

LATERAL MOVEMENT OF HERBICIDES ON GOLF COURSE FAIRWAYS AND
EFFECTS ON BENTGRASS GREENS

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Abstract

Concern has been raised that herbicides recently registered for use in warm-season turf to control perennial ryegrass could be dislodged from treated areas and deposited on neighboring cool-season grasses. In a field study, rimsulfuron was applied at 17.5 or 35 g ai/ha to perennial ryegrass in the afternoon; the following morning while dew was still present, a greens mower was driven through the perennial ryegrass and across adjacent creeping bentgrass. Irrigation had no effect on perennial ryegrass control but reduced visible track length and injury of neighboring creeping bentgrass. When treated perennial ryegrass was not irrigated prior to simulated mowing, tire tracks were evident on adjacent creeping bentgrass for up to 30 days. Gibberellic acid at 0.12 kg ai/ha and foliar iron at 1.3 kg ai/ha, applied to creeping bentgrass when tracks first appeared, did not enhance recovery of injured creeping bentgrass. Persistence and stability of [2-pyridine ¹⁴C] rimsulfuron on turf foliage was also assessed. Rimsulfuron was absorbed by annual bluegrass and perennial ryegrass equivalently and persisted equally on turf foliage. Water extractable rimsulfuron decreased from 60% at 10 minutes after treatment to 40% at 96 hours after treatment. A substantial amount of stable rimsulfuron persists on turf foliage for up to four days. Results from both studies suggest that when applying rimsulfuron near susceptible bentgrass the lowest effective rate should be used, and irrigation should follow two hours after treatment to prevent nontarget injury.

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Chapter I. Literature Review

Virginia lies in the transition zone, an area where seasonal climatic changes are extreme enough to grow warm-season turfgrass species during late spring, summer and early fall and cool-season turfgrass species during late fall, winter and early spring. Despite the fact that Virginia's climate is conducive to growing both cool- and warm-season turfgrass, neither is well-adapted year-around. Thus many Virginia golf courses maintain a two-grass fairway system of bermudagrass (*Cynodon dactylon* (L.) Pers.) overseeded with perennial ryegrass (*Lolium perenne* L.) (Virginia's Turfgrass Industry 2000). Bermudagrass has the ability to rapidly recover and withstand wear and tear (Palmtree 1975) during the summer, but undergoes a dormant state after the first killing frost and remains brown during the winter (Bingham et al. 1969). Overseeding perennial ryegrass in dormant bermudagrass can prevent damage or thinning by equipment and foot traffic, reduce weed infestation, and provide a year-around aesthetic playing surface (Mazur and Wagner 1987).

Perennial ryegrass is the most versatile cool-season grass for overseeding. There are several advantages to perennial ryegrass; it establishes quickly, can be mowed at low heights desirable for greens and fairways, and has the desired fine texture (Ward et al. 1974). These characteristics have made perennial ryegrass the most commonly used grass in Virginia for overseeded bermudagrass fairways.

Management of overseeded areas can be difficult during transition, when bermudagrass breaks dormancy and begins to green up. The desirable transition timing at

each course is the basis for how the transition period is handled (Palmertree 1975). Timing of tournaments and member preferences are considered when determining the most desirable time to return to a bermudagrass monoculture. A gradual transition is desirable to maintain an acceptable green playing surface. The ideal time to transition and maintain high aesthetics is when bermudagrass breaks dormancy, but before competition becomes a problem. Bingham et al. (1969) reported that competition between overseeded cool-season grasses and bermudagrass impedes bermudagrass green-up. Slow green-up has detrimental effects on bermudagrass health, leading to reduced tolerance to disease, drought, and winter-kill (DiPaola 1987). Both chemical and cultural methods are used to control the overseeded grass to prevent this problem. Improving perennial ryegrass tolerance to heat, drought and disease has made it more difficult to transition from a two-grass system to bermudagrass monoculture. Many cultural practices such as different mowing heights, fertilization timing, soil moisture management, coring, aeration, top dressing and vertical mowing can have an effect on transition (DiPaola 1987; Duble 1982; Horgan and Yelverton 2001; Kopec et al. 2001; Mazur and Wagoner 1987; Palmertree 1975). Conflicting results have been reported on effectiveness of using aeration, topdressing, and vertical mowing to transition back to a bermudagrass monoculture (Duble 1982; Horgan and Yelverton 2001; Mazur and Wagoner 1987).

Likewise, increased seeding rates are thought to reduce heat and drought tolerance in perennial ryegrass and cause plants to produce fewer tillers. But increased seeding rates alone did not create a smooth transition in May, the desirable time to transition in

most areas of Virginia (Kopec et al. 2001). Because cultural methods give unpredictable and inconsistent results, herbicides have been evaluated for use as transition aids.

The desired function of transition aids is to selectively control perennial ryegrass with minimal injury to warm season turfgrass. Numerous chemical options have been evaluated as transition aids; however, most evaluations have given less than promising results. Chemicals that have been assessed include diclofop, dithiopyr, metribuzin, ethephon, mefluidide, meleic hydrazide, oxadiazon, butralin, MSMA, methazole, benefin, oryzalin, glyphosate, parquat, pendimethalin, pronamide, chlorsulfuron, metsulfuron, rimsulfuron, foramsulfuron, flazasulfuron, and trifloxysulfuron (Askew et al. 2002; Barker et al. 2003; Johnson 1994; Johnson 1988; Johnson 1977; Johnson 1976; Mazur 1988). The first herbicide to control perennial ryegrass without harming bermudagrass was pronamide, which was first evaluated during the 1970's (Johnson 1976). Subsequently five additional chemicals have been registered for that same purpose, including chlorsulfuron, rimsulfuron, foramsulfuron, trifloxysulfuron, and metsulfuron. These five chemicals are all members of the sulfonylurea herbicide family and inhibit acetolactate synthase (A.K.A. acetohydroxyacid synthase). Acetolactate synthase is a key enzyme in the formation of the branched chain amino acids leucine, valine, and isoleucine (Hawkes et al. 1989). Sulfonylureas have only been commercialized since 1981, when chlorsulfuron was first registered for use in cereal crops. Sulfonylureas are popular because they require extremely low application rates, are relatively nontoxic to animals, and have high plant specificity (Obrigawitch 1998). While lower application rates are more environmentally friendly, there is still a potential of nontarget injury from sulfonylureas. Herbicides can move offsite through drift, lateral movement in rainwater

drainage, leaching, volatility and lateral movement by dislodging unabsorbed herbicide from the leaf surface. The amount of chemical moved may be enough to injure or kill a nontarget plant since these chemicals are effective at such low rates.

Chemical persistence on leaf surfaces may influence potential for lateral movement. Herbicides such as rimsulfuron remaining on the leaf surface can be moved to nontarget areas. Pure rimsulfuron has little to no stability in water under alkaline conditions, however, formulated rimsulfuron had a typical half-life of 7.5 days in alluvial soil (Martins and Mermound 1999; Schnieders et al. 1993; Scrano et al. 1999; Vicari et al. 1996). Because rimsulfuron is foliar-applied, photolysis is a threat to chemical stability until the herbicide is absorbed into the plant or environment. Rimsulfuron degradation photolysis ranged from one to nine days depending on pH (Scrano et al. 1999). Degradation time of rimsulfuron was pH dependant regardless of formulation (Martins and Mermound 1999; Schnieders et al. 1993; Scrano et al. 1999; Vicari et al. 1996). At 25°C, rimsulfuron had a half-life of 4.7, 7.2, and 0.4 days at pH 5, 7, and 9, respectively with degradation occurring primarily via a contraction of the sulfonylurea bridge (Schneiders 1993). Translocation and metabolism of rimsulfuron have been evaluated but persistence and stability of rimsulfuron has not been reported on plant foliage. Absorption, translocation, and metabolism of rimsulfuron were assessed for three nightshade species to determine differential efficacy (Ackley et al. 1999). Two nightshade (*Solanum* spp.) species absorbed nearly 75% of rimsulfuron within 48 hours after treatment, while the other specie absorbed approximately 50% (Ackley et al. 1999). Similar studies evaluated trifloxysulfuron absorption in cotton (*Gossypium hirsutum* L.), spurred anoda [*Anoda cristata* (L.) Schlecht.], smooth pigweed (*Amaranthus hybridus*

L.), jimsonweed (*Datura stramonium* L.), peanut (*Arachis hypogaea* L.), and sicklepod (*Senna obtusifolia* L.), with all species absorbing >50% of the applied herbicide (Askew and Wilcut 2002; Richardson et al. 2002). Therefore, a substantial amount of herbicide still remained on leaf surfaces.

Few studies have examined chemical relocation, and none of these from the standpoint of non-target plant injury. One study determined the amount of dislodgable 2,4-D, mecoprop, and dicamba on turf foliage by determining the extractable amount of herbicide on the leaf surface (Bowhey et al. 1987). At the highest application rate, less than 5% of the total herbicide applied was dislodgable immediately following application (Bowhey et al. 1987). Other studies evaluated potential movement of insecticides on citrus trees (*Citrus* spp.) (Hadjidemetriou et al. 1985) and cotton (Estesen et al. 1982). In both cases, researchers found greater than 50% of applied insecticide present on the leaf surface after 2 days, and detectable amounts persisted for up to 8 days.

This proposed research focuses on undesirable rimsulfuron movement and implications for nontarget injury in areas adjacent to treated turfgrass. Nontarget plant injury is of particular concern on many golf courses where non-susceptible bermudagrass is surrounded by susceptible cool-season turfgrass species. This research focused on the possible movement of rimsulfuron by a golf course greens mower and implication of chemical persistence and stability on turfgrass foliage. Results from this research will provide a better understanding of lateral movement of herbicides in a turfgrass situation.

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Chapter II. Effects of Rimsulfuron Lateral Relocation on Creeping Bentgrass¹

ABSTRACT

Concern has been raised that herbicides often used to control perennial ryegrass in warm-season turf could move laterally or “track” and injure neighboring cool-season grasses. Rimsulfuron was applied at 17.5 or 35 g ai/ha to perennial ryegrass in the afternoon; the following morning while dew was still present, a greens mower was driven through the perennial ryegrass and across adjacent creeping bentgrass. When evaluated 5, 10, and 25 days after treatment, visible track length and creeping bentgrass injury were greatly reduced by irrigating perennial ryegrass 2 hours after treatment or irrigating both perennial ryegrass and creeping bentgrass prior to simulated mowing. Visible injury of tracked turfgrass persisted for 36 days after treatment when irrigation was not applied, and as few as 5 days when both perennial ryegrass and creeping bentgrass were irrigated. Irrigation had no effect on perennial ryegrass control. Gibberellic acid at 0.12 kg ai/ha and foliar iron at 1.3 kg ai/ha, applied when tracks first appeared, did not improve recovery of injured creeping bentgrass. Results suggest when applying rimsulfuron near susceptible bentgrass one should apply the lowest effective rate, and irrigate two hours after treatment to prevent nontarget injury.

¹ Received for publication Date and in revised form Date.

Nomenclature: Rimsulfuron, 2-pyridinesulfonamide, N-(4,6-dimethoxypyrimidin-2-yl)-aminocarbonyl)-3-(ethylsulfonyl); creeping bentgrass, *Agrostis stolonifera* L.

‘Penncross’; perennial ryegrass, *Lolium perenne* L. ‘Pennant II.’

Additional index words: Dislodged pesticide; foliar iron; gibberellic acid; herbicide movement; tracking.

Abbreviations: DATR, days after tracking.

INTRODUCTION

Virginia lies in the climatic transition zone, an area where seasonal changes are extreme enough to grow warm-season turfgrass species during late spring, summer and early fall and cool-season turfgrass species during late fall, winter and early spring (Beard 2000). Many Virginia golf courses maintain a two-grass fairway system due to the variable transition zone climate (Virginia’s Turfgrass Industry 2000). During winter months, warm-season grasses are overseeded with cool-season grasses to remedy brown coloration and decreased turf density (Bingham et al. 1969).

Ideally, this two-grass system should transition back to a bermudagrass [*Cynodon dactylon* (L.) Pers] monoculture in the spring as bermudagrass breaks dormancy.

Perennial ryegrass competition during the summer growing season can have detrimental effects on bermudagrass health, leading to reduced tolerance to disease, drought, and winter kill tolerances (DiPaola 1987). Both chemical and cultural methods are used on post-dormancy bermudagrass to prevent perennial ryegrass competition and promote bermudagrass growth. Research indicates that cultural practices such as aeration,

topdressing, and vertical mowing do not completely alleviate perennial ryegrass competition and lack consistent results across environments (Horgan and Yelverton 2000; Mazur and Wagoner 1987; Duple 1982).

Rimsulfuron is a transition-aiding herbicide that was registered for use in bermudagrass turf in 2001 (Barker et al. 2003). In the months leading up to rimsulfuron registration, select individuals such as golf course superintendents and athletic field managers were provided samples of rimsulfuron for research demonstrations. A Virginia superintendent reported injury on creeping bentgrass putting greens, presumably due to mower tires that transversed an area treated with rimsulfuron. Since rimsulfuron would soon be labeled to control undesirable cool-season grasses on golf fairways, concerns were raised about the potential to dislodge rimsulfuron from treated areas and deposit the chemical onto creeping bentgrass putting greens.

Few studies have examined chemical relocation, and none of these from the standpoint of nontarget plant injury. Even at the highest application rate, less than 5% of applied 2,4-D, MCPP, and dicamba would dislodge from turfgrass foliage within one day after application (Bowhey et al. 1987). In other studies, insecticides were dislodged from citrus trees (*Citrus* spp.) (Hadjidemetriou et al. 1985) and cotton (*Gossypium hirsutum* L.) (Estesen et al. 1982). In both cases, greater than 50% of applied insecticide persisted on leaf surfaces for 2 days, and detectable concentrations were recovered after 8 days.

Although persistence of rimsulfuron on foliage has not been assessed, absorption studies on nightshade species (*Solanum* spp.) indicate that most rimsulfuron absorbs into foliage within the first two hours but at least 25% of rimsulfuron remains on plant foliage for up to four days (Ackley et al. 1999). If persistent rimsulfuron can be washed from

turfgrass foliage via irrigation, the potential to dislodge the chemical and cause injury to neighboring turfgrass may be reduced. Contrary to previous observations in non-turf crops that rimsulfuron only works through foliar absorption (Ahrens 1998), Wehtje and Walker (2002) determined maximum efficacy of rimsulfuron on annual bluegrass is achieved through root absorption. Hence, irrigation is not likely to reduce efficacy of rimsulfuron for weed control in turfgrass due to rapid foliar absorption and subsequent root absorption. Information on the potential for rimsulfuron to dislodge and cause injury to neighboring susceptible grasses is lacking. The objectives of this research were to determine if dislodgable rimsulfuron could cause nontarget bentgrass injury, if nontarget injury from dislodged rimsulfuron can be prevented with irrigation, and if remedial treatments of foliar iron and/or gibberellic acid can decrease recovery time for bentgrass injury caused by rimsulfuron.

MATERIALS AND METHODS

Three field studies were conducted at the Turfgrass Research Center in Blacksburg, VA in 2002 and 2003. Soil was a Groseclose loam (clayey, mixed, mesic, Typic Hapludalfs) with 2% organic matter and pH 6.5. Plots consisted of 2 by 2 m creeping bentgrass flanked on both sides by perennial ryegrass (Figure 1). Studies were conducted as randomized complete block designs with 12 treatments replicated 3 times. For each trial, rimsulfuron was applied to perennial ryegrass in the afternoon; the following morning while dew was still present, a greens mower was driven through the

perennial ryegrass and across adjacent bentgrass plots (Figure 1). Mower tires were rinsed between plots to prevent contamination.

The 12 treatments included a factorial arrangement of two rimsulfuron rates and four irrigation regimes with three remedial treatments and a nontreated control.

Rimsulfuron was applied at either 17.5 or 35.0 g ai/ha , the low and high label rate for overseeded perennial ryegrass control (Anonymous 2001), respectively, in all possible combinations with the four irrigation regimes that consisted of no irrigation, 0.25 cm irrigation on perennial ryegrass two hours after treatment, 0.25 cm irrigation on creeping bentgrass immediately after tracking, and both irrigating perennial ryegrass after treatment and creeping bentgrass after tracking. The three remedial treatments included foliar iron at 1.3 kg ai/ha, gibberellic acid at 0.12 kg ai/ha, or both foliar iron and gibberellic acid (Cooper 1958) after track appearance (2 to 4 days after treatment). Turf color inside and outside tracks and length of visible track were rated at five-day intervals starting at five days after tracking (DATR). The difference in turfgrass color between tracked and nontracked areas is represented by the following equation:

$$[1-(I/O)]* 100 \quad [1]$$

Where I is visually-estimated turfgrass color inside tracked areas or creeping bentgrass and O is turfgrass color outside tracked areas. Turfgrass color was rated on a one to nine scale with one representing dead or brown turfgrass, five representing acceptable turfgrass color, and nine representing dark green turf. The number of days between tracking and no visible track length were recorded separately by plot and used to determine days to complete creeping bentgrass recuperation. The nontreated control was deleted to stabilize variance. Data were considered homogenous based on the

distribution of plotted residuals. Furthermore, arcsine square-root or log transformation was evaluated but did not improve data homogeneity. All data were subjected to analysis of variance to test for appropriate main and treatment effects with partitioning appropriate for the factorial treatment arrangement. A combined analysis was performed and the three trial repetitions were considered a random variable. Appropriate interactions and main effects were tested with the mean square associated with the random variable (McIntosh 1983). Means were separated using Fisher's protected LSD at $P=0.05$. Data were pooled if interactions were not significant.

RESULTS AND DISCUSSION

When comparing irrigation treatments at 5 and 10 DATR, tracks were longest when irrigation was not applied or only the creeping bentgrass was irrigated after tracking DATR (Table 1). The most effective irrigation treatments at 10 DATR were irrigating the perennial ryegrass or both perennial ryegrass and creeping bentgrass and resulted in 1.2 and 0.1 m of visible track, respectively. This is consistent with the absorption studies on nightshade in which approximately 50% of applied rimsulfuron absorbed within six hours (Ackely et al. 1999) and data from unpublished studies indicate 40% of applied rimsulfuron remained on annual bluegrass and perennial ryegrass foliage 4 days after application (Data not shown). By 25 DATR, tracks persisted only when irrigation was not applied (Table 1). Remedial treatments of foliar iron or gibberellic acid did not improve color of injured turfgrass or decrease track length. Tracks were longer 25 DATR when gibberellic acid was applied alone or in combination with foliar

iron than if no remedial treatment was applied. Gibberellic acid has been shown to increase growth when applied to turfgrass (Cooper 1958) and likely accentuated injured turfgrass within the tracked area by increasing the growth rate of surrounding turf.

Turf Color Difference. At 5 DATR, the interaction of rimsulfuron rate and location was significant ($p < 0.0001$) for color difference. In two of three trials, increasing the rimsulfuron rate increased the percent difference in turf color between tracked and nontracked creeping bentgrass at five DATR (Data not shown). Percent difference in turf color five DATR in tracks created by rimsulfuron at 17.5 and 35.0 g ai/ha were 11 and 21, respectively during fall 2002, 13 and 16, respectively during early spring 2003, and 11 and 18, respectively in the late spring of 2003. Thus, tracks were more perceptible when the higher rate of rimsulfuron was applied to perennial ryegrass prior to crossing creeping bentgrass plots with the mower. Creeping bentgrass was stunted within tracked areas and turf foliage was chlorotic, a characteristic of sulfonylurea symptoms on susceptible plants (Porterfield et al. 2002). There was a significant trial by irrigation regime interaction in the change in turf color evaluation at 10 and 20 DATR; however rimsulfuron rate was not significant and data were pooled over the two rimsulfuron rates (Table 2). The percent color difference between tracked and surrounding turfgrass was highest when irrigation was not applied or only the bentgrass was irrigated (Table 2) or when gibberellic acid or foliar iron were applied after track appearance five DATR (Table 2). Wehtje and Walker (2002) concluded both foliar and root absorbed rimsulfuron yield the highest control, however, root absorption is more important than foliar absorption. Many sulfonylurea absorption studies have demonstrated rapid absorption into plant species (Ackley et al. 1999, Askew and Wilcut 2002, Goatley et al.

1990, Mersie and Foy 1987, Olson et al. 1999, Richardson et al. 2002). Ackely et al. (1999) indicated most of the absorbed rimsulfuron absorbed into three nightshade species within two hours after application. Therefore, even if the rimsulfuron was rinsed from creeping bentgrass foliage, irrigating after rimsulfuron relocation would likely not prevent injury due to rapid foliar absorption and continued root absorption. Tracks were most perceptible in fall 2002 at both 10 and 20 DATR (Table 2) compared to the other trials. This difference is most likely because of the time of year the study was conducted. Creeping bentgrass is a cool-season grass species and would be most active during spring and fall, resulting in slowed recovery following stress incurred during summer months (Ward et al. 1974). The larger color difference observed in the fall 2002 trial was more evident as stunting in plots treated with gibberellic acid or foliar iron. Stunting of tracked turf is probably more pronounced after remedial treatment because application of gibberellic acid increases turf growth (Cooper 1958). There was no statistical color difference at any time when either the perennial ryegrass or both perennial ryegrass and creeping bentgrass were irrigated (Table 2), the injury observed in Table 1 was stunting rather than a difference in color. At 10 and 20 DATR, there was no difference in turfgrass color between the nonirrigated plots and the remedial treatments. Both remedial treatments made track injury more perceptible, the foliar iron increased the color of noninjured turf, however not enough to show a statistical difference, and the gibberellic acid increased growth of the noninjured turf making the stunting in the tracks more evident.

Days to Recuperation. Time to complete creeping bentgrass recuperation was significantly influenced by irrigation regime but not trial. Creeping bentgrass completely

recuperated within 26 to 36 days when plots were not irrigated and did or did not receive remedial treatment of gibberellic acid and/or foliar iron (Data not shown). When creeping bentgrass was irrigated, recuperation time was reduced to 18 days; this reduction is perhaps a product of reduced absorption. Rimsulfuron continues to absorb into the foliar portions of the plant over time, but a substantial amount absorbs rapidly (Ackley et al. 1999). When the perennial ryegrass was irrigated, creeping bentgrass took as few as 10 days to recover and only 6 when both the perennial ryegrass and creeping bentgrass were irrigated (Data not shown). Increasing the rimsulfuron rate also increased recuperation time from 10.5 days when the low rate was applied to 18 days when the high rate was applied (Data not shown).

Rimsulfuron controlled perennial ryegrass equivalently, >95% eight weeks after treatment, in all trials, treatments, and rates (Data not shown). These data indicate that rimsulfuron can be dislodged from treated perennial ryegrass the morning after treatment when dew is present and can be deposited onto susceptible turfgrass via mower tires. Tracked creeping bentgrass can sustain perceivable injury as a difference in color or stunting that lasts up to 36 days. Increasing rimsulfuron rate increases both the severity and duration of injury tracks. By using the lowest effective rimsulfuron rate and irrigating the treated area prior to tracking, creeping bentgrass injury can be decreased or eliminated. Practitioners should avoid the use of turfgrass growth stimulators such as gibberellic acid and foliar iron as these products could serve to increase the perceptibility of visible injury tracks on creeping bentgrass due to increased growth of uninjured turf.

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Table 1. Effect of a 0.25 cm irrigation and remedial treatments on length of visible creeping bentgrass injury in tire tracks caused by rimsulfuron dislodged from perennial ryegrass 16 hours after treatment, pooled over three trials^a.

Irrigation	Remedial Treatment	Length of visible track		
		5 DATR ^b	10 DATR	25 DATR
		————— m —————		
None	None	5.7 a ^c	5.2 a	0.7 b
Ryegrass ^b	None	1.7 b	1.2 b	0.0 b
Bentgrass ^b	None	4.8 a	4.1 a	0.0 b
Ryegrass +Bentgrass	None	0.8 b	0.1 b	0.0 b
None	Iron ^b	5.9 a	5.4 a	1.2 ab
None	Gibberellic acid ^b	5.8 a	5.9 a	2.6 a
None	Gibberellic acid + Iron	5.9 a	5.6 a	2.9 a

^a Rimsulfuron was applied at 17.5 and 35 kg ai/ha with 0.25% nonionic surfactant to adjacent perennial ryegrass. For remedial treatments, only the high rate of rimsulfuron was evaluated.

^b Abbreviations: Bentgrass, creeping bentgrass irrigated immediately after tracking; DATR, days after tracking; Gibberellic acid, gibberellic acid applied at 0.12 kg ai/ha; Iron, foliar iron applied at 1.3 kg ai/ha; Ryegrass, perennial ryegrass irrigated two hours after rimsulfuron application.

^c Means followed by the same letter are not significantly different according to Fisher's protected LSD at P = 0.05.

Table 2. Effect of irrigation treatment on percent change in creeping bentgrass color in tire tracks caused by rimsulfuron dislodged from perennial ryegrass 16 hours after treatment and days to recuperation, pooled over two rimsulfuron rates ^a.

Irrigation	Remedial Treatment	Change in turfgrass color ^b						
		5 DATR ^c	10 DATR			20 DATR		
			Fall ^c	E Spring ^c	L Spring ^c	Fall	E Spring	L Spring
%								
None	None	13 a ^d	28 a	12 a	7 a	24 a	10 a	7 a
Ryegrass ^c	None	0 b	4 c	0 b	0 a	0 c	0 b	0 b
Bentgrass ^c	None	5 b	19 b	7 a	4 a	10 b	2 b	2 ab
Ryegrass + Bentgrass	None	0 b	0 c	0 b	0 a	0 c	0 b	0 b
None	Iron ^c	12 a	19 b	14 a	14 a	19 a	14 a	0 b
None	Gibberellic acid ^c	12 a	38 a	14 a	14 a	31 a	14 a	0 b
None	Gibberellic acid + Iron	12 a	25 a	14 a	14 a	14 a	14 a	0 b

^a Rimsulfuron was applied at 17.5 and 35 kg ai/ha with 0.25% nonionic surfactant to adjacent perennial ryegrass. For remedial treatments, only the high rate of rimsulfuron was evaluated..

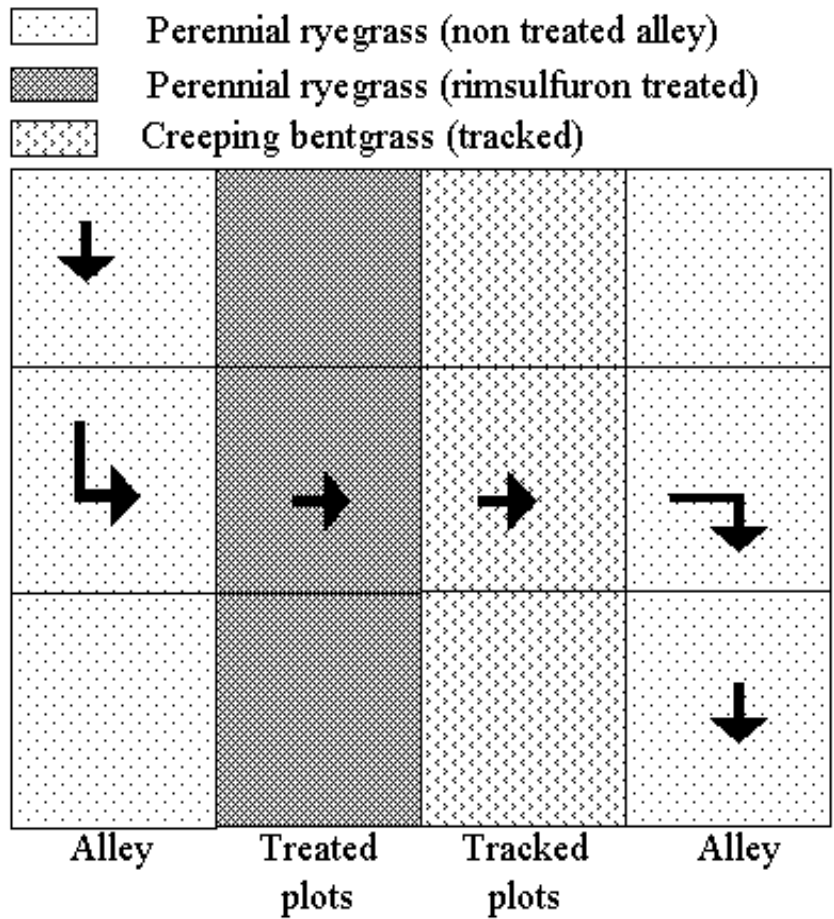
^b Change in turfgrass color was determined by comparing turf color outside of an injury track with turf color inside injury track within each plot. Percentages were determined using the following equation: $[1-(I / O)]*100$ where I is visually-estimated turfgrass color inside tracked areas and O is turfgrass color outside tracked areas.

^c Abbreviations: Bentgrass, creeping bentgrass irrigated after tracking; DATR, days after tracking; E Spring, Early spring 2003, Turfgrass Research Center, Blacksburg, VA 2003; Fall, Fall 2002, Turfgrass Research Center, Blacksburg, VA; Gibberellic acid, gibberellic acid applied at 0.12 kg ai/ha; Iron, foliar iron applied at 1.3 kg ai/ha; L Spring, Late Spring 2003, Turfgrass Research Center, Blacksburg, VA 2003; Ryegrass, perennial ryegrass irrigated two hours after rimsulfuron application.

^d Means followed by the same letter are not significantly different according to Fisher's protected LSD at P = 0.05.

^e Means followed by the same letter are not significantly different according to Fisher's protected LSD at P = 0.05.

Figure 1. Schematic of the treatment area at the Turfgrass Research Center in Blacksburg, VA that depicts treated and tracked plots. The perennial ryegrass was treated in the afternoon. The following morning a mower was driven down the alley across the treated perennial ryegrass and creeping bentgrass plots, then down the alley on the other side. Mower tires were rinsed between plots to prevent contamination.



Chapter III. Persistence of Rimsulfuron on Perennial Ryegrass and Annual Bluegrass Foliage¹

ABSTRACT

Field studies have shown that rimsulfuron can move laterally or “track” and injure neighboring cool-season grasses. Therefore, persistence and stability of rimsulfuron on turf foliage were studied. Perennial ryegrass and annual bluegrass were chosen because rimsulfuron is commonly used to control them in bermudagrass. Rimsulfuron was absorbed by annual bluegrass and perennial ryegrass equivalently and also persisted equally on foliage of these turf species. Water extractable rimsulfuron from turf foliage decreased from 57% of applied at 10 minutes after treatment to 42% of applied at 96 hours after treatment. Rimsulfuron was stable four days after application based on comparison of rinse water chromatograms to stock solution chromatograms; a substantial amount of stable rimsulfuron persists on turf foliage for up to four days. These data in conjunction with previous field studies evaluating rimsulfuron tracking indicate potential for rimsulfuron to dislodge from wet turfgrass and cause collateral damage to neighboring susceptible turf.

¹ Received for publication Date and in revised form Date.

Nomenclature: Rimsulfuron, 2-pyridinesulfonamide, N-(4,6-dimethoxypyrimidin-2-yl)-aminocarbonyl)-3-(ethylsulfonyl); perennial ryegrass, *Lolium perenne* L. ‘Pennant II’; annual bluegrass, *Poa annua* L.; creeping bentgrass, *Agrostis stolonifera* L. ‘Penncross’.

Additional index words: Absorption; herbicide degradation; herbicide relocation; herbicide stability; sulfonylurea.

Abbreviations: HAT, hours after treatment; LSS, liquid scintillation spectrometry; TLC, thin layer chromatography.

INTRODUCTION

Rimsulfuron is used on golf courses to control undesirable cool-season grasses in bermudagrass [*Cynodon dactylon* (L.) Pers] (Barker et al. 2003). In Virginia, both cool- and warm-season turfgrass is utilized on golf courses (Virginia’s Turfgrass Industry 2000). Thus, rimsulfuron-sensitive turfgrass species often border treated bermudagrass. Herbicides can move offsite through drift, lateral movement in rainwater drainage, leaching, volatility, and dislodging unabsorbed herbicide from the leaf surface. Even small amounts of rimsulfuron may be enough to injure or kill a nontarget plant (Barker et al. 2003).

Chemical persistence on leaf surfaces may influence rate of lateral movement. Pure rimsulfuron has little to no stability in water under alkaline conditions, however, formulated rimsulfuron has a typical half life of 7.5 days in alluvial soil (Martins and Mermound 1999; Schnieders et al. 1993; Scrano et al. 1999; Vicari et al. 1996). Because rimsulfuron is foliar-applied, photolysis is a possible threat to chemical stability until the

herbicide is absorbed into plants or soil. Photolysis reaction time ranges from one to nine days, but chemical stability is highly influenced by pH (Scrano et al. 1999). Degradation time of rimsulfuron is pH dependant regardless of formulation (Martins and Mermound 1999; Schnieders et al. 1993; Scrano et al. 1999; Vicari et al. 1996). At 25 C, rimsulfuron has a half-life of 4.7, 7.2, and 0.4 days at pH 5, 7, and 9, respectively and primarily occurs through a contraction of the sulfonylurea bridge (Schneiders 1993). Translocation and metabolism of rimsulfuron have been evaluated but persistence and stability on plant foliage have not. Absorption, translocation, and metabolism of rimsulfuron were assessed for three nightshade species (*Solanum* spp.) to determine differential efficacy (Ackley et al. 1999). Two of the nightshade species absorbed nearly 75% of the chemical within 48 hours after treatment, while the third species absorbed approximately 50% (Ackley et al. 1999). Similar studies evaluated trifloxysulfuron absorption on cotton (*Gossypium hirsutum* L.), spurred anoda [*Anoda cristata* (L.) Schlecht.], smooth pigweed (*Amaranthus hybridus* L.), jimsonweed (*Datura stramonium* L.), peanut (*Arachis hypogaea* L.), and sicklepod (*Senna obtusifolia* L.), with all species absorbing >50% of the applied herbicide (Askew and Wilcut 2002; Richardson et al. 2002). Although trifloxysulfuron was absorbed, a substantial percentage of the chemical remained on leaf surfaces.

Herbicide that persists on leaf surfaces may be dissolved in dew and tracked to neighboring susceptible turf, thus, causing injury (Barker et al. 2004, Unruh et al. 2003). Our objectives were to evaluate the amount and stability of ¹⁴C rimsulfuron that could be extracted from annual bluegrass and perennial ryegrass foliage with water over time.

MATERIALS AND METHODS

Perennial ryegrass and annual bluegrass seeds were germinated in sand and seedlings grown to the two-tiller stage in a greenhouse. Plants of uniform size transplanted to 50-ml screw-cap centrifuge tubes containing 25% Hoaglands solution. Plants were subsequently maintained in a growth chamber with 21/12.5 C day/night temperature and 50/80% day/night relative humidity. Light intensity was maintained at 150 $\mu\text{mol}/\text{m}^2/\text{sec}$ of PAR during the 14h day period. Prior to treatment, plants were allowed to acclimate for 7 days.

After acclimatization, plants were treated with [2-pyridine ^{14}C] rimsulfuron (Figure 1) dissolved in ethanol and 0.25 % v/v nonionic surfactant² with 1.9 MBq of specific activity. Treatment consisted of placing four 3- μl drops on the adaxial side of the second and third leaves on each of two tillers of the same plant. After application, plants were maintained in the growth chamber until harvest. Each plant received a total of 7.6 MBq of radioactivity. Non-radiolabeled herbicide was not applied to plants. Three plants were harvested at 0.06, 12, 24, 48, 72, and 96 hours after treatment (HAT). After the 12 HAT harvest, remaining plants were misted with water to simulate dew using a compressed air paint sprayer³. Simulated dew was applied each night during the study and allowed to dry naturally on plant surfaces. Care was taken to avoid watershed from leaf surfaces during misting.

At harvest, plants were cut at ground level and submersed in a vial containing 10 ml of distilled water and shaken for 30 sec to remove readily available herbicide from the

² Kinetic®, Helena Chemical Company., Collierville, TN 38017

³ Preval® Sprayer. Precision Valve Corporation., Yonkers, NY 10702.

leaf surface. The plant was removed and placed in another vial containing 10 ml of clean distilled water and again shaken for 30 seconds. After plant removal, the second distilled water vial was added to the first and rinsed with three ml of clean distilled water, also added to the first rinse vial. Next, plants were shaken using the same procedure in methanol to remove any herbicide bound to the cuticle layer. Two methanol rinses were combined in the same manner as distilled water rinses. A one ml sample of Hoagland's solution was assayed for radioactivity via liquid scintillation spectrometry⁴ (LSS) to test for exuded herbicide. Plants were dried at 60 C for at least 24 hours, oxidized using a biological oxidizer⁵, and assayed for total radioactivity via LSS. A one ml aliquot of each leaf surface rinsate was added to 20 ml of scintillation cocktail and radioactivity counts were determined utilizing LSS.

The remaining 22 ml of rinsate was used to determine herbicide stability on perennial ryegrass and annual bluegrass foliage utilizing thin layer chromatography (TLC). Methanol rinses were not subjected to TLC because extracted radioactivity was insufficient. The water rinsate was evaporated to dryness and dissolved in 0.5 ml of methanol. A 100 µl aliquot of each sample was spotted on a 20 by 20 cm silica gel TLC plate⁶. Plates were partitioned into nine 2-cm wide lanes. The first lane of each plate was spotted with 6 µl of radiolabeled rimsulfuron, which was used as a standard. The mobile phase (chloroform:methanol:acetate, 190:10:2, v/v) was used to develop plates to a 16 cm solvent front. Plates were air-dried and positions, proportions, and

⁴ LS 6500. Beckman Instrument Co., Fullerton, CA 92634.

⁵ BO306 Biological Sample Oxidizer. Packard Instrument Co., Downer Grove, IL 60515.

⁶ Silica Gel 60 F254 precoated TLC plates. EM Science, 480 Democrat Road, Gibbstown, NJ 08027.

corresponding R_f values were determined by scanning plates with a radiochromatogram scanner⁷. Radioactive trace peaks were integrated with Win-Scan® software⁸. Data were subjected to a combined analysis of variance (ANOVA) using the GLM procedure in SAS statistical software (SAS 1988). The effect of experiment repetition was considered a random variable in the combined analysis and mean squares were tested appropriately for a split-split plot treatment design (McIntosh 1983). Harvest times were considered main plots, plant or rinse partitions were subplots, and plant species were subsubplots. Data were pooled over nonsignificant effects for presentation. Appropriate regression analyses were conducted for the quantitative effect of harvest time. Other effects were separated using Fisher's Protected LSD test at $P=0.05$. Data variance was tested before ANOVA and percentage data were transformed to the arcsine of the square-root where appropriate. Other data was stabilized with log transformation where needed. To determine relationships between metabolite concentrations over time, Pearson correlations were calculated using the PROC CORR procedure in PC SAS (SAS 1988).

RESULTS AND DISCUSSION

Figure 2 depicts a chromatographic separation based on radioactive trace peaks of rimsulfuron and metabolites from an analytical standard before and after extraction procedures. Recovery of radioactivity was >90% through this study. Radioactivity in

⁷ Bioscan System 200 Imaging Scanner, Bioscan, 4590 MacArthur Blvd. NW, Washington, DC 20007.

⁸ LabLogic® Win-Scan Radio TLC Version 2.2(5) 32-bit, Distributed by BioScan, 4590 MacArthur Blvd. NW, Washington, DC 20007.

Hoagland's solution from each plant never exceeded background levels. Upon first examination, we incorrectly assumed that the large peak at R_f 0.18 was rimsulfuron and the standard did not need purification. However, after study initiation chromatographic separations of non-radiolabeled analytical standard indicated that the smaller peak at an approximate R_f of 0.52 was rimsulfuron. Published literature also confirmed that rimsulfuron has an R_f at or near 0.52 using the separation methods employed in this study (Ackley et al. 1999). Most of the radioactivity was observed at R_f 0.18 and presumed to be a metabolite of rimsulfuron. Although the primary degradation method of rimsulfuron is contraction of the sulfonyleurea bridge (Schneiders 1993), metabolites of rimsulfuron have not been reported in scientific literature and requests from the manufacturer for identification of these metabolites were denied. Two other metabolites were observed via TLC separation of the standard at R_f 0.06 and 0.74; nonetheless each accounted for 3% or less of total radioactivity applied. The metabolite at R_f 0.06 never exceeded 3% of total radioactivity at any point in the study (Data not shown). Rimsulfuron accounted for approximately 24% of applied radioactivity. Lack of purity in applied chemical did not detract from our ability to track changes in pure rimsulfuron on leaf surfaces over time because we obtained chromatographic separations of every sample. Using peak area information, we were able to calculate the amount of pure rimsulfuron in each sample rinsed from plant foliage. However, we were unable to determine the contribution of rimsulfuron to absorbed radioactivity. The inability to quantify absorbed rimsulfuron is of no consequence since our objective was to determine persistence and stability of rimsulfuron on leaf surfaces. Figure 2 also demonstrates the effect of extraction, storage, and dry-down preparation on the analytical standard. Little change occurred between the

analytical standard spotted directly on the TLC plate (solid line), and the standard subjected to extraction, storage, and dry-down techniques (dashed line).

The main effect of time was significant for rinsing percent of applied ^{14}C detected in perennial ryegrass and annual bluegrass ($p < 0.0001$) (Figure 3). Since the effect of plant species was not significant ($p < 0.05$), data from perennial ryegrass and annual bluegrass were pooled to show the response of absorbed and rinsed radioactivity over time (Figure 3). Greater than 90% of the 7.6 MBq of ^{14}C radioactivity applied was water extractable 10 min after application. After 96 hours, <50% of the total ^{14}C applied was rinsed from turf foliage (Figure 3). Although the percentage of absorbed rimsulfuron over time can't be accurately assessed, it is likely similar to total radioactivity absorbed based on observations by Ackley et al. (1999). Total absorbed radioactivity increased over time at a rate of 7% per day with a concomitant decrease of 10% radioactivity recovered in leaf rinse solution (Figure 3).

Percentage of applied rimsulfuron recovered in the water rinse from turfgrass foliage was 57% 10 minutes after treatment and decreased 5% per day for the remainder of the study (Figure 4). The rapid decrease in water-extractable rimsulfuron on leaf surfaces within the first 10 min is most likely due to rapid absorption of the herbicide. Rimsulfuron was absorbed rapidly by nightshade species (Ackley et al. 1999). Jimsonweed absorbed 10% of applied trifloxysulfuron 10 seconds after treatment and 60% of applied trifloxysulfuron four hours after treatment (Askew and Wilcut 2002). Chlorsulfuron absorption was rapid in the first 10 min for various pHs into velvetleaf (*Abutilon theophrasti* L.) roots (Mersie and Foy 1987). Olsen et al. (1999) also found sulfosulfuron absorption in the greatest quantity within the first 6 h followed by slow

absorption over time. Rapid absorption is common among herbicides in the sulfonylurea family (Ahrens 1998), but greater than 25% of applied herbicide often persists on leaf foliage for more than two days (Ackley et al. 1999, Askew and Wilcut 2002, Goatley et al. 1990, Mersie and Foy 1987, Olson et al. 1999, Richardson et al. 2002). Regardless of grass species, rimsulfuron was water extractable in the herbicidally-active form at 52, 47, and 43% at 1, 2, and 3 days after treatment, respectively (Figure 4). Since rimsulfuron accounted for only 24% of applied radioactivity in this study, it is necessary to account for the behavior of each metabolite over time. Devine et al. (1984) determined the most effective technique for determining absorbed chlorsulfuorn radioactivity utilizing leaf washes; this direct connection cannot be made in this study due to the impurity of the chemical applied to perennial ryegrass and annual bluegrass. However, this is an indication of absorption trends of sulfonylurea herbicides.

Rimsulfuron was relatively stable on leaf surfaces (Figure 5) and decreased in water-extractable rimsulfuron over time (Figure 4) are presumably due to absorption into the treated leaf based on reports of rimsulfuron and other sulfonylurea absorption (Ackley et al. 1999, Askew and Wilcut 2002, Goatley et al. 1990, Mersie and Foy 1987, Olson et al. 1999, Richardson et al. 2002). When exposed to perennial ryegrass foliage and the conditions of this experiment, the metabolite at R_f 0.18 decreased over time with a concomitant increase in the metabolite at R_f 0.74 (Figure 5). A Pearson correlation test indicted that these two metabolites were negatively correlated (-0.9448, $p < 0.0001$). It is not known what role these two metabolites might play in nontarget injury to susceptible grasses, but both were observed in a TLC separation of analytical grade rimsulfuron after one month incubation in water at pH 7.0 (Data not shown). Hence, these metabolites

likely occur in small quantities if formulated rimsulfuron is exposed to spray-tank pH in the acid or alkaline ranges that cause rapid degradation (Martins and Mermound 1999; Schnieders et al. 1993; Scrano et al. 1999; Vicari et al. 1996).

Herbicide persistence on plant foliage has been implied in many sulfonylurea herbicide absorption studies where 75% or less of the applied herbicide absorbed into the plant. Data from this study indicate that a substantial amount rimsulfuron will persist on treated annual bluegrass and perennial ryegrass foliage in the herbicidally-active form if dislodged and relocated. Field studies have shown rimsulfuron can injure creeping bentgrass when mower tires transverse perennial ryegrass one day after treatment with rimsulfuron and deposit dislodged chemical onto the creeping bentgrass (Barker et al. 2004, Unruh 2003). Injury to creeping bentgrass manifests as tire tracks that persist for up to 36 days (Barker et al. 2004). Since 43% of applied rimsulfuron was water extractable after three days (Figure 4), simply waiting for an extended period of time will not reduce the likelihood of causing nontarget injury via rimsulfuron tracking. Current registration for rimsulfuron recommends a buffer area between a treated area and susceptible turf (Anonymous 2001). However many mangers do not follow this recommendation and another solution is needed; the solution in field studies has been to wash persistent rimsulfuron from turf foliage with light irrigation prior to mowing (Barker et al. 2004).

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Figure 1. Structure of rimsulfuron. A "*" denotes the position of ^{14}C .

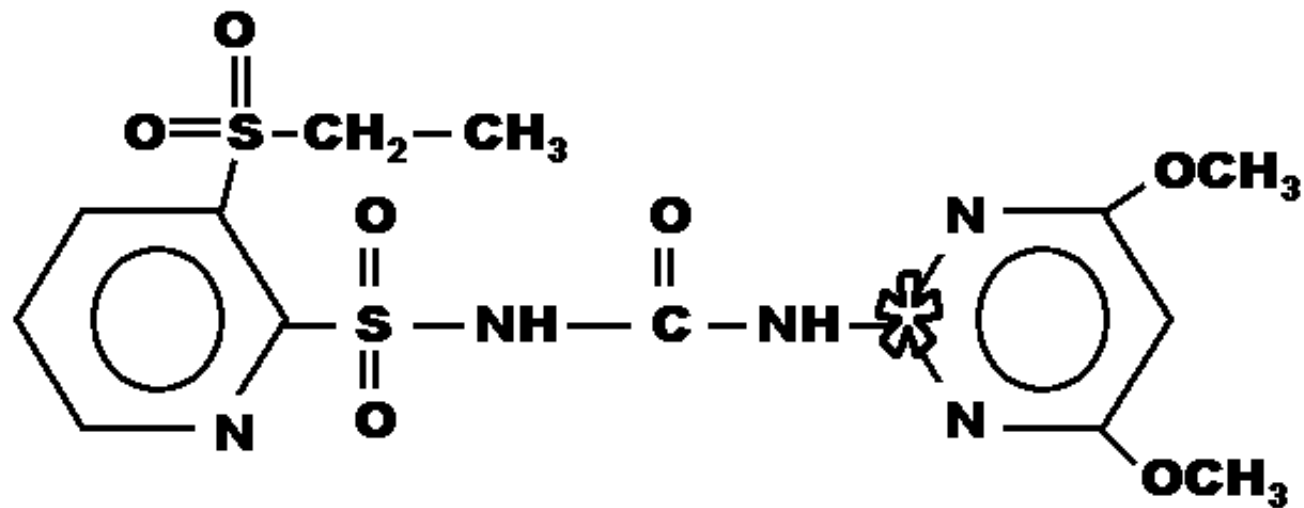


Figure 2. Radioactivity traces from thin layer chromatographic separation of [2-pyridine-¹⁴C] rimsulfuron and metabolites before and after foliage extraction procedures.

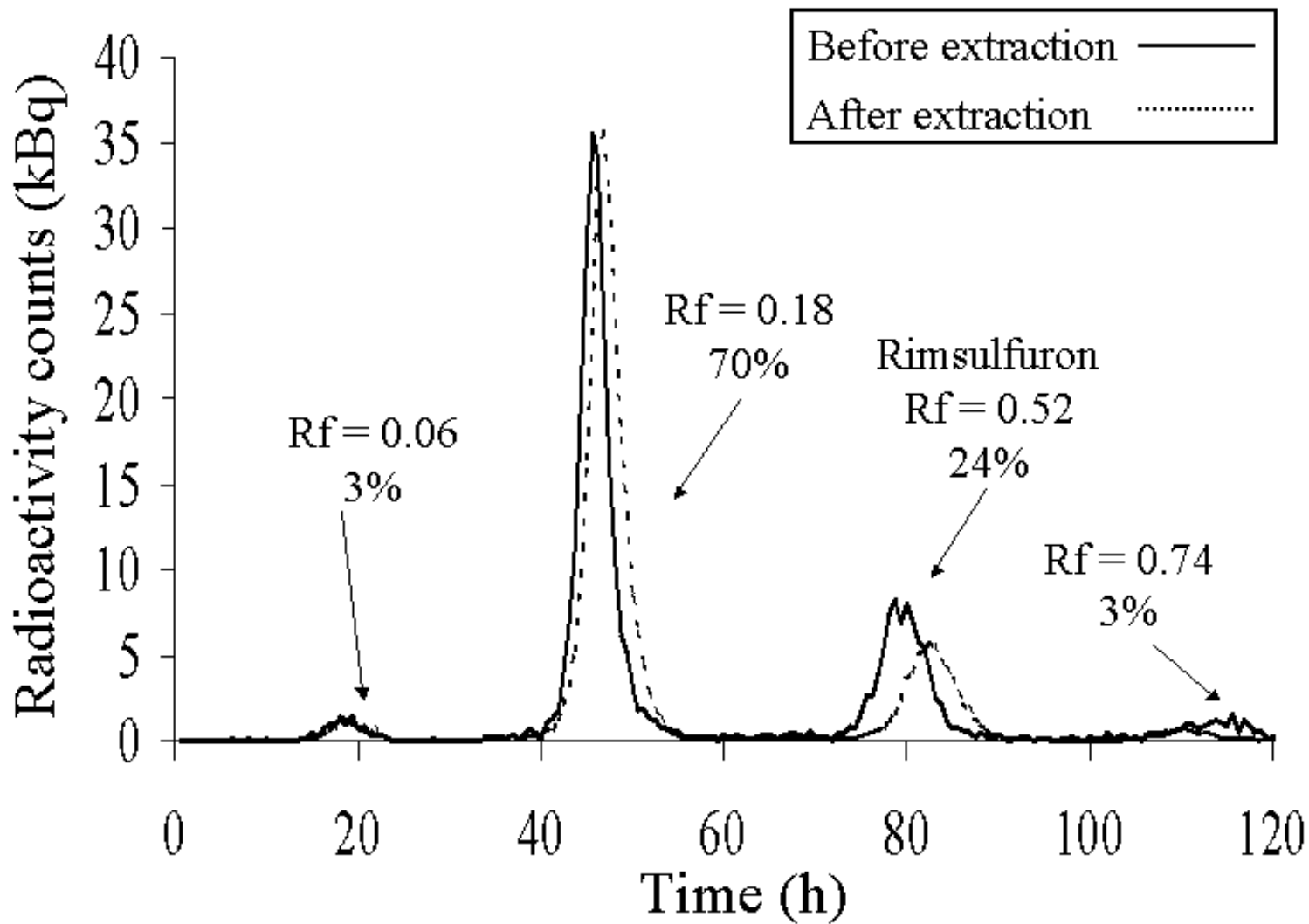


Figure 3. Percent of recovered ^{14}C from perennial ryegrass and annual bluegrass over time following application of 7.6 MBq of [2-pyridine- ^{14}C] radiolabelled rimsulfuron.

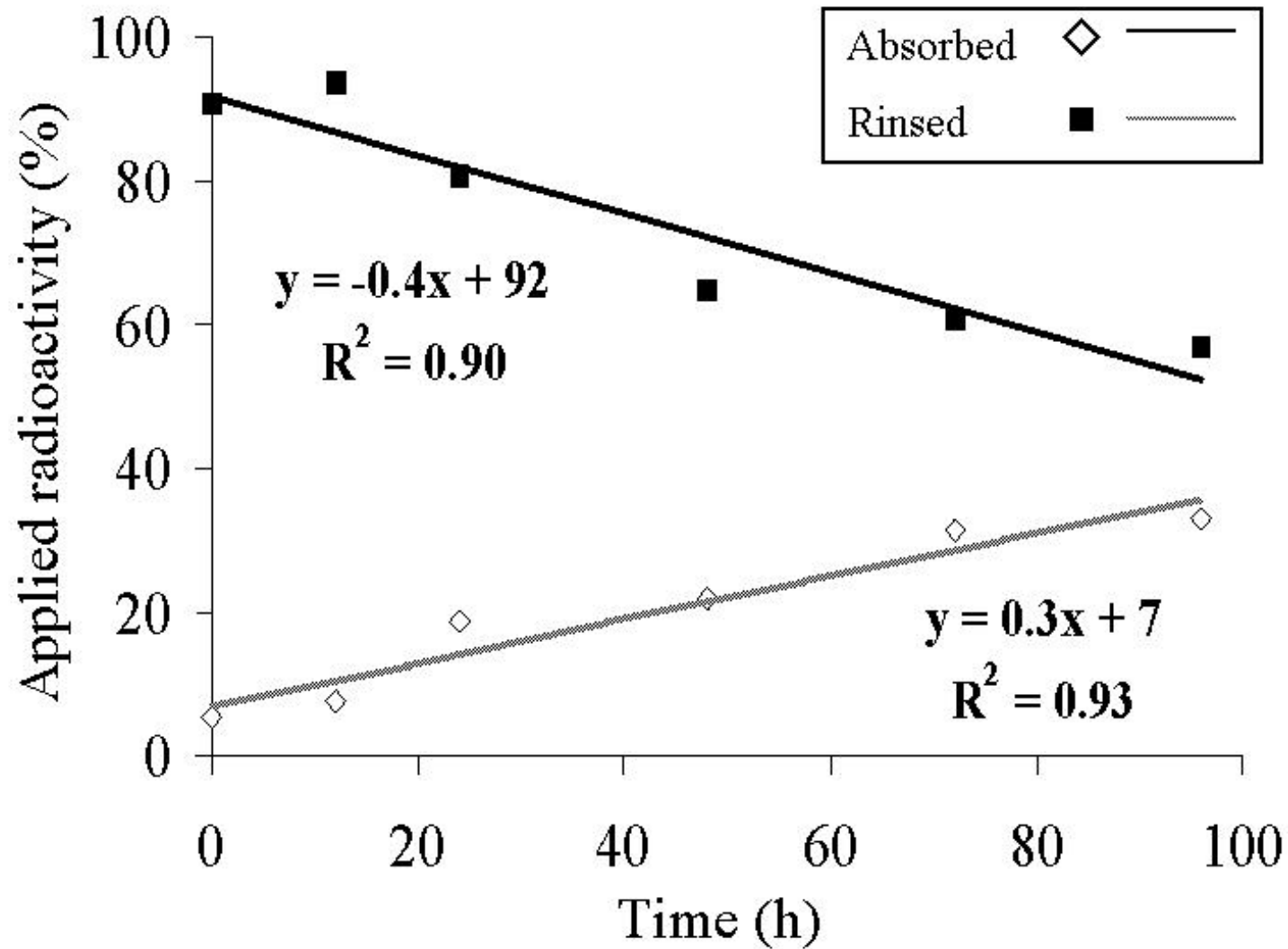


Figure 4. Percentage of applied ¹⁴C rimsulfuron extracted from foliage of perennial ryegrass and annual bluegrass over time.

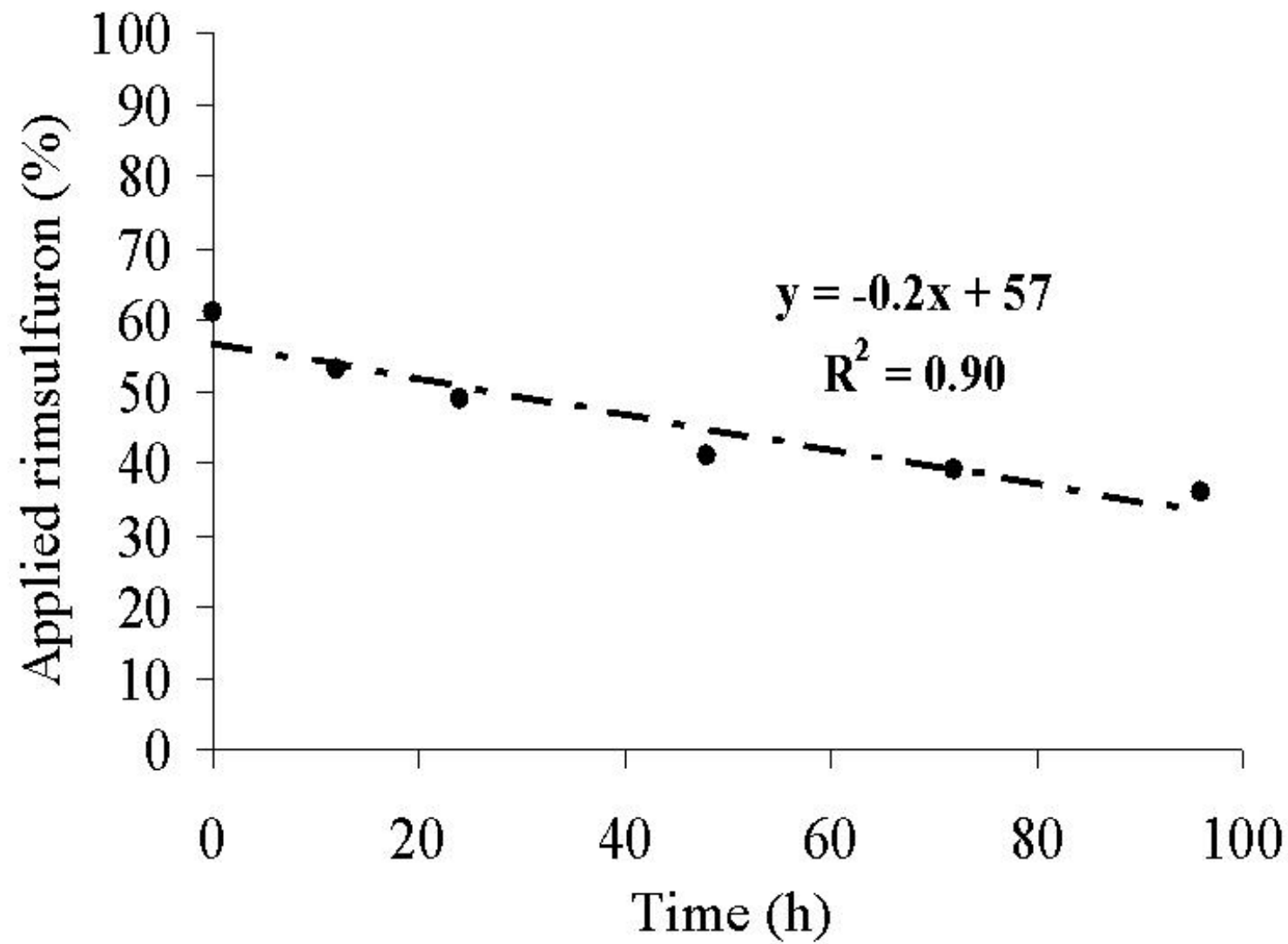
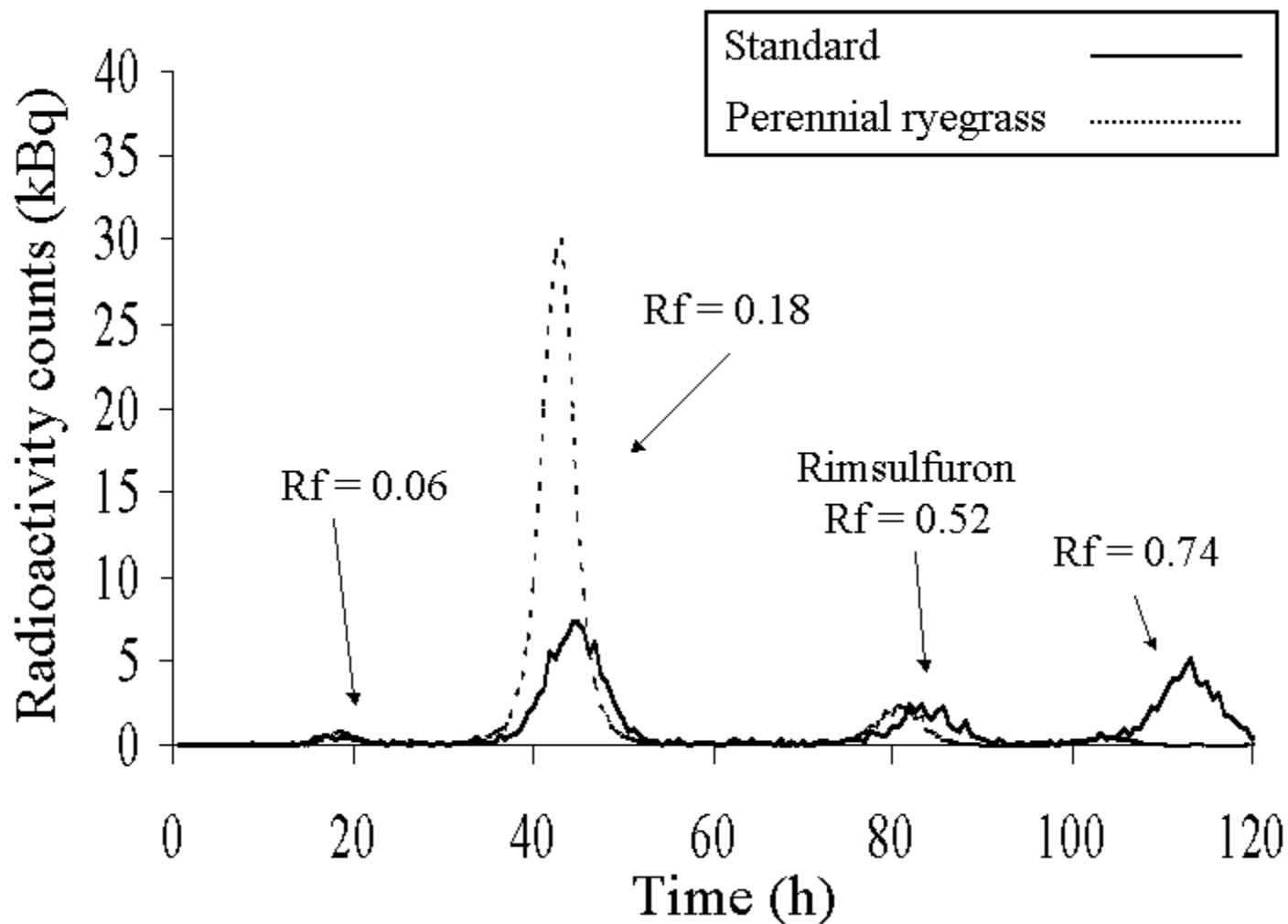


Figure 5. . Radioactivity traces from thin layer chromatographic separation of applied chemical including [2-pyridine-¹⁴C] rimsulfuron and metabolites and water extracted radioactivity from perennial ryegrass 24 hours after application.



Vitae

Whitnee Leigh Barker was born in Kokomo, IN on July 4, 1980 as the second daughter of Randy and Marcylena (Jeanie) Barker. Shortly, thereafter her family moved to Flemingsburg, KY to a dairy farm. She was active in high school participating and holding offices in many clubs and sports including SR. Beta, The National FFA Organization, Spanish Club, Science Olympiad team, in-door track, out-door track, cross-country, and basketball. She graduated cum laude from Fleming County High School in 1998. She completed her Bachelor of Science degree in Agricultural Biotechnology with a double major in Biology from the University of Kentucky in 2002. While at the University of Kentucky she received grants to fund her undergraduate research including the undergraduate research award from the Weed Science Society of America. Whitnee began her Master of Science degree at Virginia Tech in 2002.

While at Virginia Tech she has been active in the Northeastern Weed Science Society, Southern Weed Science Society, Virginia Turfgrass Conference, Agronomy Society of America, Crop Science Society of America, Soil Science Society of America, and Weed Science Society of America. Whitnee held office in the Graduate Student Organizations of the Southern Weed Science Society, and the Weed Science Society of America. She was a member of the third place team at the Northeast Weed Science contest in 2002, and the second place team in 2003. Whitnee won second place in the poster contest in 2003, and first place in the paper contest in 2004 at the Northeast Weed Science Society meetings. She was also the recipient of the Arthur J. Webber outstanding graduate student award in 2004. Whitnee plans to continue her education and earn a Ph.D.