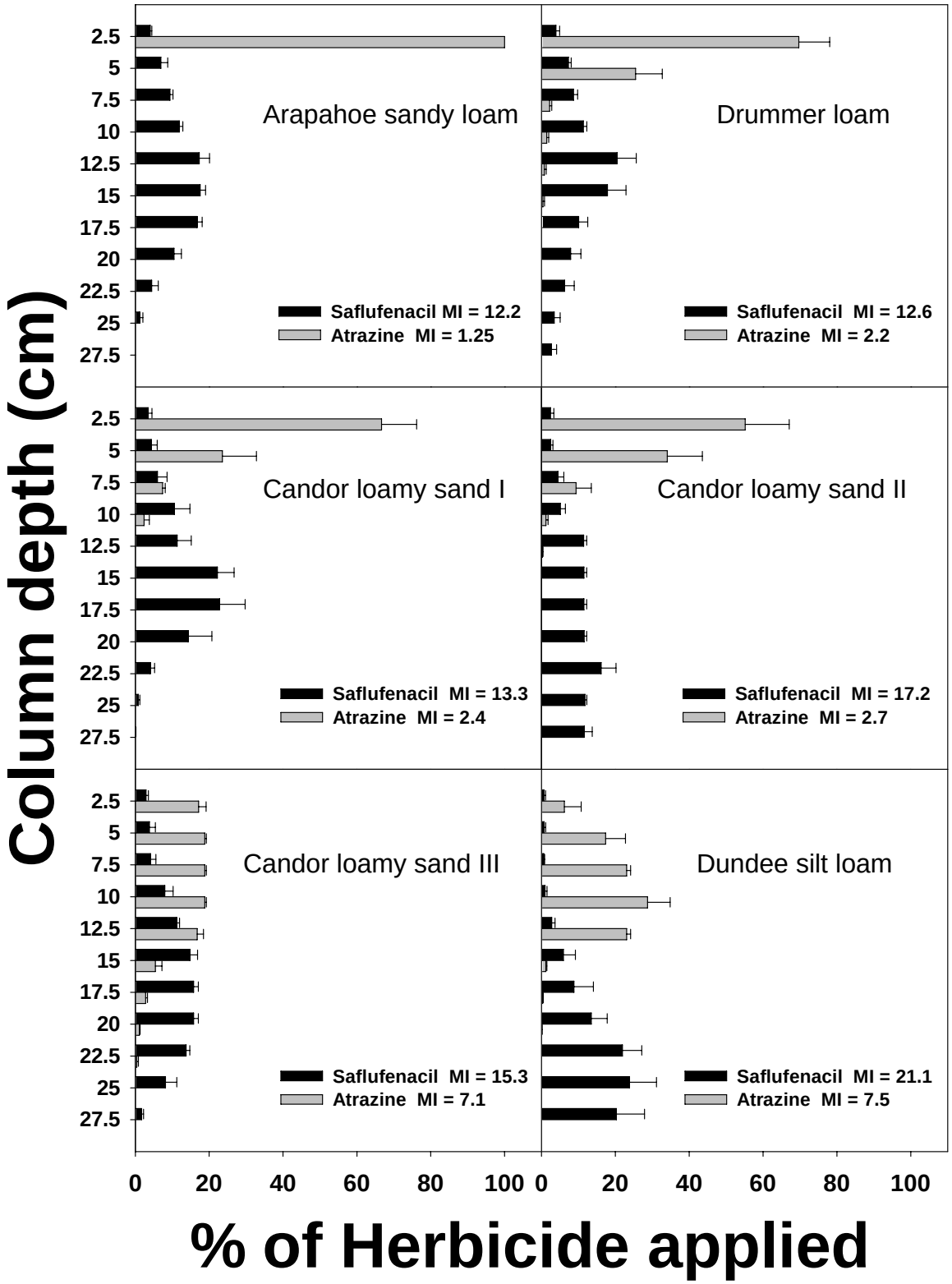
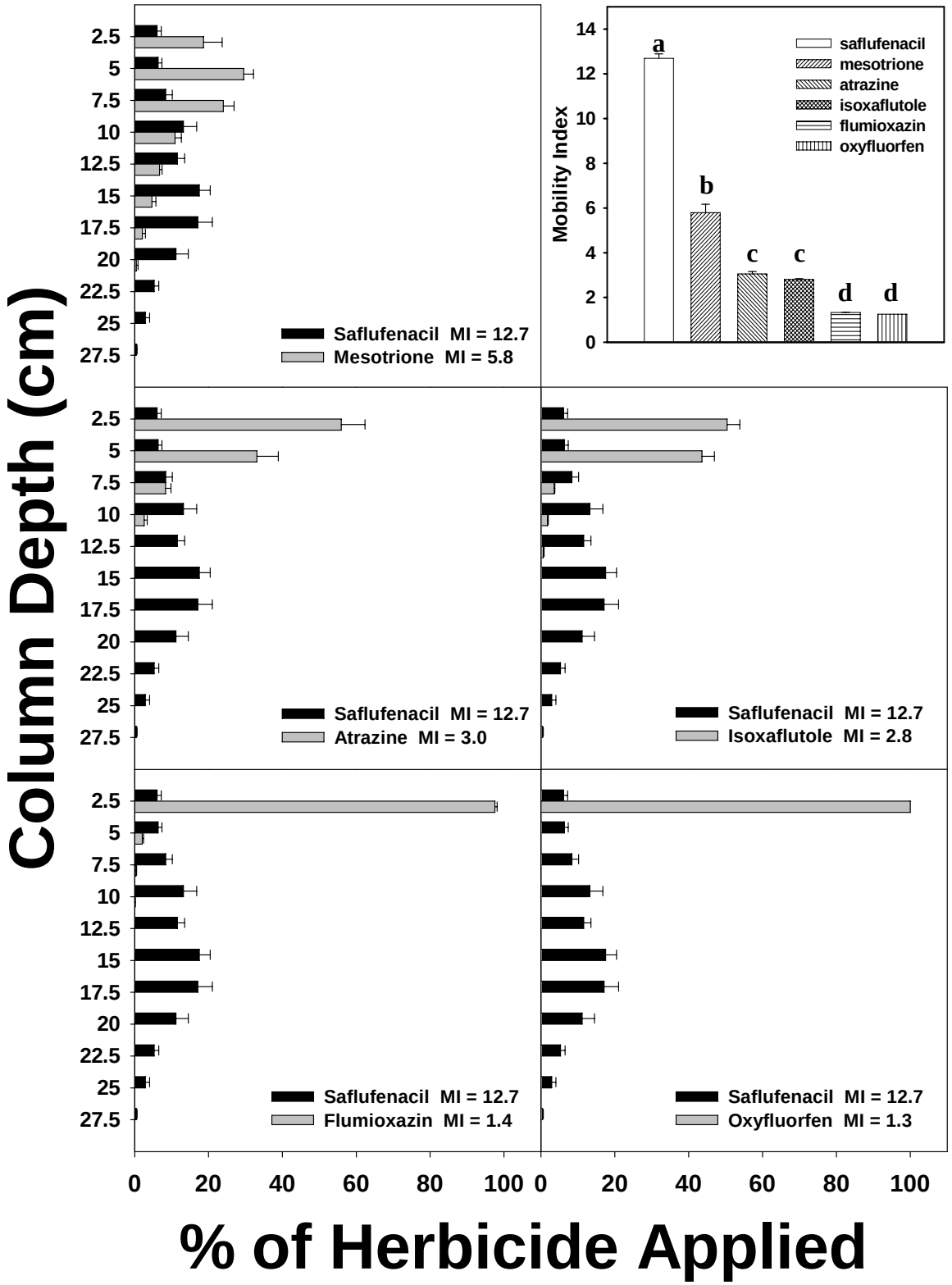

Column depth (cm)
Arapahoe sandy loam
Saflufenacil MI = 12.2
Atrazine MI = 1.25
Drummer loam
Saflufenacil MI = 12.6
Atrazine MI = 2.2
Candor loamy sand I
Saflufenacil MI = 13.3
Atrazine MI = 2.4
Candor loamy sand II
Saflufenacil MI = 17.2
Atrazine MI = 2.7
Candor loamy sand III
Saflufenacil MI = 15.3
Atrazine MI = 7.1
Dundee silt loam
Saflufenacil MI = 21.1
Atrazine MI = 7.5
2.5
5
7.5
10
12.5
15
17.5
20
22.5
25
27.5
0
20
40
60
80
100
% of Herbicide applied

Figure 4. Mobility of saflufenacil, mesotrione, atrazine, isoxaflutole, flumioxazin, and oxyfluorfen through columns packed with surface soil. Mobility index (MI) for each compound, with greater mobility index values indicating more movement through Candor loamy sand I. Mobility Index (MI) = $\sum D \times F$, where D = mean depth, F = fraction of herbicide present (Weber et al., 1999). Vertical bars are average mobility index for each herbicide. Letters above each bar indicate differences among herbicides based upon Fisher's Protected LSD at the 5% level. Error bars represent standard errors (n=4).


Column Depth (cm)
% of Herbicide Applied
Saflufenacil MI = 12.7
Mesotrione MI = 5.8
Saflufenacil MI = 12.7
Atrazine MI = 3.0
Saflufenacil MI = 12.7
Isoxaflutole MI = 2.8
Saflufenacil MI = 12.7
Flumioxazin MI = 1.4
Saflufenacil MI = 12.7
Oxyfluorfen MI = 1.3
Mobility Index
saflufenacil
mesotrione
atrazine
isoxaflutole
flumioxazin
oxyfluorfen
a
b
c
c
d
d

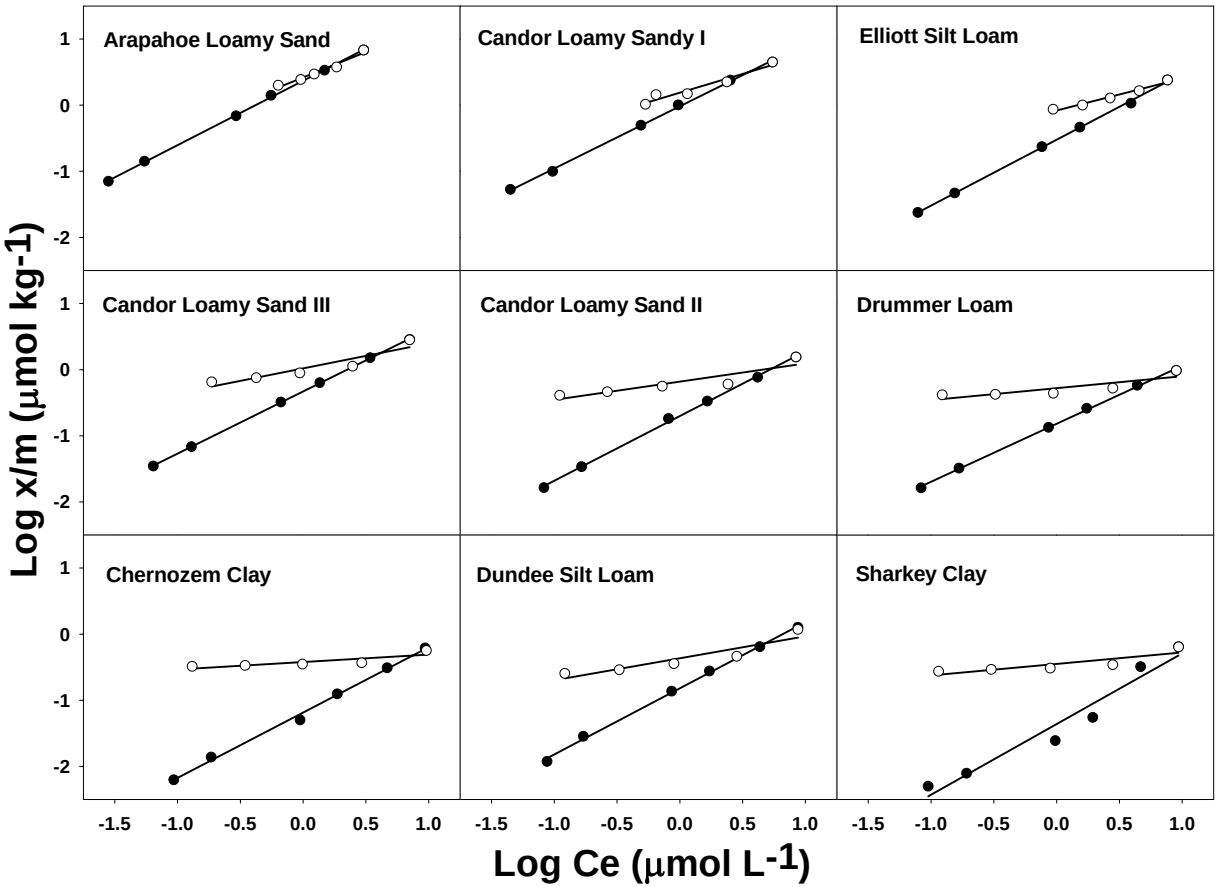


Figure 5. Sorption-desorption isotherms for saflufenacil in all soils. Open circles indicate the desorption isotherm, and closed circles indicate the sorption isotherm.

INFLUENCE OF SAFLUFENACIL SOIL PLACEMENT ON SOYBEAN (*GLYCINE MAX*) TOLERANCE

(Formatted for submission to Weed Technology)

Adam C. Hixson, Kyle E. Keller, and Jerome B. Weber*

Growth chamber and greenhouse studies were conducted to determine soybean 'Hutcheson' response to selective placement of a five-cm layer of saflufenacil-treated soil above, below, or above plus below soybean seed. Soybean shoots only, roots only, shoots + seed, roots + seeds, and shoots + roots + seeds were exposed to soil concentrations of saflufenacil at 57 and 114 µg/kg (equivalent to 40 and 80 g ai/ha). Soybean roots + seeds and shoots + roots + seeds exposure reduced plant height at least 39%, shoot dry weights at least 42%, and root dry weights at least 68%. Soybean growth reduction was greatest when root + seed and shoot + root + seed was exposed to saflufenacil. In general, shoot only and shoot + seed exposure resulted in less plant injury, height reduction, and dry weight reduction. Injury symptoms differed depending on the part of the soybean plant exposed to

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saflufenacil. Shoot exposure resulted in blackening (necrosis) of the stem at the soil surface, while root exposure caused leaf chlorosis with no stem necrosis. Difference of injury symptoms indicates more absorption and translocation of saflufenacil to leaves via roots and xylem tissue. Stem injury associated with shoot exposure appears to be primarily contact injury because little leaf chlorosis occurred.

Nomenclature: Saflufenacil, [*N*′-[2-chloro-4-fluoro-5-(3-methyl-2,6-dioxo-4-(trifluoromethyl)-3,6-dihydro-1(2*H*)-pyrimidinyl)benzoyl]-*N*-isopropyl-*N*-methylsulfamide].

Key words: soybean, site of uptake, tolerance.

Saflufenacil (Figure 1), a new herbicide for use in soybean and other crops, is a weakly acidic (pK_a = 4.4), highly aqueous soluble herbicide (30 mg/L at pH 5 and 2100 mg/L at pH 7) used to control broadleaf weeds when applied pre- or postemergence) (BASF Agricultural Products 2008). Weed control occurs when saflufenacil inhibits protoporphyrinogen oxidase in the chlorophyll biosynthetic pathway. Despite the possibility for saflufenacil to injure soybean associated with varietal difference in sensitivity, this herbicide has potential for use in soybean weed management. As weed resistance to glyphosate and acetolactate synthase (ALS) inhibiting herbicides spreads, there will be an increasing need for alternative mode of action herbicides (Heap 2008).

For soil applied herbicides, the site of uptake in plants may be an important factor in determining whether a particular herbicide would be more phytotoxic when incorporated into the soil or when applied to the soil surface. The roots and shoots of plants are the primary absorptive tissues of soil active herbicides (Bromilow and Chamberlain 1995). In either case, the effective absorptive tissue is the relatively young/immature tissue. For roots, it is the root hairs that are particularly effective in herbicide absorption. As either shoot or root tissue matures the outer layers become thickened and form a barrier to absorption of herbicides as well as other compounds. Herbicides whose main site of entry is through the roots may have little effect when applied to the soil surface unless they are moved into the root zone by rainfall or tillage. Some soil applied herbicides are absorbed by plant roots but not shoots, while others are absorbed by plant shoots and less by roots. Therefore, placement of the herbicide in the soil with respect to the site of uptake will influence herbicide efficacy and crop tolerance (Eshel and Prendeville 1967; McLean et al, 2001; Narsaiah and Harvey

1977; Walker 1973). For practical purposes soil applied herbicides are rarely found in phytotoxic concentrations in soil deeper than 7.5 cm. Plants with most of their root systems deeper than 7.5 cm normally are not greatly affected by these herbicides. Soil active herbicides that are absorbed primarily by the shoots (grass coleoptile, broadleaf hypocotyl or epicotyl) of germinating seedlings must be in the zone of soil above the seed when the shoots grow through this zone to be effective.

Soil active herbicides come in contact with the plant through one of three processes, mass flow, contact, or diffusion (Crafts and Yamaguchi 1959; Shone et al. 1974). With mass flow, herbicide molecules are carried along with soil moisture as the plant absorbs water. Contact simply implies that plants come in contact with herbicides in the soil by the roots or shoots growing into the herbicide. The diffusion process is one in which molecules move from an area of high concentration to an area of lower concentration. For any of these three mechanisms to function adequate soil moisture is required. Moisture is required for the plant to be actively growing and absorbing water. Thus, activity of soil applied herbicides is enhanced by good soil moisture conditions and reduced by limited soil moisture.

Some classes of soil active herbicides including the triazines are absorbed by the roots of plants but not the shoots. It has been reported that such herbicides as simazine and diuron are more effective when applied early in the season to allow some leaching before germination begins (Hartley 1964). Differential placement of simazine with respect to the absorptive tissue of plants is a technique used to achieve selectivity. Simazine placed on the soil surface in tree plantings is moved into the top few inches of soil with rainfall where it is absorbed by the shallow root system of germinating weeds resulting in their control (Majek

and Welker 1990). The bulk of the root system of established trees is much deeper in the soil than 2.5 to 5 cm and hence the tree root system does not come in contact with the simazine.

Weed control and crop tolerance of many dinitroanilines and chloroacetamides are dependent upon herbicide placement in the soil (Appleby and Valverde 1989; Roggenbuck and Penner 1987). For example, trifluralin is registered for control of unemerged weeds in corn when applied after the corn has developed two leaves. By the 2- leaf stage the shoots of corn and weeds have a well developed outer layer that prevents absorption of trifluralin that may contact the shoot. Since trifluralin is very immobile in the soil it does not move deeply enough into the soil to come in contact with the immature (meristematic) portions of the root system of established corn or weeds. In contrast, the shoots of germinating weed seedlings absorb trifluralin from the surface soil and are controlled. Propachlor and alachlor in the soil have been determined to be primarily shoot absorbed (Knake and Wax 1968). As a result, leaching of these herbicides below the weed seed zone significantly reduces efficacy. Cotton (*Gossypium hirsutum* L.) and corn (*Zea mays* L.) tolerance to alachlor was based primarily on depth protection and is not a result of metabolism to nontoxic forms within the plant (Eshel 1969; Narsaiah and Harvey 1977). Other studies also reported that soil placement of herbicides had a large effect on tolerance of peas and field beans (Eshel et al. 1975; Glasgow and Dicks 1980). Therefore, saflufenacil soil placement and/or soybean planting depth could be major factors in determining soybean tolerance and weed control efficacy.

Our primary objective was to determine the importance of saflufenacil positioning relative to soybean seed placement, and develop strategies to increase soybean tolerance and efficacy on key broadleaf weeds.

Materials and Methods

The soil used was Candor loamy sand (sandy, siliceous, thermic Grossarenic Kandiudult) collected from the top 15-cm soil depth near Lemon Springs, North Carolina. Soil was air-dried and passed through a 4-mm sieve. Particle size was determined by the hydrometer method (Gee and Orr 2002). Percent soil organic matter (OM) was determined using a colorimetric Walkley-Black procedure (Nelson and Sommers 1982). Soil pH was determined using a glass electrode and reference buffers on a 1:1 soil to water mixture (Peech 1965). Effective cation exchange capacity (CEC) was measured using the summation of exchangeable cations procedure described by Mehlich (1984).

A previously determined sensitive soybean variety, 'Hutcheson', was used as the bioassay species to determine site of plant uptake of saflufenacil. Experiments were conducted in a growth chamber[1] with day/night temperature of 25/15 °C and relative humidity of 80%. Following germination transferred to a greenhouse with day/night temperatures of 27/22 °C and relative humidity similar to ambient. Supplemental lighting (400 $\mu E/m^2/s$) provided a 14-h photoperiod in both areas. A nutrient solution was applied on a weekly basis starting 7 days after planting.

An aqueous solution of saflufenacil [2] was prepared to establish soil concentrations of 57 and 114 $\mu g\ kg^{-1}$, equivalent to 40 and 80 g ai/ha, that were mixed into the top five centimeters of soil. The solution provided sufficient water to bring the soil to 6% moisture content at the time of incorporation. Saflufenacil was applied in a manner similar to

Richburg et al. (1994). A four × two × two factorial treatment design was employed with four herbicide placement options, two seed placement options and two herbicide concentrations. Selective treatments were either 5 cm of saflufenacil-treated soil at 57 and 114 µg/kg below or 5 cm of treated soil above soybean seeds, with the remaining 5 cm of soil being nontreated (Figure 2). Seeds were either planted in the herbicide treated soil layer or the nontreated layer. This allowed for comparisons between seeds germinating in herbicide treated soil and germinating in nontreated soil. Treatments of 5 cm of soil above plus 5 cm of soil below seeds at 57 and 114 µg/kg and the nontreated control also were included. This treatment selection allows for comparison of saflufenacil at equivalent treatment at 114 µg/kg and is twice as concentrated as the 57 µg/kg rate placed above plus below the seeds. Selective placement was achieved by placing 5 cm of soil in the cup, then a 0.5-cm deep layer of activated charcoal[3] followed by the remaining 5 cm of soil. Four soybean seeds were planted above or below the charcoal layer for the above- or below-seed treatment, respectively, and 5 cm deep in the 5 cm above plus 5 cm below treatment and for the nontreated control. A 3:1 v/v coarse washed sand and activated charcoal mixture was used for the charcoal layers to ensure porosity needed for germinating shoots or roots to penetrate through the layer. The placement of the soybean in herbicide-treated soil allowed for herbicide uptake around the seed itself, which has been demonstrated to be important with other herbicides (Cornelius et al. 1985). Each layer of soil (185 g dry weight) was placed in the cup and brought to field capacity with the appropriate amount of water. To maximize herbicide availability, plants were surface-irrigated and subirrigated daily as needed. Germination count, shoot height, percent leaf chlorosis, stem necrosis and overall percent

growth inhibition was recorded 14 and 21 DAT. At 21 DAT, soybean plants were washed free of soil, sectioned into shoots and roots, weighed immediately and dried 48 h at 60 °C. Weights were recorded per cup and converted to shoot and root fresh and dry weight per plant using germination counts.

The experimental design was a randomized complete block design with three single-pot replicates for each treatment, and the experiment was repeated. Data for each study were transformed to percent reduction relative to the nontreated check. The nontreated check was not included in the analysis because transforming the data to percent reduction relative to the nontreated check would set the nontreated check to 0%. Using SAS[4], Analysis of variance (ANOVA) revealed no significant treatment by experiment interaction and error variances were homogeneous; consequently, data were combined over time for analysis and presentation. Means were separated with the appropriate Fisher's protected LSD test at P = 0.05.

Results and Discussion

Soil used was a Candor loamy sand with 80% sand, 12% silt, 8% clay, 2.2% OM, CEC = 5.2 cmol/kg and pH = 4.9. Saflufenacil bioavailability in this soil is medium to high (Hixson et al. 2008, unpublished data) resulting in an excellent substrate to perform this type of research. Soybean plants were able to absorb saflufenacil through both emerging shoot and root tissue (Table 1). Soybean injury was most severe when shoot, roots and seed were all exposed to the herbicide. There was a rate effect when the 57 µg/kg treatments were

compared to the 114 µg/kg. Root + seed exposure resulted in injury, stunting, chlorosis, and plant weight reduction similar to all the shoot, root, and seed exposure treatments. When the seed was planted in the untreated zone which resulted in the shoot or root allowed to grow into the treated zone, less visual injury occurred (Table 1). This shows that newly emerged tissue from the seed is very susceptible to damage by saflufenacil.

Aboveground symptomology differed when roots and shoots were exposed to saflufenacil separately. Stem necrosis (blackening) only occurred when shoots grew through herbicide treated soil (Figure 3, Table 1). Visual plant injury was usually lower when only shoots were exposed to saflufenacil with 19 and 48% for 57 and 114 µg/kg treatments, respectively (Table 1). When only roots were exposed to the herbicide, leaf chlorosis occurred, but stem necrosis was absent (Figure 4, Table 1). Although injury symptoms were different from shoot only exposure, visual plant injury was similar with 18 and 55% for 57 and 114 µg/kg treatments, respectively. Root + seed exposure resulted in greater plant injury with 47 and 73% injury for 57 and 114 µg/kg treatments, respectively (Table 1). Differences in leaf chlorosis between shoot and root exposure did not occur with the 57 µg/kg concentration, but the higher rate caused more leaf chlorosis when the roots were exposed to saflufenacil (Table 1). The stem necrosis appeared to be from contact injury, with very little absorption and translocation, while leaf chlorosis was a symptom of greater absorption and translocation from the root system.

Soybean height was consistently lower than the controls with all herbicide treated pots (Table 2). Although slight stunting occurred with the shoot only, shoot + seed, and root only exposure, greatest plant height reduction occurred with the total pot treatments and root

+ seed exposure. Soybean plant height was reduced 39 and 57% when root + seed was exposed to 57 and 114 µg/kg, respectively (Table 2). Shoot only and shoot + seed exposure resulted in less stunting with 30% height reduction for both saflufenacil concentrations. Total plant exposure caused soybean plant height reductions greater than 41 and 70% for 57 and 114 µg/kg, respectively (Table 2). This indicates severe stunting could occur if saflufenacil is able to move into the seed zone or slightly below the seed zone of soybeans.

Dry plant weight trends were similar to those associated with plant heights. In general, root reduction was greater than shoot reduction for all treatments and was the primary contributor to total plant weight reduction (Table 3, Figure 5). Root + seed exposure was similar to all total plant exposure treatments with a 42 and 73% reduction in shoot dry weight and 73 and 81% root dry weight for 57 and 114 µg/kg, respectively. Root only, shoot only, and shoot + seed treatments did not reveal any differences between plant weight reduction percentages. For these treatments, shoot reductions ranged from 15 to 24% and 19 to 30% for 57 and 114 µg/kg, respectively. Root reductions were much higher ranging from 49 to 56% and 60 to 70% for 57 and 114 µg/kg, respectively. Although significant injury still occurred with these treatments, dry plant weight reductions were always less than total plant exposure for shoots, roots, and total plant.

These data indicate that soybean injury can occur when shoots and roots are exposed separately or together. Injury symptoms differ depending on the part of the soybean plant exposed. Shoot only and shoot and seed exposure resulted in stem necrosis, with very little leaf chlorosis and stunting. Root only and root and seed exposure resulted in leaf chlorosis and stunting with no stem necrosis. Highest total plant injury occurred when the shoot, root,

and seed were exposed to the herbicide. Therefore, greatest injury will occur if saflufenacil is able to move into the soybean seed zone. Previous research (Hixson et al. 2008, unpublished data) has shown that saflufenacil is mobile in soil and with sufficient rainfall could move deeper in the soil profile. Therefore, more stunting and leaf chlorosis of susceptible soybean varieties may occur with rainfall after a preemergence or preplant application. Alternatively, if saflufenacil remains above the planting depth, less stunting occurs, but stem necrosis could cause a lodging concern.

Preliminary research on differences in tolerance among soybean varieties has shown that there are extreme differences for each variety. This will be the focus of much research in the future. Similar soybean tolerance studies have been conducted with sulfentrazone. Although sulfentrazone is labeled for use in soybeans, differences in tolerance among soybean varieties has been reported (Dayan et al. 1997; Li et al. 1999; Taylor-Lovell et al. 2001). Results from research conducted in an environmentally controlled greenhouse are difficult to extrapolate into field situations, but decisions for future research on use patterns could result. Environmental conditions may have a large affect on the amount of soybean injury caused by saflufenacil. The average field half-life (DT_{50}) at seven sites for saflufenacil is 17 d and the average aerobic half-life ($t_{1/2}$) for four soils is 15 d (BASF Agricultural Products 2008). Therefore, where conditions are warm and moist, herbicide degradation is likely to be enhanced. Because saflufenacil degrades rapidly under these conditions, less of the herbicide will be available for plant uptake at the time of soybean emergence. Cool and dry conditions could lengthen the disappearance time, and cause an increased opportunity for injury. Saflufenacil has the potential to cause severe soybean

injury under certain environmental conditions. However, recommendations of tolerant soybean varieties will reduce the potential for injury from saflufenacil. Future research will be necessary to confirm tolerance differences among soybean varieties.

Sources of Materials

[1] Conviron® reach-in growth chamber, Controlled Environments Limited, 590 Berry Street, Winnipeg, Manitoba Canada, R3H 0R9.

[2] Saflufenacil, BASF Corporation, Agricultural Products Division, 26 Davis Drive, Research Triangle Park, NC 27709

[3] Activated charcoal powder, J. T. Baker, A Division of Mallinckrodt Baker, Inc., Phillipsburg, NJ, 08865.

[4] SAS, Statistical Analysis Systems, 2003, Release 9.1, Statistical Analysis Systems Institute, Cary, NC 27513.

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Table 1. Visual soybean injury, leaf chlorosis, and stem necrosis 14 days after exposure of shoots, roots, shoots + seeds, roots + seeds, or roots + shoots + seeds to saflufenacil at 57 µg/kg and 114 µg/kg.[a,b]

		57 µg/kg			114 µg/kg		
Exposure	Seed Placement[c]	Plant injury	Leaf chlorosis	Stem necrosis	Plant injury	Leaf chlorosis	Stem necrosis
		%					
Root + Shoot + Seed	No AC	84.2a	75.8a	93.3a	95.0a	85.0a	100a
Root + Shoot + Seed	Above	55.0c	63.3b	62.1b	85.0b	80.0a	85.0bc
Root + Shoot + Seed	Below	67.5b	65.0b	59.7bc	90.0ab	88.3a	90.0b
Shoot + Seed	Above	20.8d	15.8c	50.0c	35.8e	26.7c	82.7c
Root + Seed	Below	46.7c	22.5c	0d	73.3c	45.8b	0d
Root	Above	17.5d	15.0c	0d	55.0d	53.0b	0d
Shoot	Below	19.2d	16.7c	62.4b	47.9d	25.8c	82.5c

[a] Abbreviations: AC, activated charcoal

[b] Values followed by the same letter do not differ from each other at the 5% level of significance according to Fisher's Protected LSD.

[c] Seed placement above or below the activated charcoal layer.

Table 2. Soybean height 21 days after exposure of shoots, roots, shoots + seeds, roots + seeds, or roots + shoots + seeds to saflufenacil at 57 µg/kg and 114 µg/kg.[a,b]

Exposure	Seed Placement[c]	57 µg/kg		114 µg/kg	
		Plant height	Reduction	Plant height	Reduction
		cm	%	cm	%
Control	No AC	12.6b	-	12.6b	-
Control	Above	13.8a	-	13.8a	-
Control	Below	13.5ab	-	13.5ab	-
Root + Shoot + Seed	No AC	4.40e	65.6a	1.30g	89.9a
Root + Shoot + Seed	Above	8.10d	41.3b	4.00f	70.6b
Root + Shoot + Seed	Below	5.50e	59.1a	3.30f	75.6b
Shoot + Seed	Above	10.9c	20.4c	10.8c	29.6d
Root + Seed	Below	8.20d	39.0b	5.80e	56.8c
Root	Above	11.0c	15.7c	9.60d	30.3d
Shoot	Below	11.4c	21.9c	9.50d	21.7d

[a] Abbreviations: AC, activated charcoal

[b] Values followed by the same letter do not differ from each other at the 5% level of significance according to Fisher's Protected LSD.

[c] Seed placement above or below the activated charcoal layer.

Table 3. Soybean dry plant weights 21 days after exposure of shoots, roots, shoots and seeds, roots and seeds, or roots, shoots, and seeds to saflufenacil at 57 µg/kg and 114 µg/kg.[a,b]

Exposure	Seed Placement[c]	57 µg/kg						114 µg/kg					
		Shoot	Root	Total	Shoot	Root	Total	Shoot	Root	Total	Shoot	Root	Total
		g			% Reduction			g			% Reduction		
Control	No AC	0.32ab	0.19b	0.51c	-	-	-	0.32ab	0.19b	0.51c	-	-	-
Control	Above	0.37a	0.40a	0.77a	-	-	-	0.37a	0.40a	0.77a	-	-	-
Control	Below	0.34ab	0.32a	0.66b	-	-	-	0.34a	0.32a	0.66b	-	-	-
Root + Shoot + Seed	No AC	0.16e	0.06d	0.23f	58.1a	65.3ab	61.4a	0.11d	0.05cd	0.17e	73.9a	68.0b	60.9a
Root + Shoot + Seed	Above	0.24d	0.09cd	0.33de	34.4bc	77.1a	56.5a	0.15d	0.04d	0.19e	66.0ab	90.4a	74.5a
Root + Shoot + Seed	Below	0.17e	0.07d	0.25ef	47.3ab	77.4a	62.3a	0.11d	0.05cd	0.16e	69.3ab	84.9a	75.3a
Shoot + Seed	Above	0.31b	0.19b	0.50c	15.3d	49.9c	33.4b	0.27bc	0.14b	0.41cd	26.4c	62.5b	42.9b
Root + Seed	Below	0.20e	0.09cd	0.28ef	41.5b	73.1a	61.2a	0.16d	0.06cd	0.22e	52.0b	81.3a	68.9a
Root	Above	0.29bc	0.18b	0.47c	20.2d	55.9bc	41.8b	0.36a	0.14b	0.50c	19.0c	69.6b	38.3b
Shoot	Below	0.25cd	0.16bc	0.42cd	24.4cd	48.8c	39.4b	0.24c	0.13bc	0.36d	29.5c	60.3b	39.0b

[a] Abbreviations: AC, activated charcoal

[b] Means within a column followed by the same letter are not different according to Fisher's Protected LSD at P = 0.05.

[c] Seed placement above or below the activated charcoal layer.

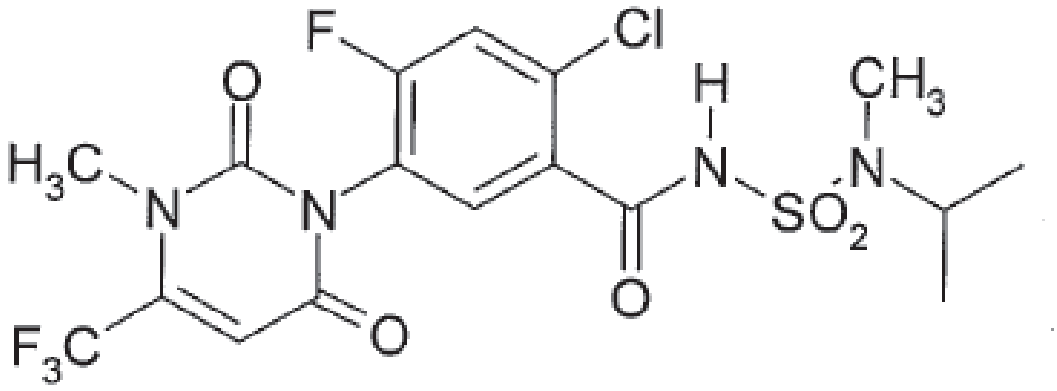

Figure 1. Chemical structure of saflufenacil.

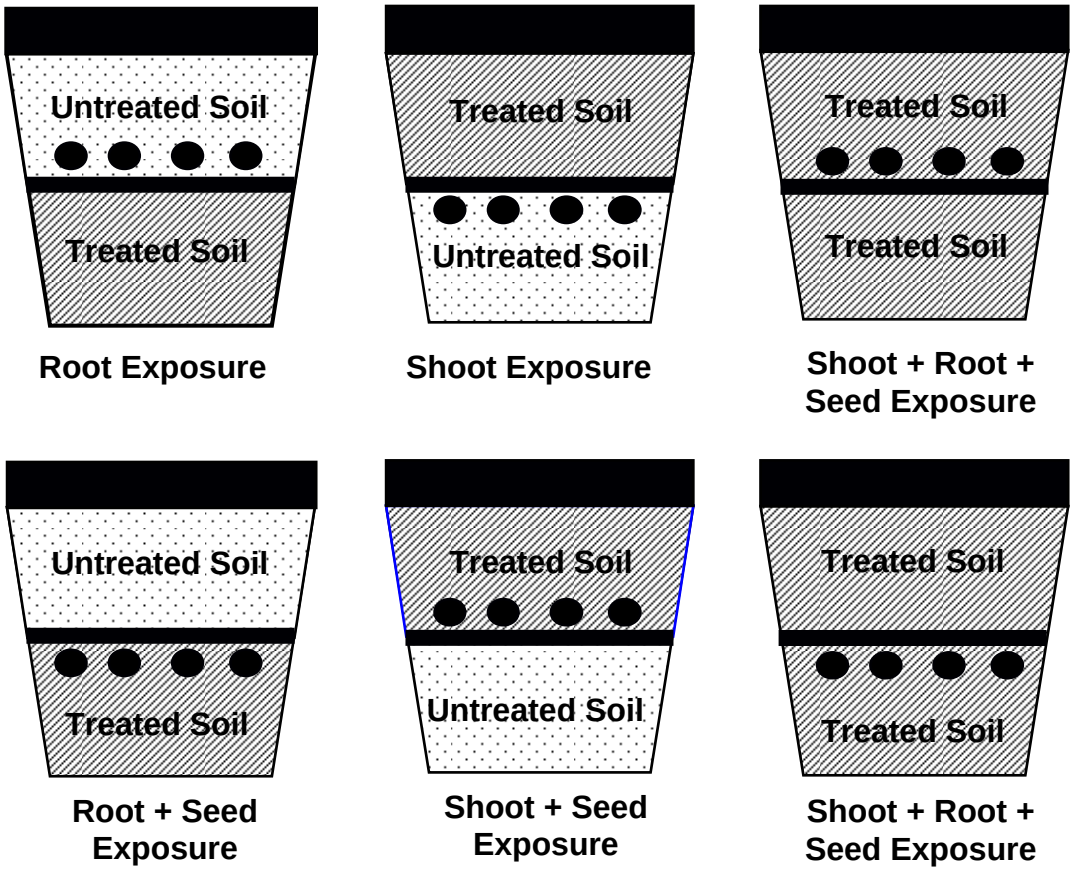

Figure 2. Schematic of treatment layouts. Black line in middle of pot represents 0.5 cm activated charcoal layer and the four ovals represent the 'Hutcheson' soybean seeds.

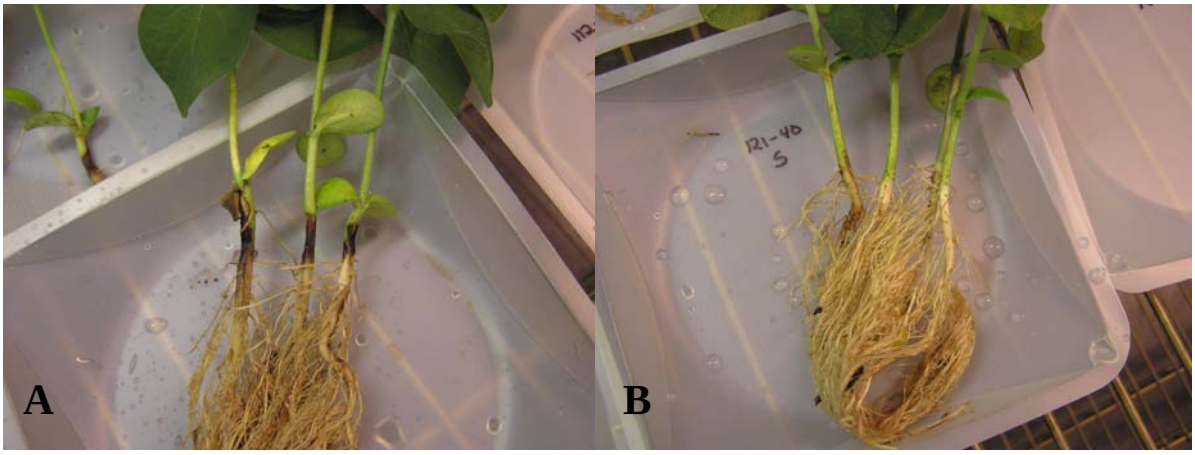

Figure 3. Stem necrosis occurring when shoots were exposed to saflufenacil (A); and no stem necrosis occurring when only roots were exposed to saflufenacil (B).

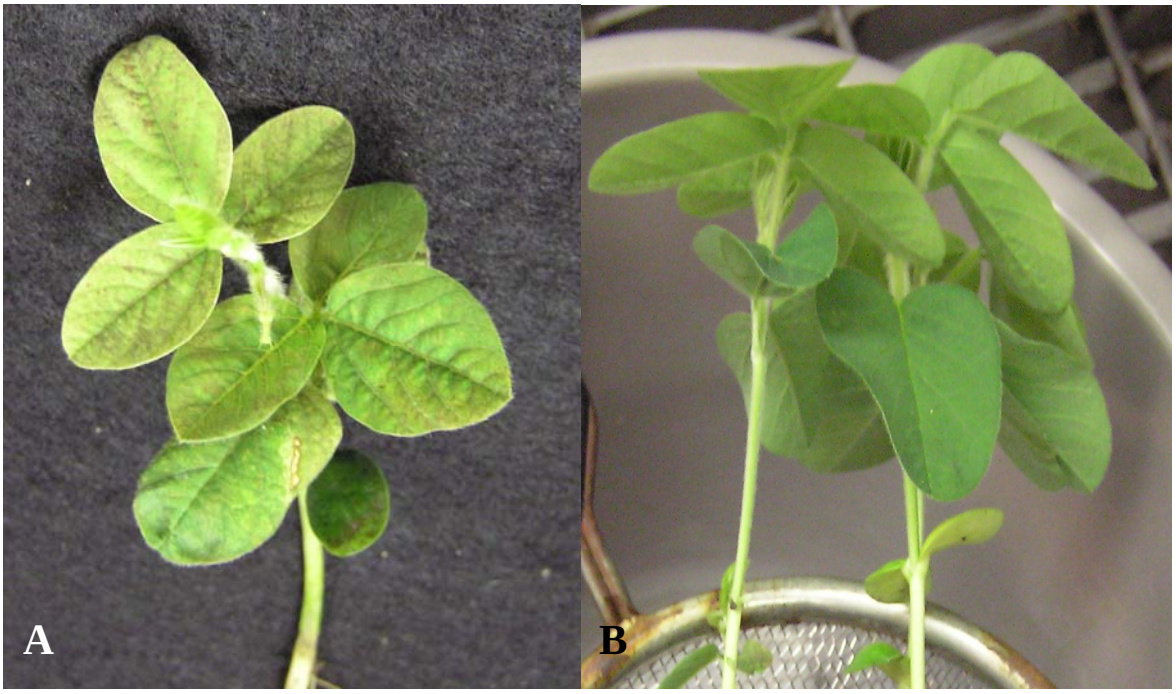

Figure 4. Leaf chlorosis and stunting occurring when roots were exposed to saflufenacil (A), and healthy leaves observed when roots were not exposed to saflufenacil (B).

Figure 5. Left to right: No saflufenacil, shoot + seed exposure, and root + seed exposure. Soybean plants were exposed to 114 µg/kg.